Structure and Properties of Complex Transformation Products in Nb/Mo-Microalloyed Steels

by

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Abstract

Advanced line pipe steels are microalloyed with Nb to promote the formation of complex microstructures leading to the required mechanical properties. In addition to its role during thermo-mechanical processing Nb in solution affects significantly the austenite decomposition kinetics and the resulting microstructure. A systematic study has been carried out to quantify the influence of Nb on the austenite decomposition in a commercial X80 line pipe steel containing 0.06C-0.034Nb-0.24Mo-0.012Ti-0.0005N (in wt. %) for a variety of austenite grain sizes and cooling rates that are relevant for the heat affected zone.

To quantify the influence of Nb on transformation kinetics, two distinct amounts of Nb in solution were obtained through carefully designed reheat treatments prior to continuous cooling transformation tests conducted with a Gleeble 3500. The amount of Nb in solution was quantified based on ageing experiments. To investigate the combined influence of Nb and Mo on austenite decomposition two laboratory cast low-carbon steels containing 0.06 wt. % Nb and 0.045 wt. % Nb and 0.145 wt. % Mo, respectively, were compared with the X80 steel. The obtained transformation products include irregular ferrite, upper and lower bainite and martensite/austenite.

Electron backscatter diffraction (EBSD) was used to distinguish upper and lower bainite based on their orientation relationship with the prior austenite and to quantify microstructural features which are relevant for the tensile properties. Based on the quantitative measures obtained from the EBSD analysis structure-property relationships were developed to predict the yield strength, uniform elongation and ultimate tensile strength of the studied X80 line pipe steel. An effective grain size was defined including martensite/austenite to consider grain refinement and the kernel average misorientation was used to quantify dislocation strengthening.

A phenomenological model was applied and modified to capture the austenite decomposition of the X80 steel considering the effect of prior austenite grain size, amount of Nb in solution and cooling rate. The amount of martensite/austenite depends on the surrounding matrix
microstructure and is predicted as a function of the transformation start temperature with an empirical fit.
Preface

This research work was conducted as part of an NSERC grant awarded to The University of British Columbia in collaboration with TransCanada PipeLines Ltd. and Evraz Inc. NA. For the studies presented in this thesis, I was the primary researcher and responsible for experimental design and sample preparation, data collection, analysis and interpretation. Results and data published by other members of the project were considered and incorporated where suitable and reference is made in the particular sections throughout the thesis, i.e. [11, 121, 135, 149, 150].

My supervisor, Dr. Matthias Militzer, was involved in all stages of my work and provided guidance and assistance. Additional guidance with the modelling of the austenite decomposition was provided by Dr. Thomas Garcin. The development of structure-property relationships was carried out in cooperation with Dr. Warren J. Poole. Some of the tensile data as well as the corresponding heat treated material for EBSD samples used to develop the structure-property model were supplied by Dr. Michael Gaudet.

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$\alpha$ Ferrite

$\beta_1$ Coefficient describing solute drag of Nb in ferrite start model

$\beta_2$ Coefficient describing solute drag of Nb in bainite start model

$\varepsilon_{\text{true}}$ True strain

$\gamma$ Austenite

$(\varphi_1, \phi, \varphi_2)$ Euler angles

$\lambda_1, \lambda_2$ Fit parameters in the ferrite start model to relate the critical carbon concentration for nucleation site saturation to the austenite grain size

$\nu$ Sub-grain boundary angle

$\psi$ Cooling rate

$\rho$ Dislocation density

$\theta$ Work hardening rate

$\xi$ Characteristic length scale capturing the distance for dynamic recovery

$A$ Area of bainite nucleation in bainite start model

$AR$ Aspect ratio

$B$ Magnitude of the Burgers vector

$b$ Rate parameter in the JMAK equation
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<td>$B_N$</td>
<td>Bainite nucleation temperature</td>
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<td>$B_s$</td>
<td>Bainite start temperature</td>
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<td>$B_T$</td>
<td>Bainite transition temperature in</td>
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<td>$CE$</td>
<td>Carbon equivalent</td>
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<td>$c_1$</td>
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<td>$G$</td>
<td>Shear modulus</td>
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<td>$G_N$</td>
<td>Critical driving pressure for bainite formation</td>
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<td>$H$</td>
<td>High angle grain boundary density</td>
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<td>$H_A$</td>
<td>Effective grain size</td>
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</table>
$HV$  Vickers hardness

$HV_0$  Initial Vickers hardness after austenite to ferrite transformation

$dHV_i$  Hardness increase between initial hardness and peak hardness

$dHV_{max}$  Hardness increase between initial hardness and peak hardness when all Nb is in solution prior to ageing

$k$  Constant describing the dislocation storage during deformation

$dl$  Length change of bainite lath in bainite start model

$l_1, l_2$  Fit parameters describing linear growth velocity of bainite laths

$l'_1, l'_2$  Fit parameters in bainite start temperature

$logK_s$  Solubility product of NbCN

$m$  Fit parameter describing grain size dependence of rate parameter b in JMAK equation

$M$  Taylor factor

$n$  Avrami exponent in the JMAK equation

$N$  Number of Bainite nuclei in bainite start model

$R_a$  Radius of ferrite nucleus in ferrite start model

$R^*$  Radius of ferrite nucleus when site saturation is reached in ferrite start model

$T$  Temperature

$t$  Time

$T_N$  Ferrite nucleation temperature
\( T_s \)  
Transformation start temperature

\( X \)  
Fraction transformed in the JMAK equation

\( X_C^0 \)  
Nominal carbon fraction

\( X_C^\alpha \)  
Equilibrium carbon concentration in ferrite

\( X_C^\gamma \)  
Equilibrium carbon concentration in austenite

\( X_C^{sol} \)  
Fraction of carbon in solid solution

\( X_C^* \)  
Critical carbon concentration related to nucleation site saturation in ferrite start model

\( X_N^0 \)  
Nominal nitrogen fraction

\( X_Ti^0 \)  
Nominal titanium fraction

\( X_{Nb}^{sol} \)  
Fraction of Nb in solid solution

\( \sigma_\rho \)  
Dislocation strengthening

\( \sigma_0 \)  
Material dependent base strength

\( \sigma_{HA} \)  
Grain size strengthening

\( \sigma_{true} \)  
True stress in MPa

\( \sigma_{yield} \)  
Experimentally measured yield strength (0.02 offset)
## List of Abbreviations

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<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>BCC</td>
<td>Body-centred cubic</td>
</tr>
<tr>
<td>CCT</td>
<td>Continuous cooling transformation</td>
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<tr>
<td>CGHAZ</td>
<td>Coarse grained heat affected zone</td>
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<tr>
<td>CPP</td>
<td>Close packed plane</td>
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<tr>
<td>EBSD</td>
<td>Electron backscatter diffraction</td>
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<tr>
<td>FCC</td>
<td>Face-centred-cubic</td>
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<tr>
<td>FGHAZ</td>
<td>Fine grained heat affected</td>
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<tr>
<td>GND</td>
<td>Geometrically necessary dislocation</td>
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<tr>
<td>HAGB</td>
<td>High angle grain boundary</td>
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<td>HAZ</td>
<td>Heat affected zone</td>
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<td>ICHAZ</td>
<td>Intercritical heat affected zone</td>
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<tr>
<td>IQ</td>
<td>Image quality</td>
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<tr>
<td>IR</td>
<td>Irregular ferrite</td>
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<tr>
<td>IPF</td>
<td>Inverse pole figure</td>
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<tr>
<td>JMAK</td>
<td>John-Mehl-Avrami-Kolmogorov</td>
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<tr>
<td>KAM</td>
<td>Kernel average misorientation</td>
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<td>KS</td>
<td>Kurdjumov-Sachs</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td><strong>LAGB</strong></td>
<td>Low angle grain boundary</td>
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<td><strong>LB</strong></td>
<td>Lower bainite</td>
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<tr>
<td><strong>M/A</strong></td>
<td>Martensite/austenite</td>
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<tr>
<td><strong>NW</strong></td>
<td>Nishiyama-Wassermann</td>
</tr>
<tr>
<td><strong>LUMet</strong></td>
<td>Laser ultrasonics for metallurgy</td>
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<tr>
<td><strong>PFM</strong></td>
<td>Phase field model</td>
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<tr>
<td><strong>OIM</strong></td>
<td>Orientation Imaging Microscopy</td>
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<tr>
<td><strong>OR</strong></td>
<td>Orientation relationship</td>
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<tr>
<td><strong>PAGB</strong></td>
<td>Prior austenite grain boundary</td>
</tr>
<tr>
<td><strong>PAGS</strong></td>
<td>Prior austenite grain size</td>
</tr>
<tr>
<td><strong>RA</strong></td>
<td>Retained austenite</td>
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<tr>
<td><strong>SCHAZ</strong></td>
<td>Subcritical heat affected zone</td>
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<tr>
<td>( t_{8.5} )</td>
<td>Cooling time between 800 and 500°C</td>
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<tr>
<td><strong>TMCP</strong></td>
<td>Thermo-mechanical controlled processing</td>
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<tr>
<td><strong>TRIP</strong></td>
<td>Transformation induced plasticity</td>
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<tr>
<td><strong>UB</strong></td>
<td>Upper bainite</td>
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<tr>
<td><strong>UTS</strong></td>
<td>Ultimate tensile strength</td>
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</table>
Acknowledgements

While it seemed just as intimidating to write my acknowledgements as it seemed to write any other chapter of this manuscript when I first sat down to write my PhD thesis, it is now a pleasure to extend my gratitude to those who accompanied me on this (longer (and maybe better) than expected) journey.

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Ja genau, oui oui, ano ano.


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Chapter 1: Introduction

Metallurgical advances have strongly influenced society for more than 3,000 years, with the use of iron-alloys dating back to the Iron Age. Advances in steel making during the era of the Industrial Revolution in the 18th and 19th century marked the start of modern steel technology and laboratory based steel research flourished in the late 19th and early 20th century when the use of metallographic techniques led to the coupling of microstructure and material properties [1]. Rolling practices were improved and the limitations of using carbon additions as primary strengthening method emerged when the failure of weld structures was related to brittle phases. The concept of toughness was introduced in the late 1940s and the relationship between strength and toughness and the ferrite grain size [2], [3] prompted steel makers to lower the rolling temperatures leading to refined microstructures and improved mechanical properties [4]. In 1958, the first commercial niobium-bearing high strength steel plates were introduced and the basic understanding of the influence of Nb on microstructure and mechanical properties in C-Mn steels was established in the early 1960s [5]. New rolling practices were established where the finish rolling is carried out under the so-called non-recrystallization condition. This processing scheme was a breakthrough in the development of modern high strength low-alloy (HSLA) steels.

Advanced HSLA steels are used for bridges, heavy industrial machinery, car components, and structural components. In addition, applications in the energy sector include oil and gas pipelines, transmission towers, on- and off-shore platforms, and long tower sections for wind turbines. Remote areas of oil and gas fields require long distance pipelines as the most economic and
environmentally friendly delivery system to bring oil and gas from the fields to the market. Particularly in North America, there is an increased interest to explore new sources of oil and gas in the Arctic. Here, additional challenges to the material properties arise from permafrost, thaw settlement, frost heave and soil movement and call for the improvement of available line pipe steels to meet the high strength and toughness requirements even in harsh environments. In addition, improved strength allows for the reduction of steel volume which results in tremendous costs savings for structural applications, involving handling and transportation fees [6], [7], which becomes increasingly important for remote areas or off-shore locations.

The development of Nb-microalloyed steel grades initiated in the 1960s and 1970s. Line pipe steels such as X52 or X65 were limited in strength with microstructures comprising polygonal ferrite and pearlite to ensure sufficient toughness [8], [9]. The advances in thermo-mechanical controlled processing (TMCP) have led to enhanced rolling techniques since the 1980s [10]. Niobium is the key microalloying element in thermo-mechanical controlled processing. Finish rolling practices in the non-recrystallization regime lead to highly deformed pancaked austenite that, in combination with accelerated cooling, results in fine ferritic microstructures with higher strength and toughness compared to traditional ferrite/pearlite microstructures. The base material of currently used line pipe steels such as X70 or X80 mainly consists of fine grained irregular ferrite, including randomly distributed martensite/austenite islands and complex precipitates [11], [12]. The next generation of X100 and X120 grades are designed to constitute highly dislocated bainitic structures leading to superior strength [7]. However, increased hardenability results in high susceptibility to brittle fracture. While X100 steel has already been used for demonstration and test purposes by TransCanada PipeLines Ltd., the commercial application of this steel is still in the development phase.

The installation of pipelines involves the girth welding of pipe sections in the field. Thus, weldability is an important criterion for the alloy design [13]–[15]. While carbon is the primary strength controlling element in low-alloy steels, it promotes embrittlement of the heat affected zone and therefore reduces the weldability. The reduction of carbon content in HSLA steels is
compensated for with the addition of microalloying elements such as niobium, titanium, vanadium, and molybdenum. Microalloying elements lead to high strength through solid solution strengthening, precipitation hardening, microstructural refinement and dislocation strengthening, Figure 1-1. It is noteworthy that grain refinement is the only strengthening mechanism that also increases the toughness.

In addition to niobium, titanium plays an important role in TMCP as TiN inhibits austenite grain growth and is stable at high temperatures. Molybdenum is added for additional strength through increased hardenability: carbon activity is decreased in the presence of molybdenum, delaying or suppressing polygonal ferrite and especially pearlite formation during austenite decomposition, which results in a shift to lower transformation temperatures, thereby promoting highly dislocated microstructure constituents of the hot rolled material such as irregular ferrite and bainite.

These fine microstructures are required for high strength in combination with excellent toughness even at low temperatures. However, in the heat affected zone (HAZ) the encountered microstructures can vary significantly from those of the base material. The time-temperature profile experienced during welding changes along the distance from the fusion line (see Figure 1-2) creating a steep temperature gradient within the HAZ which results in a graded microstructure with varying mechanical properties.
Figure 1-2: Schematic of the thermal profile across the heat affected zone that varies as a function of the distance from the fusion line

This work is part of a larger research project at the University of British Columbia to develop an integrated microstructure-property model for the HAZ of a commercial X80 line pipe steel grade proposed for applications in the Arctic in collaboration with NSERC, TransCanada PipeLines Ltd. and Evraz Inc. NA. The aim of this work is to study the combined influence of niobium and molybdenum on the microstructure evolution during austenite decomposition and to connect microstructural features to the resultant tensile properties. While a vast amount of studies are available in the literature for the transformation behavior from pancaked austenite, the knowledge gained through this study will be valuable for the design of welding procedures to ensure that the heat affected zone microstructure provides the required strength and toughness.
Chapter 2: Literature review

2.1 Introduction

2.1.1 Classification of line pipe steels

The classification of line pipe steels in North America follows the American Petroleum Institute (API) standards. Steel grades such as API X65 or API X80 refer to the minimum required yield strength in ksi, i.e. 65 or 80 ksi, respectively, and are often referred to as X65 or X80. The requirements for the tensile strength of line pipe steels have increased by a factor of two from 1960 to today, Figure 2-1. X80 steels are currently used for large diameter pipelines, while higher grades such as X100 and X120 are still under development [17]. The advances are mainly due to the combination of microalloying, low carbon contents and thermo-mechanical controlled processing (TCMP) as well as welding techniques such as double submerged arc welding (DSAW). DSAW includes both inside and outside welds which are usually performed in separate processes. During submerged arc welding the welding arc is submerged in flux to shielding the molten metal from atmospheric contamination. DSAW pipe is used in high pressure gas and oil transmission lines, both onshore and offshore.
Initial steel grades such as X52 or X65 started with a microstructure consisting of polygonal ferrite and pearlite [8], [9], [19]. This microstructure offers sufficient toughness at limited strength levels. Continuous development resulted in higher strength and toughness properties based on advanced microalloying strategies as well as grain refinement induced by accelerated cooling. Hence, X70 line pipe steel meets higher strength in combination with improved toughness and higher brittle fracture resistance which is mainly achieved through grain refinement and the promotion of non-polygonal microstructure constituents such as irregular ferrite. Figure 2-2 compares the microstructure of X65 and X80 which demonstrates the grain refinement achieved through irregular ferritic microstructures characteristic for X70 and higher grades.

In the development of more advanced high-strength steels with a focus on low-temperature toughness, the processing strategy for the production for X80 consists of thermo-
mechanical controlled rolling followed by accelerated cooling from above the ferrite start temperature. This rolling strategy typically leads to a microstructure of fine grained irregular ferrite, including randomly distributed martensite/austenite islands and complex precipitates [11], [12]. These microstructures allow for increased operating pressures of large diameter pipelines, while the wall thickness can be decreased for economic reasons.

Figure 2-2: a) Microstructure of X65 consisting of polygonal ferrite and pearlite preprinted from ref. [9] with permission of Elsevier; b) X80 microstructure showing fine non-polygonal ferrite; reprinted from [20] with permission of ASME

In conventional stress-based pipeline design, the pipeline is designed around the containment of gas where the required strength is related to the operating pressure. Of particular concern in terms of material performance are the properties of the girth welds and associated heat affected zones. In addition to the requirements of the stress-based design, the strain-based design takes into account the strain demand in the longitudinal direction that would arise from ground movement associated with frost heaves or settling in areas of unstable permafrost [17]. For Arctic construction the strain-based design is now standard as the pipeline must traverse areas of continuous or discontinuous permafrost and is subjected to low operating temperatures. Strain-based design calls for stress-strain curves of a particular shape which is determined by the ratio of stress to strain at given strain values leading to a so-call ‘roundhouse’ stress-strain curve where the strain increases smoothly near the yield stress, preventing the occurrence of yield point elongation.
The next generation of X100 and higher grades also follows the strain-based design to constitute highly dislocated bainitic structures. Compared to a yield strength of 550 MPa and an ultimate tensile strength of 620 MPa for X80 steel, X100 line pipe steel shows superior strength with a reported yield strength higher than 680 MPa and tensile strength higher than 800 MPa [7]. While X100 steel has already been used for demonstration and test purposes by TransCanada PipeLines Ltd., increased hardenability resulting in high susceptibility to brittle fracture has been preventing the commercial application [21], [22].

2.2 Role of alloying elements

Suitable additions of alloying elements contribute to an increase in strength through microstructural refinement, solid solution strengthening and precipitation hardening, as well as through the promotion of highly dislocated transformation products [10]. Solid solution strengthening is closely related to the alloy content, while grain refinement and precipitation strengthening depend on the complex interaction of alloy composition and thermo-mechanical treatment.

A higher content of alloying elements is generally necessary in order to reach the X80 strength level. It is therefore important to find the optimum balance between the strength of the base metal, on the one hand, and the heat affected zone toughness, on the other hand [23]. While carbon is the primary strength controlling element in steels, the carbon content is drastically reduced to 0.03-0.09 wt. % in modern line pipe steels to ensure weldability. An empirical measure of the weldability is given by the carbon equivalent which is defined by the International Institute of Welding for steels containing more than 0.18 wt. % C as:

$$CE = C + \frac{Mn}{6} + \frac{Cr}{10} + \frac{Ni + Cu}{15}$$

(2-1)

Here, the alloying content of each element is given in wt. %. A modified carbon equivalent for low-carbon steels containing less than 0.18 wt.% is proposed by Ito and Bessyo [24]:
Both formulas demonstrate the strong effect of carbon while the modified equation clearly indicates the reduced negative impact of other alloying elements on weldability in modern low-carbon steels [10]. Alloying elements used in line pipe steels promote the formation of highly dislocated low temperature transformation products which leads to increased strength and toughness.

Upon cooling from the austenite state various mechanisms govern the austenite decomposition transferring the crystal lattice of the parent austenite to numerous transformation products. In addition to the phases represented in the Fe-Fe₃C phase diagram, i.e. ferrite and pearlite, other structures occur, e.g. martensite and bainite. The addition of alloying elements influences the transition between austenite and ferrite. The alloying elements of iron based alloys are generally classified into two categories according to their effect on the stability of austenite. The first class of alloying elements are austenite stabilizers that widen the temperature range for stable austenite by decreasing the austenite-to-ferrite transformation temperature. Examples of austenite stabilizers are carbon, manganese, nitrogen, nickel, and cobalt. Ferrite stabilizers include metallic elements such as molybdenum, vanadium, niobium, chromium or aluminum and non-metallic elements such as silicon, phosphorus or sulphur. One has to note, that in addition to thermodynamic factors, alloying elements also influence transformation kinetics.

Typically, alloying elements segregate to austenite grain boundaries and lower their energy, thereby delaying the nucleation of new phases upon cooling. Moreover, they hinder interface motion through particle pinning [25] and solute drag [26], both of these lowering the interface mobility and the effective driving force for phase transformations. A combination of these factors results in retardation of the austenite-to-ferrite transformation. Thus, the formation of bainite and martensite is more likely to occur.
As stated above, the properties of line pipe steels depend on a combination of alloy composition and processing strategy. Nb is the key micro-alloying element in thermo-mechanical controlled processing (TMCP) as it strongly retards recrystallization in hot rolled austenite, thereby enabling rolling practices in the non-recrystallization regime. Figure 2-3 schematically shows the concept of thermo-mechanical controlled processing and the influence of Nb on the microstructure evolution comparing a Nb-free steel to a Nb-added steel. While Nb-microalloyed line pipe steels generally contain Ti to impede austenite grain growth by particle pinning of TiN at high temperatures, the schematic focuses on the influence of Nb precipitation in the Nb-added steel. Following the schematic from left to right, Nb continuously precipitates with decreasing temperature during the rolling process. Large precipitates in the order of 100-300 nm inhibit austenite grain growth at high temperatures through particle pinning. In later stages smaller precipitates in the range of 50 nm retard or prevent recrystallization of the deformed austenite leading to highly deformed pancaked austenite. Comparing the ferrite grains formed from the fully recrystallized austenite in the Nb-free steel to the ferrite grains transformed from in the Nb-added steel, grain refinement is achieved due to additional nucleation sites at ledges or deformation bands in the pancaked austenite. Remaining Nb continues to precipitate in ferrite during cooling, contributing to the strength of the material through precipitation hardening.
Figure 2-3: Schematic showing the influence of Nb on microstructure evolution during thermo-mechanical controlled processing (TMCP); reprinted from ref. [27] with permission of IOP Publishing

Figure 2-4 shows the strong influence of Nb on the non-recrystallization temperature compared to vanadium. Other micro-alloying elements such as Ti and Al are also known to increase the non-recrystallization temperature, however, less efficient than Nb. According to Cuddy and Raley [28] alloying additions of Nb below 0.08 wt. % are sufficient to increase the non-recrystallization temperature reach temperatures in the finish rolling regime of low-carbon steels leading to strongly pancaked austenite prior to cooling which offers additional nucleation sites for ferrite formation, as seen in Figure 2-3, promoting a fine ferrite grain structure of the as-hot rolled material.
Figure 2-4: The effect of Nb microalloying additions on the non-recrystallization temperature of austenite in a low-carbon -Nb- and –Mo steels; reprinted from [29] with permission of Springer

The advanced alloying strategies of line pipe steels based on Nb-Ti or Nb-Ti-V concepts, which can include further microalloying elements such as Mo, result in complex precipitates. A variety of precipitates comprised of different morphologies and dimensions is found in state-of-the-art high strength line pipe steel [7], [11], [30]–[34] and several advantages can be gained from the interaction of different carbide or nitride forming species.

Line pipe steels generally contain an under-stoichiometric ratio of Ti and N (less Ti) to obtain TiN with sizes in the range of 20 to 100 nm that provide efficient pinning of austenite grain boundaries. In addition to Ti-rich particles, a second family of coarser precipitates has been observed with irregular shape and sizes in the range of 5 to 100 nm [11], [34]. Most of these precipitates are found to be Nb-rich carbonitrides and a small amount of them is identified as Mo₂C.
TiN has a low solubility in austenite and ferrite and is very stable even at high temperatures. It is assumed to form in the melt prior to solidification [34] and is therefore suitable to limit austenite grain growth during processing and within the heat affected zone close to the fusion line [11], [33], [35]. In steels containing Ti, Nb, and Mo large cubic TiN precipitates serve as nucleation sites for fine Nb and/or Mo containing precipitates that nucleate as spherical caps on one or more faces of the TiN core. Such a combination of precipitates is defined as complex precipitates [32], [34]. An example is shown in Figure 2-5a, where a coarse Ti precipitate (1) acts as nucleation site for smaller Ti/Nb- and Nb-rich precipitates (2)-(4). The precipitates formed at lower temperatures are typically Nb-rich carbides or carbonitrides if sufficient nitrogen is available after TiN and/or AlN precipitation. Nb-rich precipitates may contain further alloying elements, e.g. Mo. Nucleation of NbC requires heterogeneous nucleation sites such as grain boundaries, dislocations, or second phase particles [36].

Figure 2-5: Precipitates in X80 steel; a) Coarse Ti- precipitate (1) with Ti/Nb- rich (2, 3) and Nb-rich (4) precipitates; b) Finer Nb-rich precipitates; c) very fine Nb-rich precipitates; reprinted from ref. [37] with permission of the author

As Mo delays the Nb precipitation in austenite, more Nb is available to from fine NbC in ferrite, potentially contributing to precipitation strengthening. Steels containing Nb and Mo typically exhibit fine and uniformly distributed MC-type carbides. Some of the Nb-rich precipitates are located at grain boundaries. Finer particles with sizes of 1 to 3 nm are
homogeneously distributed within grains [11], [34], [38] and along sub-grain boundaries, Figure 2-5c. Vanadium is another frequent micro-alloying addition and forms almost no precipitates in austenite and is therefore available for precipitation hardening during or after the austenite-to-ferrite transformation [39].

2.3 Transformation products in low-carbon steels

2.3.1 Polygonal ferrite/ pearlite

Polygonal ferrite forms at high temperatures when the austenite is cooled at sufficiently low cooling rates. Ferrite nucleation starts below the \( \text{Ae}_3 \) temperature at grain boundaries and continues to grow along austenite grain boundaries resulting in grain boundary allotriomorphs, followed by growth into equiaxed grains [40]. Carbon is rejected from growing ferrite into the surrounding austenite as the maximum solubility in ferrite is significantly lower with 0.02 wt. %. Consequently, austenite is enriched with carbon and different concentrations arise in ferrite and austenite. Ferrite growth is thus primarily controlled by long-range diffusion of carbon atoms. In low-carbon steels the rate controlling mechanism shifts from a diffusion controlled mechanism to a mixed-mode regime, i.e. both long range carbon diffusion and interface related reactions such as solute drag control the interface propagation [40]–[42].

Ferrite formation is often accompanied by pearlite, when the remaining austenite approaches the eutectoid composition and consists of colonies of alternating lamella of ferrite and cementite. Carbon diffusion is the rate controlling parameter for pearlite formation, which requires sufficiently high temperatures. In low-carbon steels, pearlite nucleates at the austenite-ferrite interface followed by subsequent lamellar growth of a pearlite colony into austenite. As the transformation temperature is lowered the driving pressure for the reaction is increased but the diffusivity of carbon is decreased such that the pearlite inter-lamellar spacing is reduced.
2.3.2 Irregular/ quasi polygonal ferrite

Irregular ferrite forms at lower temperatures than polygonal ferrite and therefore contains a higher dislocation density resulting from the volume change during the transformation of the face-centred-cubic (FCC) to the body-centred cubic (BCC) structure. Irregular ferrite mainly nucleates heterogeneously at grain boundaries and the transformation can be accomplished by short-range diffusion across the transformation interface. The partitioning of interstitial or substitutional atoms, which may occur at the migrating interfaces, results in irregular grain boundaries and substructures [40], [42], [43]. The highly dislocated substructures and retained austenite or martensite/austenite constituents entrapped in irregular ferrite crystals can be observed under the optical microscope. The temperature range in which irregular ferrite forms is intermediate to the high temperatures of polygonal ferrite formation and the bainite start temperature [44].

2.3.3 Upper and lower bainite

Bainite exhibits characteristics of diffusional transformations such as the carbide precipitation in upper and lower bainite, while the crystallography, i.e. the orientation relationship with the parent austenite, is found to be a near Kurdjumov-Sachs orientation relationship as it is the case for martensitic transformation products [45]. This has led to a controversy about its transformation mode, i.e. the changes in composition at the onset of the bainite reaction, the growth mechanism of the ferritic component and the source of carbide precipitation. Two main schools of thought are still present, consisting of those who believe that bainite is a diffusional or reconstructive transformation product and those who believe that bainite forms by a mechanism which is essentially displacive in nature. The discussion has provoked numerous papers questioning the arguments of the respective opponents rather than bringing new experimental evidence [46]–[52]. In the following a brief overview of the cornerstones in the discussion about the bainite reaction is given before its morphology is described in more detail.
The term bainite was first introduced several years after Bain and Davenport [53] described their observations resulting from improvements to the interrupted isothermal transformation technique and constructed the first time-temperature-transformation diagram in 1930. Bainite was described as an acicular mixture of ferrite and cementite and Zener [54] introduced the hypothesis that bainite forms as supersaturated solution by the migration of a glissile interface similar to martensite. To explain the observed incomplete transformation, he suggested that carbon is rejected from the supersaturated ferrite into the remaining austenite before the next unit of bainite forms leading to carbon enrichment of the austenite as if bainitic ferrite had never been supersaturated with carbon.

While Zener did not provide any experimental evidence Ko and Cottrell [55] reported a surface relief in lower bainite supporting Zener’s hypothesis by assuming the surface relief was due to dislocation glide in connection with a coordinated movement of atoms across the interface. However, at the same time they reported that the transformation rate was much lower than that of martensite, suggesting that the interface migration is diffusion controlled. Hultgren [56] on the other hand concluded, based on microstructure observations, that bainite forms with a ledge wise growth mechanism.

It was soon shown that Widmanstätten ferrite also gives a surface relief [57] and today there seems to be wide agreement [58]–[60] that a surface relief is not sufficient evidence to prove a martensitic type of growth by shear. It was also suggested that bainite sub-units form successively by a displacive mechanism under faster transformation rates than the observed overall rates and it is now accepted that a displacive mechanism does not always lead to rapid and diffusionless growth [61].

Several studies offered explanations for the observed growth rates of bainite as controlled by carbon diffusion [62] and in a debate between Hehemann, representing the opinion of the displacive theory, and Aaronson and Kinsman, representing the diffusional growth
theory, Heheman concludes “It is difficult to argue against these diffusion controlled models.” [46].

In subsequent years the discussion about the growth mechanism of bainite slowed down until Bhadeshia and Edmonds [63] provided new arguments based on microstructural observations and thermodynamic analysis claiming that bainite grows by a displacive transformation mechanism; the growth being accompanied by a shape deformation which is an invariant–plane strain with a large shear component. They conclude that the transformation is diffusionless but carbon atoms partition into the residual austenite, shortly after growth is arrested. The precipitation of carbides is therefore considered a secondary event similar to the tempering of martensite.

The classification of bainite into upper and lower bainite is commonly accepted irrespective of the uncertainties concerning the transformation mechanism at the interface [61]. Both types of bainite consist of aggregates of plates or sheaves of ferrite, separated by untransformed austenite, cementite or martensite. Bainitic ferrite comprises a very high dislocation density and upper bainite forms at higher temperatures, resulting in a series of parallel ferrite laths separated by continuous or semi-continuous layers of carbide or retained austenite.

Upper bainite exhibits a large number of low-angle misorientation boundaries, while lower bainite exhibits a higher proportion of high-angle misorientations [64]. Lower bainite forms at lower temperatures where ferrite takes the form of laths or plates and contains an intra-ferritic distribution of carbide particles due to limited diffusivity [65]. Both types of bainitic sheaves may appear similar under optical microscopy so that higher resolutions or additional information is needed for their distinction.

In general, carbides are likely to be finer and the etching response darker in lower bainite. Figure 2-6 shows examples of thin foil electron micrographs of upper bainite formed at 550°C in a 0.1wt. % C steel, showing sheaves of bainitic ferrite and layers of carbides, and
lower bainite formed at 300°C in a 0.6wt. % C steel, showing intra-ferritic carbides, respectively.

![Figure 2-6](image)

**Figure 2-6:** a) Upper bainite in 0.1% C steel transformed at 550°C; b) Lower bainite in 0.6% C steel transformed at 300°C; reprinted from ref. [66] with permission of Springer

The intra-ferritic carbides in lower bainite adhere to the same orientation relationship as those in tempered martensite with the difference that three variants are found in martensite while lower bainite contains carbides of one orientation as can be seen in Figure 2-6.

### 2.3.4 Orientation relationships (OR) of bainitic transformation products and austenite

Bainitic transformation products are found to show a particular orientation relationship with the parent austenite which offers a quantitative distinction of different types of bainite independent of morphology and carbide distribution. An OR describes the misorientation between two crystallographic lattices and can be quantified by parallel planes and directions of parent and product phases [67]. Several crystallographic orientation relationships have been observed for the $\gamma \rightarrow \alpha$ transformation in steels, including the Bain OR, Pitch OR, Nishiyama-Wassermann OR, Kurdjumov Sachs OR and Greninger-Trojano OR. The misorientation between these ORs is small and a distinction, especially when analyzing experimental data, is rather difficult. Table 2-1 gives an overview of these orientation relationships.
Table 2-1: Overview of orientation relationships between parent FCC and product BCC phase

<table>
<thead>
<tr>
<th>Orientation relationship</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kurdjumov-Sachs</td>
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<tr>
<td>Bain</td>
</tr>
<tr>
<td>Nishiyama-Wassermann</td>
</tr>
<tr>
<td>Pitch</td>
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<tr>
<td>Greninger-Troiano</td>
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<tr>
<th>Orientation relationship</th>
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<tbody>
<tr>
<td>Kurdjumov-Sachs</td>
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<tr>
<td>Nishiyama-Wassermann</td>
</tr>
<tr>
<td>Pitch</td>
</tr>
<tr>
<td>Greninger-Troiano</td>
</tr>
</tbody>
</table>

The most intuitive transformation path from the FCC to the BCC crystal structure was proposed by Bain in 1924. Although the Bain OR between the FCC and BCC is the simplest OR, it is never observed experimentally in steels but can be considered a first approximation when considering the FCC to BCC transformation [68], [69]. Most experimental studies report a near Kurdjumov-Sachs (KS) or Nishiyama-Wassermann (NW) orientation relationship.

Figure 2-7 shows a schematic of the Bain, KS and NW orientation relationship between the FCC and BCC lattice represented in grey and white, respectively. The Bain relation includes a contraction of the BCC lattice along the z-axis by about 21% and expansions around the x- and y-axes by about 12% to obtain the transformation structure. Both the Nishiyama-Wasserman and the Kurdjumov-Sachs orientation relationship are defined by a \(\{111\}_\gamma\) plane parallel to a \(\{110\}_\alpha\) plane, with certain parallel directions within these planes. The KS OR requires a \(<110>_\gamma\) direction within the \(\{111\}_\gamma\) plane to be parallel to a \(<111>_\alpha\) direction within the \(\{110\}_\alpha\) plane. The NW OR only differs in the parallel directions, requiring a \(<112>_\gamma\) direction parallel to \(<110>_\alpha\).
According to the cubic symmetry the KS orientation relationship yields 24 variants resulting from four \{111\}_\gamma planes, each being parallel to one \{110\}_\alpha plane and containing three different \langle110\rangle_\gamma directions. Each \langle110\rangle_\gamma direction can be parallel to two different \langle111\rangle_\alpha directions.

Figure 2-7: Schematic of orientation relationships between the austenite (FCC) and (BCC) phases; a) Bain OR; b) Nishiyama–Wassermann OR; c) Kurdjumov–Sachs OR; black arrows indicate part of the motion initiating the transformation; dashed arrows indicate the invariant direction which is shared by the parent and product phases, after Sandoval et al. [68] with permission of IOP Publishing

Depending on austenite conditioning and cooling path different selections of the 24 KS variants may occur during the austenite decomposition and this can, in particular, be used to discriminate different bainitic transformation products. With increasing transformation temperature, the experimentally observed deviation from the close packed planes according to the exact KS OR increases, while the deviation from the close packed direction only differs slightly.
Table 2-2 lists the 24 KS OR variants according to their close packed plane. The variants can be grouped into three Bain groups with the following correspondence: B1: ([001]γ//[001]α, [100]γ//[110]α, [010]γ//[110]α); B2: ([100]γ//[001]α, [010]γ//[110]α, [001]γ//[110]α); B3: ([010]γ//[001]α, [001]γ//[110]α, [100]γ//[110]α).

Table 2-2: Twenty-four variants according to KS OR grouped into four close packed plane groups and intervariant misorientation with respect to variant V1

<table>
<thead>
<tr>
<th>Variant no.</th>
<th>Plane parallel</th>
<th>Direction parallel</th>
<th>CP group</th>
<th>Bain group</th>
<th>Misorientation from V1 (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1</td>
<td>(111)γ//[011]α</td>
<td>[101]γ//[110]α</td>
<td>CP1</td>
<td>B1</td>
<td>00</td>
</tr>
<tr>
<td>V2</td>
<td>(111)γ//[011]α</td>
<td>[011]γ//[110]α</td>
<td>CP1</td>
<td>B2</td>
<td>00</td>
</tr>
<tr>
<td>V3</td>
<td>(111)γ//[011]α</td>
<td>[011]γ//[110]α</td>
<td>CP1</td>
<td>B3</td>
<td>00</td>
</tr>
<tr>
<td>V4</td>
<td>(111)γ//[011]α</td>
<td>[101]γ//[110]α</td>
<td>CP1</td>
<td>B4</td>
<td>00</td>
</tr>
<tr>
<td>V5</td>
<td>(111)γ//[011]α</td>
<td>[101]γ//[110]α</td>
<td>CP1</td>
<td>B1</td>
<td>00</td>
</tr>
<tr>
<td>V6</td>
<td>(111)γ//[011]α</td>
<td>[011]γ//[110]α</td>
<td>CP1</td>
<td>B2</td>
<td>00</td>
</tr>
<tr>
<td>V7</td>
<td>(111)γ//[011]α</td>
<td>[101]γ//[110]α</td>
<td>CP1</td>
<td>B3</td>
<td>00</td>
</tr>
<tr>
<td>V8</td>
<td>(111)γ//[011]α</td>
<td>[011]γ//[110]α</td>
<td>CP1</td>
<td>B4</td>
<td>00</td>
</tr>
<tr>
<td>V9</td>
<td>(111)γ//[011]α</td>
<td>[101]γ//[110]α</td>
<td>CP1</td>
<td>B1</td>
<td>00</td>
</tr>
<tr>
<td>V10</td>
<td>(111)γ//[011]α</td>
<td>[011]γ//[110]α</td>
<td>CP1</td>
<td>B2</td>
<td>00</td>
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<td>CP1</td>
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<tr>
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<td>(111)γ//[011]α</td>
<td>[101]γ//[110]α</td>
<td>CP1</td>
<td>B1</td>
<td>00</td>
</tr>
<tr>
<td>V14</td>
<td>(111)γ//[011]α</td>
<td>[011]γ//[110]α</td>
<td>CP1</td>
<td>B2</td>
<td>00</td>
</tr>
<tr>
<td>V15</td>
<td>(111)γ//[011]α</td>
<td>[101]γ//[110]α</td>
<td>CP1</td>
<td>B3</td>
<td>00</td>
</tr>
<tr>
<td>V16</td>
<td>(111)γ//[011]α</td>
<td>[011]γ//[110]α</td>
<td>CP1</td>
<td>B4</td>
<td>00</td>
</tr>
<tr>
<td>V17</td>
<td>(111)γ//[011]α</td>
<td>[101]γ//[110]α</td>
<td>CP1</td>
<td>B1</td>
<td>00</td>
</tr>
<tr>
<td>V18</td>
<td>(111)γ//[011]α</td>
<td>[011]γ//[110]α</td>
<td>CP1</td>
<td>B2</td>
<td>00</td>
</tr>
<tr>
<td>V19</td>
<td>(111)γ//[011]α</td>
<td>[101]γ//[110]α</td>
<td>CP1</td>
<td>B3</td>
<td>00</td>
</tr>
<tr>
<td>V20</td>
<td>(111)γ//[011]α</td>
<td>[011]γ//[110]α</td>
<td>CP1</td>
<td>B4</td>
<td>00</td>
</tr>
<tr>
<td>V21</td>
<td>(111)γ//[011]α</td>
<td>[101]γ//[110]α</td>
<td>CP1</td>
<td>B1</td>
<td>00</td>
</tr>
<tr>
<td>V22</td>
<td>(111)γ//[011]α</td>
<td>[011]γ//[110]α</td>
<td>CP1</td>
<td>B2</td>
<td>00</td>
</tr>
<tr>
<td>V23</td>
<td>(111)γ//[011]α</td>
<td>[101]γ//[110]α</td>
<td>CP1</td>
<td>B3</td>
<td>00</td>
</tr>
<tr>
<td>V24</td>
<td>(111)γ//[011]α</td>
<td>[011]γ//[110]α</td>
<td>CP1</td>
<td>B4</td>
<td>00</td>
</tr>
</tbody>
</table>

The maximum misorientation within one Bain group is 10.5° between variant 1 and 2. Variants belonging to different Bain groups are divided by high angle grain boundaries.

Gourges at al. [70] defined crystallographic bainite packets based on electron backscatter diffraction (EBSD) studies. Crystallographic packets comprise parallel ferrite laths that are separated by high-angle boundaries (defined as >10°) and often contain several low-angle packets. These packets result from variant selection during the γ→α transformation.

Takayama et al. [71] quantitatively investigated the temperature dependence of variant pairing in bainite and martensite of low-carbon low-alloy steel. They found three types of
microstructures formed in the temperature range between 580 and 450°C and called them type I, II and III. A schematic of the arrangement of Bain groups with a prior austenite grain and the resultant HAGBs and LAGBs for type I, II, and III is shown in Figure 2-8.

Type I is formed at higher temperatures and is comprised of regions belonging to the same Bain group. Variants with low misorientations such as V1/V4/V8 are favored within that Bain group. This results in regions without high angle grain boundaries (HAGBs) as only low angle grain boundaries are formed within each Bain group. At lower temperatures, i.e. 450°C in their study, type II bainite is formed which is characterized by variants belonging to the same close packed plane (CPP) group while different Bain groups form adjacently. Each CPP group contains 6 variants, 2 of each Bain group. While variants of all Bain groups are found, the twin related variant pair V1/V2 with an axis angle misorientation of [011]60° is prevalent. Generally variants of different Bain groups are divided by HAGBs leading to an increase of HAGB area in type II compared to type I. Bainite transformed at intermediate temperatures shows a mixture of type I and II.

![Schematic of variant pairing within one prior austenite grain for different transformation products indicating the most frequently occurring variant pairs.](image)

Figure 2-8: Schematic of variant pairing within one prior austenite grain for different transformation products indicating the most frequently occurring variant pairs. a) bainite formed at 580°C; b) bainite formed at 450°C; and c) lath martensite. Each color represents one Bain group, high and low angle grain boundaries are represented in black and white, respectively. Reprinted from ref. [71] with permission of Elsevier.
Type III is classified as martensite. Similarly to bainite of type II, variants of the same CPP group are formed adjacently however, within one CPP group variants of the same Bain group are formed next to each other resulting in an increased amount of LAGBs.

The temperature dependence of variant pairing in type I and II is explained based on the driving pressure for bainite formation. The driving pressure for transformation is small at high transformation temperatures, resulting in a specific variant selection. Two factors play an important role in the selection of variants during austenite decomposition, i.e. the interface energy of the newly formed phase and the self-accommodation of transformation strain in the austenite surrounding the newly formed bainite laths. At higher temperatures the austenite is softer and can more easily accommodate transformation strain, therefore, the grain boundary area becomes the dominating energy and variants within one Bain group are supposed to be favored due to the reduced grain boundary energy between low misorientation axes. The strength of austenite increases with decreasing temperature, which encourages the formation of different variants and self-accommodation of the transformation strain.

Some variants belonging to the same Bain group are observed to grow simultaneously within one prior austenite grain even though they are separated by a variant belonging to a different Bain group [72]. This was observed by Terasaki et al. via laser scanning confocal microscopy during continuous cooling simulation in a steel containing 0.1C-1.0Ni-0.8Mn-0.4Mo-0.04V (in wt. %). The authors suggest that variants belonging to the same Bain group require the same amount of driving pressure for the Bain deformation along the <001> axis and therefore transform at the same time during cooling. They show that certain boundaries between variants that do not form at the same time promote blocky martensite/austenite [73]. These boundaries are found between V1/V4/V8 and are defined by <011> 10.53°. This can be explained by the carbon enrichment of the remaining austenite during the phase transformation. While certain bainite variants grow at higher temperatures, the carbon concentration in the surrounding austenite increases and stabilizes the austenite,
which remains as blocky martensite/ austenite constituents after the formation of an adjacent variant that is separated by LAGBs.

2.3.5 Martensite

The martensitic transformation requires a very high driving force and occurs during rapid cooling at temperatures below the martensite start temperature. The transformation of the cubic face centred austenite crystal lattice into the body centred tetragonal crystal lattice of martensite occurs by shear which requires atoms to move considerably less than one interatomic distance. The coordinated movement of atoms induces an increase in volume of about 3% accompanied by a shape change which is observed as a relief structure on the surface of transformed martensite. Elastic tensions induced by the shape change can be accommodated or reduced by slip or twinning. The high dislocation or twin density is responsible for the substantially increased hardness of martensite [74].

The morphology of martensite depends on the alloy composition and in particular on the carbon content. Stormvinter et al. [75] studied de-carburized samples with a carbon gradient to isolate the influence of carbon content on the morphology of martensite units formed during cooling. They found that a lath morphology is dominant below 0.6 wt. % C and plate martensite is dominant above 1.0 wt. % C. Martensite laths consist of parallel lath-shaped units a few µm long and less than 1 µm thick with a high density of dislocations, while martensite plates are characteristically tilted with respect to their habit plane and the apparent homogeneous nature of this distortion is best described as an invariant plane strain [45]. Due to the absence of long range diffusion there is no change in composition involved and iron and alloying elements remain in the same relative lattice positions.
2.3.6 Martensite/Austenite (M/A)

During the decomposition of austenite into ferrite, i.e. irregular ferrite or bainite, in continuously cooled low-carbon and microalloyed steels, austenite is locally enriched with carbon during the transformation and is thereby stabilized. Hence, some of the parent austenite does not transform and may be retained to room temperature or partially transform below the martensite start temperature to produce the martensite/austenite constituent [76], [77]. Ferritic or bainitic transformation products may take many morphologies and retained austenite or M/A constituents mirror the shapes of the matrix structure in which they are embedded [40]. For steels containing overall carbon contents greater than 0.06 wt. %, the carbon content in the M/A constituents has been found experimentally to be about 1.1–1.3 wt. % [78].

A detailed analysis of the M/A constituent in a Nb-microalloyed steel by Shanmugam et al. [79] reveals alternative layers of martensite and retained austenite within M/A constituents. TEM observations showing the morphology and selected area diffraction pattern, revealing the orientation relationship between austenite and martensite are shown in Figure 2-9.

Li and Baker [78] reported four different morphologies of M/A particles including blocky like particles, also described as islands [15], [80], [81], connected or nearly connected particles along prior austenite grain boundaries, elongated stringer particles along bainitic ferrite laths and M/A-C particles consisting of M/A and a second phase, i.e. carbide and ferrite. M/A islands were reported with sizes between 0.5 and 5 µm and elongated particles were found with a length of up to 10 µm and a width between 0.2 to 2 µm.
Figure 2-9: a) Bright field TEM micrograph of M/A constituent; b) Dark field TEM micrograph of the same area; c) Selected area diffraction pattern analysis of retained austenite and martensite; d) Schematic of layers within M/A constituent; reprinted from ref. [79] with permission of Elsevier

Terasaksi and Komizo [73] observed blocky M/A between particular variant pairs, i.e. at the boundaries of close packed planes and correlated the shape and composition of M/A to the amount of low angle grain boundaries (LAGB) within a given Bain group. For a low LAGB density the M/A particles are mostly elongated retained austenite with little martensite. Within a Bain group comprised of a high LAGB density the M/A constituents contain a higher fraction of martensite and are blocky. They suggest that the morphology of bainitic ferrite influences the stability of austenite which governs the formation process of M/A.
2.4 The heat affected zone (HAZ)

2.4.1 HAZ formation

In addition to superior mechanical properties, line pipe steel grades are designed to feature good weldability [13]–[15]. When pipe sections are girth welded in the field the heat affected zone experiences a rapid thermal cycle, depending on the welding procedure and distance from the fusion line, such that the resulting microstructure in the HAZ can deviate substantially from that of the base metal. Depending on peak temperatures and dwelling times austenite grain growth and dissolution of carbonitrides may occur [35]. As a result, the austenite grain size and the content of microalloying elements such as Nb in solution, which determine the austenite decomposition upon cooling and thus the resulting microstructure, vary significantly across the HAZ. Figure 2-10 shows different sections of the HAZ resulting from the temperature gradient during the welding process.

![Figure 2-10: Sections of the heat affected zone perpendicular to the fusion zone and relevant temperature ranges in the Fe-Fe₃C phase diagram; reprinted from [82] with permission of Elsevier](image)

High peak temperatures close to the fusion zone lead to the coarse grained heat affected zone (CGHAZ). Full or partial dissolution and coarsening of microalloying precipitates
reduces grain boundary pinning and leads to substantial austenite grain growth [28]. Due
to cooling rates in excess of 100°C/s in addition to high peak temperatures and large
austenite grain sizes, the transformation temperature in the CGHAZ is well below the \( A_{\text{e}3} \) temperature which promotes low temperature transformation products such as lower
bainite and martensite. Martensite formation in the heat affected zone is generally
undesirable as it may lower the weld toughness and increase the risk of hydrogen cracking
[83].

The fine grained heat affected (FGHAZ) also undergoes full austenitization at lower peak
temperatures where limited austenite grain growth results in a microstructure comprised of
ferritic transformation products including carbon-rich second phases. Partial austenite
formation in the intercritical heat affected zone (ICHAZ) promotes the formation of
martensite/austenite constituents. A major concern is the reheating of the CGHAZ into the
intercritical region in multi-pass welding scenarios as the intercritical coarse grained heat
affected zone is prone to martensite formation [84]. Far away from the fusion zone, the
peak temperatures are below the \( A_{\text{e}3} \) temperature and no transformation takes place in the
subcritical heat affected zone (SCHAZ) while tempering of the base material may occur to
some extent.

2.4.2 The significance of Nb and Mo for the austenite decomposition

While Nb is primarily added as part of the thermo-mechanical controlled processing, Nb
in solid solution has a strong effect on the transformation start temperature. A shift of the
transformation start to lower temperatures is consistently reported for Mo and Nb
containing steels [85]–[87]. Different suggestions are available in the literature for the
mechanisms by which Nb affects the transformation kinetics. In particular, it is assumed
that Nb atoms segregate to the prior austenite grain boundaries where they lower the grain
boundary energy which in return retards the nucleation of ferrite [87]. In addition, solute
Nb and Mo strongly reduce the carbon activity in austenite which leads to a decrease in the
ferrite growth rate [32], [88], [89]. Since Mo retards the Nb precipitation, their individual effects on reducing the carbon activity are additive in NbMo steels [16].

In addition to Nb in solution, Nb bearing precipitates can also interfere with the migrating interface by employing a pinning pressure, which is effective in retarding the recrystallization in austenite [86], [90]. However, particularly in ferrite, the effect of Nb in solution seems to be more prominent. Precipitation of niobium-containing particles in austenite therefore lowers the overall retarding effect of Nb on austenite decomposition due to the reduced amount of Nb in solution and thus leads to the formation of higher temperature transformation products compared to Nb in solid solution [87]. Given the temperature gradient along the HAZ, Nb dissolution varies considerably which promotes austenite grain growth in the CGHAZ while Nb remains precipitated in the FGAHZ contributing to microstructural variations in the HAZ of microalloyed steels.

Park et al. [91] investigated the dissolution and precipitation kinetics of Nb(C,N) in both strained and strain-free austenite of a Nb-microalloyed steel containing 0.08C- 1.21Mn- 0.2Si- 0.038Nb – 0.0017N (in wt. %) using electrical resistivity. The dissolution temperature for a holding time of 600 s was found to be 1230°C. This value is higher than the calculated value for the Nb(C,N) dissolution temperature using Irvine’s equation (1144°C) or Thermo-Calc (1097°C) which is due to the shorter holding time of 600 s compared to 1 hour in Irvine’s approach or equilibrium conditions assumed in Thermo-Calc.

The relative mole fraction of Nb(C,N) re-precipitating after full dissolution was obtained by applying the lever rule to the measured electrical resistivity obtained during isothermal holding at different temperatures. Details of the resistivity measurements can be found elsewhere [92]. Figure 2-11 shows the variation of the precipitated fraction of Nb(C,N) at different holding temperatures. Nb(C,N) precipitation is fastest at 900°C and after 20 min more than 90% of Nb is precipitated.
Mo decreases the activity and diffusivity of carbide forming species such as Nb and therefore delays the precipitation of NbC in austenite [93]. Mo additions also suppress the formation of pearlite or polygonal ferrite during continuous cooling, similar to the effect of Nb in solid solution [94]. The resultant finer and sub-structured microstructure constituents result in increased strength compared to polygonal structures [32], [95] whereas the increased hardenability and promotion of martensite/ austenite (M/A) constituents can be detrimental to the resulting toughness [96].

Continuous cooling transformation studies have been carried out to capture the influence of alloy composition, cooling rate and deformation on the austenite decomposition in microalloyed steels. The influence of deformation is neglected here as it is not relevant for the HAZ. Isasti et al. [97] compared steels with varying amounts of Nb (i.e. 0.03 wt. % and 0.06 wt. %), with and without Mo addition (0.31 wt. %), with a plain carbon steel. A shift to lower transformation temperatures was observed for the 0.03 wt. % Nb-steel in comparison with the plain carbon steel, reducing the amount of polygonal ferrite formed.
The transformation was not further delayed with the addition of 0.06 wt. % Nb, which suggests that a saturation of the effect of Nb was approached. The addition of 0.031 wt. % Mo to the 0.06 wt. % Nb-steel causes a shift in the transformation temperature for cooling rates between 10 and 50°C/s while only a slight shift in the transformation temperature is observed at slow cooling rates between 0.1 and 5°C/s and at very high cooling rates (100°C/s – 200°C/s). When transforming form the undeformed austenite, the appreciable amount of Nb outweighs the effect of Mo, which is in agreement with similar observations by Lee et al [31] and Junhua et al [96].

Cizek et al. [42] report a reduction of the polygonal ferrite field and a noticeable decrease for the transformation start temperatures of acicular structures caused by the addition of niobium and molybdenum, respectively. The study conducted by Zhao et al. [95] shows that the addition of 0.32 wt. % Mo (at a constant content of Nb of 0.04-0.045 wt.%) has an evident effect on the transformation start temperature, suppressing or delaying the formation of polygonal ferrite and pearlite.

Zhang et al. [98] investigated the austenite-to-ferrite transformation during simulated welding thermal cycles with short dwelling times at 1350 ºC and non-linear cooling with varying $t_{8.5}$ (the time between 800°C and 500°C). When adding 0.026 wt. % Nb the transformation start temperature reportedly decreased consistently by 20°C for a $t_{8.5}$ between 10s and 300s. At faster cooling, the transformation start temperature was not strongly affected by the Nb addition. The authors suggest that Nb has not been fully dissolved during heating and the short dwelling time at the peak temperature and therefore has a negligible effect at fast cooling while slower cooling enables further dissolution prior to the austenite-to-ferrite transformation.

2.4.3 Mechanical properties of the HAZ

The mechanical properties of the HAZ often deviate strongly from the well-designed base material due to the variation in microstructure constituents as mentioned above. Major
concerns are the toughness of the CGHAZ and the intercritical coarse grained HAZ, as well as the influence of hard phases such as M/A constituents [80], [99], [100]. Figure 2-12 shows an overview of microstructural features influencing the performance of the HAZ in correlation with crack initiation and propagation. The schematic shows a large martensite/austenite constituents as crack initiation site, while packet boundaries deflect the crack. Fine laths structures with a high density of packet boundaries are therefore desirable. Cracks initiating at several large M/A constituents can connect and lead to cleavage fracture.

![Schematic showing microstructure feature of the HAZ microstructure in correlation with crack imitation and propagation](image)

**Figure 2-12:** Schematic showing microstructure feature of the HAZ microstructure in correlation with crack imitation and propagation; reprinted from ref. [101] with permission of Elsevier

Several researchers studied the strength and toughness of the base material [102], [103] and the HAZ [23], [64], [101], [104]–[106]. A significant amount of work has been done on the influence of M/A on the performance of HAZ microstructure, especially in regard to the resistance to fracture, i.e. [107]–[109]. Crack initiation as well as de-cohesion of M/A constituents from the matrix have been observed [78].
Long et al. [64] related the change in mechanical properties caused by M/A features to the change in morphology of retained austenite for a constant M/A volume fraction. Thin austenite films along prior austenite grain boundaries result in higher impact toughness than small blocky retained austenite which is found to have a lower mechanical stability [110]. Li et al. [111] found a correlation between the prior austenite grain size and the resultant M/A constituents. While the M/A fraction was not influenced by the prior austenite grain size, coarse austenite grains promoted coarse M/A along prior austenite grain boundaries and a refinement of the M/A phase was achieved by refining the prior austenite grain size.

Especially the presence of necklace type M/A noticeably increases the susceptibility of cleavage micro-crack nucleation. However, examples of M/A constituents acting as crack arrestor for secondary cracks have been observed and if the amount and size is low the effect of M/A less detrimental. A combination of the matrix microstructure and M/A constituents has to be considered when investigating the crack propagation [78].

The use of EBSD has become a valuable tool to correlate microstructural observations with the resultant mechanical properties. A correlation of the tensile properties based on EBSD data was proposed by Hell et al. [112] and crack propagation in the HAZ of X100 steel was investigated by Li et al. [110] using EBSD. Figure 2-13a shows the deflection of a crack at high angle grain boundaries in green (15 - 45°) and yellow (>45°). The magnified optical micrographs show broken M/A constituents at a prior austenite grain boundary.
Hutchinson et al. [113] considered two microalloyed steels that were subjected to heat treatments simulating the HAZ over a range of heat input conditions and cooling rates. The impact toughness was evaluated by means of Charpy impact tests. A range of microstructures that look rather similar under the optical microscope showed different toughness values. Further investigation involved EBSD, applying a five dimensional boundary analysis. They found that lower transformation products, which were mostly bainitic, comprise a high density of boundaries dominated by misorientations having \( <110 > \) and \( <111 > \) rotation axes and the habit planes of the ferrite laths close to \{110\}. The average spacing of these boundaries varied with steel composition and cooling rate. Decreased lath sizes resulted in decreasing toughness and the authors suggest that the close spacing between lath boundaries inhibits plasticity at stress concentrations and favors
initiation of fracture due to the high boundary density at \( \{110\}_\alpha \) planes as they are coinciding with the \( \{110\} \) slip plane in ferrite [113].

A modified Hall-Petch equation is often used including an average grain size obtained by EBSD to capture the tensile behavior of HSLA steels. Shukla et al. [114] used the linear intercept to successfully predict tensile strength of a thermo-mechanically processed ultra-low-carbon, high-molybdenum bearing steel. The investigated microstructures were a mixture of fine polygonal and irregular ferrite. The combined effect of dispersion strengthening caused by incoherent precipitate particles and dislocation strengthening was also considered to predict the yield strength.

Iza-Medina and Gutierrez [115] studied several types of microstructures in a C-Mn-Nb steel, which they classified as ferrite-pearlite, bainite, quenched and quenched and tempered structure. Starting from the Hall-Petch equation they included grain size measurements based on the misorientation angle obtained by EBSD to extend the equation to bainitic and martensitic microstructures. Additional strengthening mechanisms from Nb precipitation, free interstitial solutes and transformation dislocations were included. The estimated dislocation strengthening contribution worked well in the case of martensite while the dislocation density of bainite seemed to be consistently overestimated.

### 2.5 Microstructure modelling

#### 2.5.1 Overview

Phenomenological models to capture and predict the austenite decomposition are often based on experimental observations using dilatometry during isothermal or continuous cooling transformation. The isothermal kinetics of phase transformations is frequently described by the model proposed by Kolmogorov [116], Johnson and Mehl [117], and
Avrami [118], where the volume fraction $X$ of the newly formed phase is given by:

$$X = 1 - \exp(-bt^n) \quad (2-3)$$

This equation, describing sigmoidal growth, is known as the John-Mehl-Avrami-Kolmogorov (JMAK) equation, where $b$ is a temperature dependent rate parameter. The JMAK exponent $n$ is a factor that depends on the nucleation conditions and growth geometries. The parameters $b$ and $n$ are often empirically determined, and are reflective of growth and nucleation conditions. Commonly, the rate parameter $b$ is defined as a function of chemical composition, temperature, carbon supersaturation, prior austenite grain size, strain, and/or cooling rate.

To apply the JMAK equation to industrial processes including non-isothermal heat treatments, the JMAK equation can be adapted to the principle of additivity provided $n=\text{const.}$ by taking the derivative of equation (2-3) with respect to time [119]:

$$\frac{dX}{dt} = n(-b)^n (1-x) \left( \frac{1}{\ln(1-x)} \right)^{\frac{1-n}{n}} \quad (2-4)$$

A complete process model for hot strip rolling of various low-carbon microalloyed steels containing Nb-Ti-V as the main microalloying elements was proposed by Militzer et al. [120]. The model accounts for the effects of cooling rate, initial austenite grain size and retained strain on the austenite to ferrite transformation. The temperature at which 5% transformed is reached is taken as the transformation start temperature. The transformation start temperature model considers early carbon diffusion controlled growth of ferrite nucleated at austenite grain corners. A limiting carbon concentration in the remaining austenite is introduced above which ferrite nucleation is inhibited and the calculated transformation start temperature coincides with reaching the critical carbon content at all austenite grain boundary positions. Subsequent ferrite growth is then modelled using the JMAK equation, assuming additivity to be valid during the ferrite formation regime. A
transition temperature between polygonal and non-polygonal ferrite formation is empirically established as a function of retained strain for Nb/Ti-The transformation start model was later extended to include the solute drag effect of Nb on the austenite-to-ferrite transformation kinetics and a separate model was proposed to predict the bainite start temperature [121].

The JMAK approach in combination with Scheil's approach of additivity was recently applied to a vanadium-microalloyed steel containing 0.274C- 1.5Mn- 0.48Si- 0.12V-0.02Ti (in wt.%) by Azghandi et al. [122] to predict the fractions of ferrite, pearlite, and bainite, transformed during continuous cooling. The model consists of eight sub-models including ferrite transformation start temperature, ferrite growth, pearlite start temperature, pearlite growth, bainite start temperature, bainite growth, martensite start temperature and the resultant hardness. The model prediction of the austenite decomposition kinetics is in close agreement with the experimental observations and yields calculated hardness value within 7% of the experimentally measured hardness.

The growth kinetics of ferrite in Fe-C alloys can also be described by one-dimensional carbon diffusion models adopting spherical geometry, where the overall kinetics can be predicted reasonably well [123]. At lower carbon concentration (below 0.2 wt. % C) as it is the case for line pipe steels, it is important to also consider the interface reaction. In the mixed-mode modelling approach the mode of control is predicted to vary from a diffusion controlled mode at very low undercooling towards an interface controlled mode at high undercoolings [124]. A physically based austenite-to-ferrite transformation model for low-carbon steels was proposed by Fazeli and Militzer [125], with an emphasis that it can be applied to industrial heat-treatment paths. The model considers the carbon diffusion in the remaining austenite, the interface reaction, and solute drag.

In addition, meso-scale models, e.g. phase field model (PFM), cellular automata [126] and Monte Carlo [127] methods, provide insight into transformation mechanisms as well as
resulting grain structures. In particular, the phase field approach has recently emerged as a versatile tool to describe microstructure evolution, e.g. solidification, solid-state transformation, recrystallization and grain growth [128]. Interfacial parameters and nucleation scenarios are crucial input information that is frequently used in an empirical way to fit experimental observations thereby limiting the predictive capability of the PFM approach. Nevertheless, PFM simulations can provide invaluable qualitative and semi-quantitative insight into phase transformation mechanisms in steels with complex microstructural morphologies [129].

Schmitt et al. proposed a 3-dimensional phase field approach describing the deformation induced martensitic transformation at a loaded austenite surface [130]–[132]. Dislocation movement is modeled by a crystal plasticity setting using different slip systems. The model is able to predict several martensite variants and nucleation is triggered by plastic deformation followed by the autocatalytic formation of further martensitic plates.

A PFM that is applicable to rapid heat-treatment cycles relevant for the HAZ was developed for austenite grain growth in 2D and 3D taking the pinning/dissolution effects of Nb bearing particles into account by using an effective mobility concept [133]. In addition, a PFM was developed for the austenite decomposition and applied to the HAZ of X80 line pipe steel to predict the simultaneous formation of polygonal ferrite and bainite. The formation of carbide-free bainite is considered and a suitable anisotropy approach is proposed for the austenite-bainite interface mobility. The PFM is coupled with a carbon diffusion model and an effective interface mobility is introduced to implicitly account for the solute drag effect of Nb [134].
2.6 Summary of the literature review

High-strength line pipe steels have been subject to research for more than three decades and numerous studies have been conducted to individually investigate the influence of Nb and Mo on phase transformation. Both elements are reported to shift the austenite to ferrite transformation to lower temperatures, promoting non-polygonal microstructure constituents. It has been shown that the effect of Nb on phase transformation depends on whether it is precipitated or in solid solution. Further, it has been observed that Mo influences the precipitation kinetics of Nb and consequently the amount of Nb in solution. Models have been established to capture the austenite decomposition in Nb and Mo containing steels. However, the amount of Nb in solution depends on the austenitizing condition and the proposed models do not account for the resulting change in the influence of Nb on phase transformation. A comprehensive study dedicated to the systematic change of Nb in and out solution and the synergistic effect with Mo could not be found.

Complex microstructures are formed in the HAZ and their optical and crystallographic morphologies have been studied by several researchers. Advances in electron microscopy lead to the increased use of EBSD as a tool to understand phase transformation paths and orientation relationships. Several studies point out the relations between different thermal cycles and microstructural features of line pipe and HSLA steels. More knowledge needs to be gained on the quantitative description of these complex microstructures to build structure-property relationships that are capable to capture the structure-property relationships for the various transformation products encountered in the heat affected zone.
Chapter 3: Objectives and scope

The aim of this work is to study the combined influence of Niobium and Molybdenum on the microstructure evolution during austenite decomposition in low-carbon steels with a particular focus on austenite conditioning and cooling rates that are relevant for the microstructure evolution in the heat affected zone of girth welds in line pipe steels and to connect microstructural features to the resultant tensile properties.

Within the scope of this thesis a phenomenological model will be developed to describe the dependence of the austenite decomposition in the HAZ on the amount of Nb in solution, the prior austenite grain size and the cooling rate. The literature review has shown that there is an orientation relationship between the prior austenite and the transformation products in steels. These concepts will be applied to an X80 line pipe steel to design an experimental strategy to quantitatively describe the encountered HAZ microstructures. A model will be created to predict the tensile properties based on the experimentally quantified microstructure features.

The scope of this project can be divided into five sections as follows:

- The precipitation kinetics of Nb in austenite will be determined to quantify the amount of Nb in solution prior to austenite decomposition in X80. Ageing tests will be carried out to quantify the Nb precipitation kinetics at 900°C.
- The influence of Nb in and out of solution on the austenite decomposition in X80 will be studied and CCT diagrams will be established to capture the influence of the amount of Nb
in solution on the austenite decomposition for a range of austenite grain sizes and cooling rates. In addition, austenite decomposition in steels with varying Nb and Mo levels will be analyzed to describe the combined effect of Nb and Mo on austenite decomposition.

- The phenomenological transformation model will account for the amount of Nb in solution, the prior austenite grain size and the cooling rate to predict the ferrite and bainite start temperature, the ferrite-bainite transition temperature as well as the ferrite and bainite growth kinetics.

- Relevant standard metallographic techniques will be applied to identify the overall microstructure types and to choose relevant cases for in-depth characterization with more advanced tools. The focus will be on the use of electron backscatter diffraction (EBSD) to utilize the orientation relationship between the prior austenite and the transformation products with the aim to distinguish different types of bainite and to quantify the formation of martensite/austenite constituents.

- The results from the EBSD analysis will be used to establish structure-property relationships for X80. A model will be developed to predict yield stress, uniform elongation, and ultimate tensile strength based on EBSD measurements.
Chapter 4: Materials and experimental methodology

4.1 Materials

The investigated line pipe steel with a chemistry as shown in Table 4-1 was provided by Evraz Inc. NA in the form of hot rolled pipe. The as-received X80 steel mainly consists of irregular ferrite, including randomly distributed martensite/austenite islands and complex precipitates, Figure 4-1. The precipitates range in size from 3 to 100 nm and can be grouped into 4 categories: coarse TiN particles, small and large Nb(C,N) precipitates and coarse Mo₂C particles [11].

Figure 4-1: a) As-received X80 steel showing irregular ferrite and martensite/austenite islands; b) Bright field TEM micrograph showing Nb, Ti and Mo containing precipitates in the as-received material from ref. [11]; reprinted with permission of Springer
To further study the combined effect of Nb and Mo on austenite decomposition two laboratory cast steels were investigated. The chemical composition and $A_{e3}$ temperatures as obtained from Thermo-Calc (TCFE7 database) for all investigated steels are reported in Table 4-1. It is noteworthy that the $A_{e3}$ temperatures of all steels are essentially the same. Although the X80 steel has a higher Mo and lower Mn content than the laboratory steels it contains Ni which is an austenite stabilizer.

Table 4-1: Chemical composition of investigated steels in wt. % and $A_{e3}$ temperature

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Nb</th>
<th>Mo</th>
<th>Ti</th>
<th>Ni</th>
<th>Al</th>
<th>Cu</th>
<th>N</th>
<th>$A_{e3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>X 80</td>
<td>0.06</td>
<td>1.65</td>
<td>0.11</td>
<td>0.034</td>
<td>0.24</td>
<td>0.012</td>
<td>0.40</td>
<td>0.088</td>
<td>0.13</td>
<td>0.005</td>
<td>823 °C</td>
</tr>
<tr>
<td>Nb</td>
<td>0.058</td>
<td>1.78</td>
<td>0.09</td>
<td>0.06</td>
<td>-</td>
<td>0.004</td>
<td>0.02</td>
<td>0.036</td>
<td>0.003</td>
<td>0.006</td>
<td>822°C</td>
</tr>
<tr>
<td>NbMo</td>
<td>0.058</td>
<td>1.84</td>
<td>0.09</td>
<td>0.045</td>
<td>0.145</td>
<td>0.006</td>
<td>0.022</td>
<td>0.063</td>
<td>0.008</td>
<td>0.005</td>
<td>823°C</td>
</tr>
</tbody>
</table>

The first laboratory steel is microalloyed with Nb. The initial microstructure consists of a mixture of ferrite and pearlite, see Figure 4-2a. The second laboratory steel contains both Nb and Mo and shows a mixture of ferrite/pearlite and bainite, see Figure 4-2b. The bainitic constituents in the NbMo-steel result in a hardness of (203±2) HV, which is higher than that of the Nb-steel, i.e. (195±2) HV.

Figure 4-2: As-received material of laboratory materials; a) Nb-steel; b) NbMo steel
4.2 Experimental methodology

4.2.1 Introduction

A Gleeble 3500 thermo-mechanical simulator (Dynamic System Inc., Poestenkill, NY) was used to conduct austenite grain growth and continuous cooling transformation tests to produce various microstructures typical for the heat affected zone (HAZ) of girth welds. Tests were conducted under high vacuum, at 1.3x10^{-5} Pa, and the temperature was measured and controlled by NiCr-Ni (type K) thermocouples at temperatures up to 1250 °C and PtRh-Pt (type S) thermocouples at higher temperatures, spot welded to the sample centre. The thermocouple was used to read and regulate the temperature based on the programmed thermal cycle.

Strip sample with a length of 60 mm and width of 10 mm were used for austenite grain size measurements. The sample thickness for Laser Ultrasonics for Metallurgy (LUMet) measurements was 1.5 mm while thinner samples with a width of 1 mm were used for water quenching when preparing samples for metallographic austenite grain size measurements. Austenite decomposition kinetics were monitored by means of a mechanical contact dilatometer and tubular samples with 8 mm outer diameter, 1 mm wall thickness and 20 mm length were used for the dilatometry measurements.

4.2.2 Austenite conditioning

The thermal profile along the heat affected zone varies with the distance from the fusion line and as a result austenite grain sizes and amounts of Nb in solution vary simultaneously. Higher peak temperatures are reached close to the fusion line resulting in larger austenite grain sizes and a higher amount of Nb in solution. To compare the effect of different amounts of Nb in solid solution on the austenite-to-ferrite phase transformation for different austenite grain sizes and cooling rates, thermal cycles were designed to vary the amount of Nb in solid solution for a given austenite grain size.
To control the austenite grain size independent of the Nb content a solutionizing treatment was carried out prior to all reheat treatments. The solutionizing treatment shown in Figure 4-3a is based on the dissolution temperatures for Nb-containing precipitates in the investigated steels, as shown for the X80 steel in Figure 4-3b.

![Figure 4-3: a) Solutionizing treatment and b) dissolution of TiN, NbC and Mo$_2$C in X80 line pipe steel calculated with Thermo-Calc TCFE7](image)

NbC was assumed to fully dissolve during heating at 10°C/s to 1300°C and holding for 7s, which is confirmed with a Nb dissolution model developed for the investigated X80 steel by Banerjee et al. [11]. Subsequent quenching to room temperature using He gas ensured that Nb remained in solid solution. The peak temperature of the following heat treatment determined the austenite grain size. Reheating was carried out at a heating rate of 100°C/s to prevent NbC re-precipitation during heating. Samples were reheated to different temperatures where they were held for 0.5s prior to cooling at ≈120°C/s to 900°C. Continuous cooling transformation (CCT) tests were carried out at different cooling rates from 900°C to room temperature. To vary the amount of Nb in solution, a holding time of 20 min at 900°C was incorporated to re-precipitate Nb in austenite prior to austenite decomposition. A similar approach was used by Fazeli [135] where samples were first heated to 1250°C to bring Nb into solution and then rapidly cooled to 900°C where holding times
between zero and 20 min were incorporated before samples were cooling at 1°C/s. Based on the shift in transformation start temperature Fazeli concluded that Nb is fully precipitated after 20 min at 900°C. A schematic of the thermal cycles carried out for CCT tests is shown in Figure 4-4. Samples were either cooled at position 1 where Nb is fully dissolved or at position 2 where Nb is partially re-precipitated in austenite.

**Figure 4-4: Schematic of thermal cycles carried out for continuous cooling transformation tests**

### 4.2.3 Austenite grain size measurements

A recently developed technique using laser ultrasonics for metallurgy (LUMet) [35], [136], [137] was applied to determine austenitizing conditions for the laboratory steels listed in Table 4-1. The LUMet is attached to the Gleeble 3500 and provides in-situ grain size measurements during heat treatments. Here, it is used to determine the peak temperature of the reheat treatment carried out subsequent to the solutionizing treatment to obtain the desired austenite grain sizes for CCT studies.

A laser pulse with a typical spot size of 2 mm creates a wideband ultrasound wave by ablating a thin layer from the sample surface. As the wave propagates through the sample thickness it is
scattered by grains in elastically anisotropic polycrystalline materials such as steels. The attenuation, i.e. the reduction in amplitude, is detected as the wave travels back and forth between the sample surfaces and can be related to the scattering due to grain boundaries, dislocations and porosities. To obtain the average grain diameter from the attenuation, the frequency of the ultrasound wave, the operating temperature and a temperature dependent material parameter need to be considered [136].

Once austenitizing conditions were determined using the LUMet the austenite grain sizes were validated for the selected conditions applying metallographic techniques. Austenite grain size measurements for X80 are based on metallography. To prepare samples for metallographic analysis of austenite grain structures samples were water quenched and subsequently tempered in a tube furnace under argon atmosphere at 500 °C for 24 hours. The tempering promotes grain boundary segregation of elements such as P and S thereby improving the etching response to reveal austenite grain boundaries [138]. A solution of saturated aqueous picric acid was used to reveal the prior austenite grain boundaries. The grain size was measured as equivalent area diameter (ASTM E1382-97) and converted to volumetric grain size by multiplication with the factor 1.2 [139]. A minimum of 500 grains was analyzed for each condition.

### 4.2.4 Nb precipitation in austenite

Ageing experiments were carried out to determine the precipitation kinetics of Nb in austenite. Prior to ageing, the as-received material was solutionized as described in section 4.2.2 using strip samples (60 x 10 x 1 mm). After solutionizing the samples were reheated to 950°C and held for 0.5 s to establish a reproducible starting microstructure with a small austenite grain size. Samples were then held at 900°C for various times between zero and 60 min allowing for Nb re-precipitation in austenite before cooling to room temperature. The resulting samples with different amounts of Nb in solid solution were then aged at 570°C and the precipitation hardening was quantified by means of hardness measurements after each ageing treatment. Vickers hardness
measurements were conducted at 1 kg load and 15 s dwell time; an average of five hardness measurements is reported.

The samples were subject to several subsequent ageing treatments until the peak hardness was detected. The difference in peak hardness was then related to the amount of Nb available for precipitation during ageing, i.e. the nominal amount of Nb (204 ppm) minus the amount that has precipitated in austenite prior to the ageing treatments.

To prepare the ageing samples, a stepped cooling process was employed after the holding time at 900°C to obtain ferritic microstructures with different levels of Nb in solution; the applied thermal treatments are shown in Figure 4-5. To limit precipitation prior to the austenite-to-ferrite transformation, accelerated cooling at 30°C/s was applied from 900°C to 700°C before the cooling rate was reduced to 10°C/s between 700°C and 610°C where the samples were held isothermally for 7 s to promote ferrite formation. The transformation kinetics were confirmed by means of dilatometry. Subsequent cooling to room temperature was carried out at 10°C/s.

Figure 4-5: Schematic showing the thermal cycle used to prepare ferritic samples containing different amounts of Nb in solution for subsequent ageing at 570°C
The starting microstructures for the ageing treatments with Nb fully in solution (0 minutes holding at 900°C) and Nb precipitated after 20 min holding time at 900 °C are shown in Figure 4-6. Nb in solution yields irregular ferrite while the microstructure obtained after 20 min holding is overall similar but also includes more equiaxed grains.

![Figure 4-6: Initial ageing microstructure for X80 steel; a) Nb fully in solution (0min holding at 900°C); b) Nb precipitated (20min holding at 900°C)](image)

Ageing was carried out in a tube furnace under argon atmosphere. The measured heating rate in the tube furnace was 2–3°C/s depending on how many samples were heat treated at the same time and slowed down as the target temperature of 570°C was approached. The heating rate consistently slowed down when the sample temperature had reached 550°C, Figure 4-7b. The time to reach 550°C (heating) was therefore subtracted from the overall time in the furnace to obtain the effective ageing time. The ageing was carried out in an accumulative manner, i.e. each sample was aged several times and the hardness was noted each time.

To ensure reproducibility during the nucleation stage which is expected to occur at the beginning of ageing, the first ageing treatment was carried out in the Gleeble where a heating rate of 60°C/s was applied to prevent precipitation at temperatures below 570°C. The samples were held at 570°C for 5 min and cooled at 6°C/s. Figure 4-7a shows the initial ageing treatment carried out in the Gleeble and the thermal profiles of subsequent treatments in the tube furnace are shown in Figure 4-7b. Samples naturally cooled down at about 6°C/s after each treatment carried out in the furnace.
Continuous cooling transformation tests

Continuous cooling transformation (CCT) tests were carried out to capture the influence of austenite grain size, cooling rate and the amount of Nb in solid solution on the austenite decomposition of the investigated steels. Tubular samples were used for the dilatometry measurements. The thermocouple was spot welded to the sample centre where the mechanical contact dilatometer was attached to the sample. Helium gas was purged through the hollow sample while the temperature was controlled by direct resistance heating to allow for homogenous cooling at a constant cooling rate. The lever rule (ASTM A1033) was applied to calculate the transformation kinetics based on the different thermal expansion coefficients of austenite and ferrite. The transformation start temperature was determined at the measured fraction transformed of 0.05. Lottey [140] carried out several repeated CCT tests with a Nb/Ti-microalloyed steel containing 0.05C- 1.65Mn- 0.071Nb- 0.196Mo- 0.021Ti (in wt. %) to quantify the experimental accuracy in determining the transformation start temperature. An error of ±4°C was reported and is adopted for the current study as both steel chemistry and experimental set up are similar.
4.2.6 Microstructure characterization using optical microscopy

The identification and quantification of different transformation products for all CCT specimens was performed using standard metallographic techniques and a Nikon EPIPHOT 300 series inverted optical microscope equipped with a digital camera. Images were taken at magnifications of 200 and 500 times, respectively. Samples were prepared by mechanical grinding of the surface using SiC paper up to 1200 grit followed by mechanical polishing using 6 µm and 1 µm diamond paste. All samples were etched with 2 % Nital solution for 20-40 seconds.

The observed transformation products include irregular ferrite, upper and lower bainite as well as martensite/austenite (M/A). Figure 4-8 shows a schematic of the morphology based criteria to distinguish these phases.

![Schematic of morphological features characterizing transformation products with optical microscopy based on Nital etch]

Irregular ferrite has serrated grain boundaries forming ferrite grains of varying irregular shapes with sparse second phase contained within the grains. Prior austenite grain boundaries are not distinguishable in the Nital-etched microstructure. Upper bainite shows second phase features within bainite packets, while prior austenite grain boundaries are clearly visible. Packets of lower bainite show dark feathery appearance of bainite laths originating at prior austenite grain

Figure 4-8: Schematic of morphological features characterizing transformation products with optical microscopy based on Nital etch; a) irregular ferrite; b) upper bainite; c) lower bainite
boundaries. The prior austenite grain structure can be traced based on the growth direction of parallel laths.

The manual point counting method according to ASTM E562-89 was applied using a square grid superimposed on micrographs taken at a magnification of 500x. The ratio of the grid points falling onto a given phase to the total number of grid points provides the phase fraction. Figure 4-9 shows an example of a mixture of upper and lower bainite etched with 2% Nital. While some regions can be clearly distinguished as upper or lower bainite based on the criteria stated above, other regions are more challenging. The black circles mark intersections that fall on regions comprising lower bainite which are identified based on parallel laths. The arrows indicate regions that fall onto phase boundaries or mixed regions and might be characterized differently by different researchers. It is most important to be consistent with the characterization of these features. A minimum of 5 micrographs each containing an overlay of 1750 grid points was quantified for each sample to ensure statistic measurements of the present transformation products.

Subsequently, the samples were re-polished and LePera reagent [141] containing equal volumes of 4% picral and 10% aqueous sodium metabisulfite (Na₂S₂O₅) solution was used to etch samples for the analysis of M/A constituents. This etchant reveals M/A particles white or light yellow in a
brown tinted bainitic or ferritic matrix. The image analysis software ImageJ was used to determine the area fraction, size and shape of M/A constituents. The numerical images were transformed into a binary image and a threshold was applied to highlight the M/A constituents from the background. Particles touching the edge of the picture were excluded from consideration. The thresholding of the M/A phase involves optical evaluation which requires consistent procedures. To minimize measurement errors at least 5 micrographs, yielding $3 \times 10^4$ particles on average, were analyzed for each condition and a sensitivity analysis was carried out overlapping the particle outlines resulting from different threshold limits on top of the original LePera micrograph to find the appropriate threshold for each micrograph. Figure 4-10 shows the overlay (in red) of particles identified as M/A, based on the threshold, on top of the original micrograph. Based on the threshold sensitivity, the accuracy of the measurements was found to be in the range of $\pm 0.15$ of the determined average value.

Figure 4-10: LePera-etched micrograph and overlay of particles identified based on image analysis to determine area fraction and size of M/A constituents
4.2.7 Microstructure characterization using electron backscatter diffraction (EBSD)

Samples were prepared according to the mechanical polishing procedure outlined in section 4.2.6 before the final surface preparation was completed with electro-polishing using a solution of 95% acetic acid and 5% perchloric acid. Electro-polishing was performed with a current density of 50mA/cm², corresponding to a voltage of ≈16V, for 20-30 seconds. The samples were then rinsed under running water and cleaned in an ethanol ultrasound bath.

Electron backscatter diffraction was carried out with a DigiView IV EBSD Camera system from EDAX attached to a Zeiss Sigma field emission scanning electron microscope. The samples were tilted at an angle of 70° and an acceleration voltage of 20 kV was applied at a working distance of 10 to 12 mm. A square grid with a step size of 50 nm was used to scan the sample surface. EBSD analysis was performed with TSL Orientation Imaging Microscopy (OIM) data analysis software. For software parameters and set up, please refer to Appendix A.

Each point in the obtained EBSD map is attributed a phase and crystallographic orientation. The selected lattice structures for phase identification are face-centred cubic and body-centred cubic crystal structure. The orientation is defined based on the sample reference frame, while a misorientation is an orientation defined with another crystal orientation frame as reference instead of the sample reference frame. In addition to the identification of phase and orientation, the obtained data allows for definition of grain boundaries and local misorientations between neighbouring pixels. Grain boundaries with misorientation angles >15° were considered high angle grain boundaries (HAGBs), while grain boundaries between 2°-15° were considered low angle grain boundaries (LAGBs).

The studied transformation products can be divided into ferritic or bainitic body-centred cubic matrix and the second phase, i.e. martensite/ austenite. Hence, the EBSD data was divided into several data sets for detailed analysis of the matrix microstructure and second phase constituents, respectively. The first data set contained retained austenite (RA), the second set included...
martensite and the last data set contained the remaining BCC matrix microstructure. The detailed procedure to obtain these data sets is explained below.

For the quantification of retained austenite and martensite no automated cleaning method was applied to the EBSD data. In a first step, retained austenite was identified and separated from the remaining phases based on its FCC crystal structure. Clusters of four pixels or more were considered as an object; smaller clusters were removed from the map. The applied step size of 50 nm thus led to the smallest identified objects in the range of 100 nm. The amount of RA was determined as area fraction.

Due to the high dislocation density and distortion of the atomic lattice resulting from the martensitic transformation, the image quality of martensite is very low. The image quality (IQ) is a measure of intensity of the Hough peaks which is linked to the sharpness of the detected Kikuchi bands. Any distortion of the crystal lattice within the diffracting volume will produce more diffuse diffraction patterns resulting in lower image quality [142]. While the image quality is a measure of the perfection of the crystal lattice, several other factors influence the IQ including sample preparation and EBSD settings. Therefore, the image quality is not an absolute value but a function of the material and the set up. However, the IQ can be used to give a description of the strain distribution within a given sample. Several studies can be found in literature where the image quality is related to distortions caused by a high dislocation density to distinguish martensite from other phases or to determine the fraction recrystallized [143]–[145].

Within the investigated transformation products of the current study the tetragonal body-centred crystal structure could not be distinguished based on the Kikuchi patterns. Instead areas of randomly indexed points were obtained in all maps. In the inverse pole figure map, shown in Figure 4-11, the martensite appears as clusters of points with random orientation. BCC crystal structure was assigned to the majority of these points, while the remaining points were assigned the face-centred cubic structure.
The quantification of martensite was carried out in three steps, starting from the EBSD raw data, including the matrix and second phase constituents, see Figure 4-12a. First, points with an orientation deviating more than 5° from their neighbours were removed from the matrix, Figure 4-12b, and a new data set was created only including the non-partitioned points, Figure 4-12c. These points with a misorientation of more than 5° from their neighbours are referred to as randomly indexed points in the following. As no cleaning procedure was applied to the data, the new data set comprising clusters of randomly indexed points also included falsely indexed points. These falsely indexed points originate from uncertainties in the evaluation of the Kikuchi pattern but do not generally involve lattice distortions. The image quality of points falsely indexed due to overlapping patterns at grain boundaries or due to pseudo-symmetry is therefore higher than the IQ of the highly dislocated martensite.

In a second step, the image quality was considered. The IQ distribution of the martensite data sets showed a pronounced tail at high IQ values, see Figure 4-12c, which originated from falsely indexed points not representing martensite. Due to its high dislocation density martensite has a lower IQ than the falsely indexed points.
Figure 4-12: a) EBSD raw data of matrix and second phase; b) data set containing matrix without randomly indexed points; c) data set of randomly indexed points with a misorientation of more than 5° from their neighbours. The image quality is shown for each data set.

The highest values of the IQ distribution were selected, highlighting the corresponding points in the EBSD map, see Figure 4-13a. The IQ values were normalized for each data set and a sensitivity analysis of three representative cases shows a variation of the final martensite area fraction of less than ±0.01 for a range of normalized IQ values between 0.4 and 0.5 used as threshold values. A threshold value of 0.4 is selected as an appropriate cut-off to separate the points falsely indexed due to pseudo-symmetry or overlapping patterns from the points representing martensite. The highlighted points with a normalized IQ > 0.4 were then removed from the data set, resulting in the final data set only including randomly indexed points with a normalized IQ below 0.4.
In a third step, the EBSD map only including clusters of points representing martensite was analyzed with the image analysis software ImageJ to measure the area fraction, size and shape of martensite constituents. As any identified object was defined to consist of four points or more clusters comprising less than 4 points were neglected. Due to the random orientation of each point in the martensite data set, the OIM software did not recognize clusters but considered each point as a single point due to the high misorientation between neighbouring points. ImageJ recognizes each point separately and allows for the grouping of points irrespective of their orientation so that clusters smaller than four points could be identified and removed.

For the analysis and characterization of the remaining BCC microstructure a data set was created excluding all points that had previously been identified as martensite or austenite. This data set
was cleaned using a neighbour correlated confidence index clean-up method in which each pixel is evaluated based on its surrounding neighbours. Points with a confidence index below 0.2 were then excluded from further analysis. The kernel average misorientation (KAM) was calculated based on the 3rd nearest neighbor which results in a kernel size of 49 pixels. The KAM is the average of the misorientation between the pixel in the kernel center and each pixel within the kernel as shown in Figure 4-14.

![Figure 4-14: Schematic of kernel size used to calculate kernel average misorientation showing the pixel in the kernel centre (outlined in red) and its 3rd nearest neighbors (blue)]](image)

### 4.2.8 Determination of the orientation relationship between prior austenite and transformation products

The BCC matrix shows an orientation relationship with the prior austenite that is close to the Kurdjumov-Sachs orientation relationship (KS OR). The retained austenite present in the microstructure allows for the determination of areas that have transformed from a single prior austenite grain. Thus, the orientation relationship can be studied without the need for complicated austenite reconstruction programs.
The orientation of a parent austenite grain is given in terms of Euler angles \((\varphi_1, \Phi, \varphi_2)\) and the rotation matrix is given by:

\[
\begin{pmatrix}
\cos \varphi_1 \cos \varphi_2 - \sin \varphi_1 \cos \Phi \sin \varphi_2 & \sin \varphi_1 \cos \varphi_2 + \cos \varphi_1 \cos \Phi \sin \varphi_2 & \sin \Phi \sin \varphi_2 \\
-\cos \varphi_1 \sin \varphi_2 - \sin \varphi_1 \cos \Phi \cos \varphi_2 & -\sin \varphi_1 \sin \varphi_2 + \cos \varphi_1 \cos \Phi \cos \varphi_2 & \sin \Phi \cos \varphi_2 \\
\sin \varphi_1 \sin \Phi & \cos \varphi_1 \sin \Phi & \cos \Phi
\end{pmatrix}
\] (4-1)

The Euler angles describing the transformation from austenite to ferrite following KS OR are \((5.77^\circ, 48.19^\circ, 5.77^\circ)\) \[146\]. Based on the FCC symmetry of the austenite, the KS OR yields 24 possible variants that fulfill \(\{111\}_\gamma||\{011\}_\alpha<101>\gamma||<111>\alpha\). Figure 4-15 shows the orientation of a given prior austenite grain represented in the (001) pole figure and the corresponding 24 variants following KS OR. The calculated variants are then compared with EBSD data of the transformation products formed within that prior austenite grain.

![Figure 4-15: (001) pole figure of a) the parent austenite and b) calculated 24 variants following the Kurdjumov-Sachs orientation relationship](image-url)
4.2.9 Phenomenological modelling approach

A phenomenological model was created to describe the austenite decomposition of the studied X80 steel based on the CCT tests. The model is designed to capture the effect of Nb in solid solution, prior austenite grain size and cooling rate and consists of five sub-models including (i) ferrite start temperature, (ii) ferrite growth, (iii) ferrite/ bainite transition temperature, (iv) bainite start temperature, (v) bainite growth kinetics.

The ferrite start model was originally proposed for plain carbon steels by Militzer et al. [147] and later extended to include a solute a solute-drag effect of Nb by Fazeli and Militzer [135]. The model was applied to the CCT tests starting with ferrite and the least square method was used to optimize two adjustable fit parameters to account for the solute drag-effect of Nb in solution and a critical carbon enrichment, respectively.

The transition from ferrite to bainite is based on the critical driving pressure proposed by [148] and a polynomial fit is used to describe the temperature at which the driving pressure for bainite formation falls below the free energy of ferrite which is calculated using Thermo-Calc.

The model to describe the transformation start temperature for fully bainitic cases is based on an empirical model previously proposed by Fazeli et al. [121]. The original model was modified to suit the experimentally observed transformation start temperatures, i.e. an initially included grain size dependence was omitted and the least square method was used to determine three adjustable fit parameters.

Ferrite and bainite growth were modelled based on the Johnson-Mehl-Avrami-Kolmogorov (JMAK) approach. As transformation occurs during continuous cooling, additivity has to be applied, (equation (2-4)). The rate parameter $b$ was determined separately for ferrite growth, bainite growth following ferrite formation and bainite growth without previous ferrite formation and three fit parameters were used to account for the temperature dependence and austenite grain size. A linear dependence of theses fit parameters on the Nb content was established based on the
two Nb conditions of the CCT tests, i.e. Nb fully in solution and Nb partially precipitated. The details of individual models will be described in more detail in chapter 8.

To predict the tensile properties of the investigated X80 steel, experimental results from tensile tests carried out by Gaudet [149] were used and three additional tests using sub-sized specimen as shown in Figure 4-16, were carried out according to the procedure established by Gaudet to include a polygonal ferritic microstructure which has not been considered previously.

Figure 4-16: Schematic of sub-sized tensile specimen after Gaudet [149]

Taking into account the results from the EBSD analysis the model is used to predict the yield strength, uniform elongation and the ultimate tensile strength. The details of the model will be described in chapter 8.
Chapter 5: Austenite conditioning

5.1 Introduction

Austenite decomposition is governed by the prior austenite grain size, the cooling rate and the amount of Nb in solution. To study the individual effects of these parameters several austenite grain sizes with distinct amounts of Nb in solution were studied for the X80 steel. To vary the amount of Nb in solution prior to austenite decomposition complex reheating cycles were employed. The amount of Nb in solution was quantified with subsequent ageing tests.

In addition, suitable reheat conditions were established in two laboratory steels with varying amounts of Nb and Mo to obtain comparable austenite grain sizes in all investigated materials for subsequent austenite decomposition studies.

5.2 Austenite grain growth in X80

The austenite grain size is determined by the thermal profile, i.e. heating and cooling rates as well as soaking time and temperature, and the amount of alloy carbides and nitrides such as TiN and NbC that may inhibit austenite grain growth through particle pinning of the austenite grain boundaries. TiN is assumed to be stable at temperatures up to 1440°C, see Figure 4-3b. However, with increasing temperature the amount of Nb in solution increases, thereby reducing the pinning pressure of niobium carbides and promoting austenite grain growth. Both, the amount of Nb in solution and the austenite grain size influence the subsequent austenite-to-ferrite transformation.
Thus, to study the separate influence of the austenite grain size on austenite decomposition, the amount of Nb in solution was kept constant by having either all or a specified amount of Nb in solid solution. Therefore, all samples were first solutionized prior to a second reheating step used to establish the austenite grain size.

To limit re-precipitation of Nb and decarburization at high temperatures, high heating rates and short holding times of 0.5 s at the reheat temperature were applied to obtain different austenite grain sizes. Previous studies by Banerjee et al. [11] showed that the influence of the heating rate on austenite grain growth in the investigated X80 line pipe steel is negligible for heating rates above 100°C/s.

To obtain different amounts of Nb in solution for a given austenite grain size, specimens were cooled at ≈120°C/s from the reheat temperature to 900°C from where cooling was started at different rates through the transformation temperature range either immediately upon reaching 900°C or after holding there for 20 min, see Figure 4-4. The holding time at 900°C leads to re-precipitation of Nb, therefore varying the Nb content in solution, without any substantial concurrent austenite grain growth [11].

Several reheat temperatures following this approach were suggested by Tafteh [150] yielding austenite grain sizes of 5, 40, and 80 μm, respectively. Due to the high peak temperature necessary to obtain an austenite grain size of 80 μm the solutionizing and reheating treatment were combined.

For this study, an intermediate grain size between 5 and 40 μm was also desired to ensure that sufficient data would be gathered during the continuous cooling transformation tests where the austenite decomposition starts with ferrite rather than bainite. Figure 5-1 shows the thermal cycles and respective quenched-in prior austenite grain structures resulting from reheating to 1250°C, 1150°C and 1050°C, respectively, subsequent to the solutionizing treatment. The prior austenite grain boundaries are clearly visible and the grain sizes were determined as equivalent area diameter and then converted to volumetric grain size. The grain size distributions are shown for each
reheating condition indicating the average grain size assuming an accuracy of ±10% to account for measurement errors.

The metallographically measured grain sizes of this study and relevant values from the literature that were adopted for this study are summarized in Table 5-1. A reheat temperature of 1250°C was found to yield an austenite grain size of 26 µm and was adopted for the continuous cooling transformation tests.

Figure 5-1: Prior austenite grain structures and grain size distributions for X80 resulting from different reheat temperatures; a) 1250°C; b) 1150°C; c) 1050°C

The metallographically measured grain sizes of this study and relevant values from the literature that were adopted for this study are summarized in Table 5-1. A reheat temperature of 1250°C was found to yield an austenite grain size of 26 µm and was adopted for the continuous cooling transformation tests.
Table 5-1: Metallographically measured austenite grain sizes in the X80 steel for different reheat conditions having all Nb in solution

<table>
<thead>
<tr>
<th>Solutionizing treatment</th>
<th>Heating rate</th>
<th>Peak temperature</th>
<th>Holding time</th>
<th>Austenite grain size</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓</td>
<td>1,000°C/s</td>
<td>950°C</td>
<td>0.5s</td>
<td>5 µm *</td>
</tr>
<tr>
<td>✓</td>
<td>100°C/s</td>
<td>1050°C</td>
<td>0.5s</td>
<td>8 µm</td>
</tr>
<tr>
<td>✓</td>
<td>100°C/s</td>
<td>1150°C</td>
<td>0.5s</td>
<td>12 µm</td>
</tr>
<tr>
<td>✓</td>
<td>100°C/s</td>
<td>1250°C</td>
<td>0.5s</td>
<td>26 µm</td>
</tr>
<tr>
<td>✓</td>
<td>100°C/s</td>
<td>1350°C</td>
<td>0.5s</td>
<td>42 µm *</td>
</tr>
<tr>
<td>✓</td>
<td>10°C/s</td>
<td>1350°C</td>
<td>35s</td>
<td>80 µm *</td>
</tr>
</tbody>
</table>

*adopted from [150]

The error of the austenite grain size measurements is estimated to be within ±10% based on studies by Giumelli [151] dedicated to the measurement of austenite grain sizes where a 95% confidence interval was applied to different techniques, e.g. equivalent area diameter and linear intercept method. As the austenite grain boundaries were clearly revealed for all cases in this study, this estimate is a conservative measure.

5.3 Austenite grain growth in Nb and NbMo-steels

To investigate the combined influence of Nb and Mo on austenite decomposition two laboratory cast steels containing 0.06 wt. % Nb (Nb-steel) and 0.045 wt. % Nb and 0.145 wt. % Mo (NbMo-steel) were compared with the X80 line pipe steel (0.034 wt. % Nb, 0.24 wt. % Mo). Please see table 4-1 for the detailed steel compositions.

To compare the transformation kinetics of the three steels, different reheat temperatures were chosen to obtain comparable austenite grain sizes for all steels. An intermediate grain size of 26 ±5 µm was aimed for as a representative grain size. Suitable reheat temperatures for the Nb- and
NbMo-steels were determined using laser ultrasonics for metallurgy (LUMet) to monitor austenite grain growth during the reheating process. The austenite grain sizes obtained from the chosen time-temperature profiles were verified on quenched-in samples with metallographic measurements. Figure 5-2 shows the austenite grain size evolution of the Nb-steel during the solutionizing treatment where the sample is heated at 10°C/s to 1300°C and then held for 7 seconds and during the subsequent reheating at 100°C/s to 1300°C followed by immediate quenching with helium gas.

Dilatometry measurements showed that austenitization is completed at ≈900°C for both heat treatments. The grain size evolution for the solutionizing treatment shows minimal grain growth between 900°C and 1100°C followed by substantial grain growth at higher temperatures. At 1300°C an austenite grain size of 50 µm is reached which increases further to 55 µm during the holding at 1300°C. During the subsequent reheating treatment the initial austenite grain size at 900°C starts with a value of 20 µm followed by an apparent decrease to 10 µm at 1100°C before the austenite grain size starts to increase. The apparent decrease in austenite grain size does not reflect physical processes and is therefore considered to be an artefact of the LUMet measurement. This artefact was consistently observed for the reheat treatments after solutionizing and is assumed to be related to the substantial differences in the starting microstructures at room temperature prior to the ferrite-to-austenite transformation. The solutionizing treatment starts from the as-received material consisting of polygonal ferrite and pearlite while the reheating starts form the solutionized material which comprises martensite and bainite formed from a coarse prior austenite, see Figure 5-2. The influence of the starting microstructure on the austenite formation in the studied steels is not known in detail and further investigation would be needed which is outside the scope of this thesis. However, the observed austenite grain size evolution starting from the martensitic microstructure obtained from the solutionizing treatment consistently showed the same behavior at typical grain coarsening temperatures, i.e. the austenite grain size starts to increase at ≈1100°C with an initial grain size around 10 µm at 1100°C. The part between 900°C and 1100°C is not relevant to establish the desired reheat temperatures and was therefore not further considered.
Figure 5-2: In-situ measurement of austenite grain growth in Nb-steel; a) thermal profile and start microstructure for solutionizing treatment; b) thermal cycle and start microstructure for reheating; c) LUMet measurement of instantaneous austenite grain size

Based on the reheat treatment to 1300°C shown in Figure 5-2b reheat temperatures of 1230°C and 1200°C were selected for subsequent grain growth measurements with the LUMet with the goal to establish a reheat condition resulting in an austenite grain size of approximately 26 µm. The thermal profiles are shown in Figure 5-3. To prevent an overshoot of the peak temperature the heating rate was decreased to 30°C/s when the temperature reached a value 30°C below the respective peak temperature and a holding time of 0.5 s at the peak temperature was incorporated.
Figure 5-3: Thermal profiles for in-situ measurement of austenite grain growth in Nb-steel;  
   a) reheat temperature 1230°C; b) reheat temperature 1200°C

Figure 5-4 shows the grain size evolution for the Nb-steel during reheating to different peak temperatures, i.e. 1230°C and 1200°C, subsequent to the solutionizing treatment. An increase in the austenite grain growth rate is observed when the heating rate is decreased to 30°C/s prior to reaching the peak temperature where isothermal grain growth occurs during the short holding time.

Based on the LUMet measurements, a reheat temperature of 1200°C was found to yield an austenite grain size in the range of 28 µm. An additional sample was reheated to 1200°C (subsequent to solutionizing) which was water quenched after the 0.5 s holding time at 1200°C for metallographic austenite grain size measurements which resulted in a value of 23 µm, falling into the desired range, see Figure 5-4b.
Figure 5-4: a) in-situ measurement of austenite grain growth in Nb-steel; b) prior austenite grain structure resulting from reheating to 1200°C and grain size distribution from metallographic measurements

Similar austenite grain growth was expected for the NbMo-steel as Nb was in solution and did not contribute to particle pinning of the austenite grain boundaries. However, the LUMet measurements, shown in Figure 5-5a, suggest a slightly larger austenite grain growth rate resulting in a grain size of 30 µm for a peak temperature of 1200°C. Additional grain growth tests were carried out for a peak temperature of 1175°C resulting in an austenite grain size of 24 µm. As the metallographic measurement showed a slightly lower value than the LUMet measurements in case of the Nb-steel, a reheat temperature between 1175 and 1200°C, i.e. 1185°C, was chosen for the sample that was water quenched for metallographic grain size measurement. The reheating to 1185°C yielded an austenite grain size of 22 µm (based on metallography) which falls into the desired range for subsequent CCT tests.
Figure 5-5: a) In-situ measurement of austenite grain growth in NbMo-steel; b) Prior austenite grain structure resulting from reheating to 1185°C and grain size distribution from metallographic measurements

5.4 Nb re-precipitation in X80

For the X80 steel, the Nb level in solution was varied by holding the solutionized samples at 900°C for 20 min prior to continuous cooling tests. To quantify the amount of Nb in solution after 20 min, several samples were prepared with holding times at 900°C between zero and 60 min, subsequent to the solutionizing treatment. These samples were then aged in the ferrite state. The hardness of each sample obtained after the holding time at 900°C depends on several parameters including solid solution strengthening, transformation hardening and precipitation hardening. An initial heat treatment was carried out for 5 min at 570°C during which the hardness dropped for all samples. This drop is assumed to be related to the release of internal stresses and the annihilation of transformation induced dislocations. The subsequent increase in hardness during ageing is exclusively attributed to precipitation strengthening of Nb and the hardness increase is calculated
between the peak hardness and the hardness after the initial treatment, $HV_0$. The contribution of Mo induced precipitation hardening is assumed to be the same for all ageing conditions (i.e. all Mo is in solution at 900°C) while only the amount of Nb changes during the holding time. The observed lack of precipitation hardening for a holding time of 60 min at 900°C indicates that the contribution of Mo is negligible.

The age-hardening response of samples containing different amounts of Nb in solution prior to ageing at 570°C is shown in Figure 5-6 and a summary of the hardness increase is given in Table 5-2.

![Figure 5-6](image.png)

**Figure 5-6:** Evolution of hardness during ageing at 570°C subsequent to various holding times at 900°C yielding different amounts of Nb in solution

For no holding at 900°C all Nb is in solution (i.e. 204 ppm) and a maximum increase in hardness of 18 HV is obtained during ageing. With continuous holding time at 900°C less Nb is available
for precipitation during ageing and the hardness gain decreases. An increase of 1 HV is measured after 40 min holding time at 900°C. It has to be noted that this increase is within the magnitude of the measurement error. While hardness measurements provide sufficient accuracy when all Nb is available for precipitation, it is challenging to monitor changes when only a small amount of Nb remains available for precipitation. After 60 min holding at 900°C no further hardening is observed during ageing and it is concluded that all Nb has precipitated during this holding time at 900°C.

### Table 5-2: Vickers hardness obtained during ageing at 570°C (in HV)

<table>
<thead>
<tr>
<th>Holding at 900°C</th>
<th>0 min</th>
<th>2 min</th>
<th>6 min</th>
<th>20 min</th>
<th>30 min</th>
<th>40 min</th>
<th>60 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial hardness</td>
<td>218±1.9</td>
<td>213±1.4</td>
<td>210±2.4</td>
<td>209±2.9</td>
<td>207±1.8</td>
<td>204±0.9</td>
<td>203±1.7</td>
</tr>
<tr>
<td>Peak hardness</td>
<td>236±1.8</td>
<td>230±0.74</td>
<td>223±2.9</td>
<td>216±0.8</td>
<td>210±0.7</td>
<td>205±0.75</td>
<td>203±0.7</td>
</tr>
<tr>
<td>Hardness increase</td>
<td>18±3.7</td>
<td>17±2.14</td>
<td>13±5.3</td>
<td>7±3.7</td>
<td>3±2.5</td>
<td>1±1.6</td>
<td>0±2.4</td>
</tr>
</tbody>
</table>

The normalized fraction of Nb precipitated, \( f(t_{900°C}) \), is obtained by relating the change in hardness increase after different holding times in the austenite state prior to ageing to the maximum hardness increment, which is obtained when the total amount of Nb is available for precipitation, i.e. for 0 min holding time at 900°C:

\[
f(t_{900°C}) = \frac{dHV_{max} - dHV_i}{dHV_{max}}
\]

(5-1)

Here \( dHV_i \) is the hardness increase for a specific holding time at 900°C according to Table 5-2 and \( dHV_{max} \) is the maximum hardness increment, obtained after 0 min holding time at 900°C.
The normalized fraction precipitated is shown in Figure 5-7a. After 20 min holding at 900°C about 67% of the Nb is precipitated. The precipitation kinetics can be described with a JMAK equation, i.e.:

\[ f_{\text{JMAK}} = 1 - \exp(-bt^n) \]  

(5-2)

with the experimentally observed fit parameters \( b = 1.68 \times 10^{-2} \text{ s}^{-1.4} \) and \( n = 1.4 \).

The amount of Nb remaining in solid solution in the matrix \( X_{\text{Nb}}^{\text{sol}} \) can be related to the equilibrium solubility of Nb in the steel using the solubility product for NbCN proposed by Irvine et al. [152]:

\[ \log K_s = -\frac{6670}{T} + 1.31602 \]  

(5-3)

\[ K_s = [X_{\text{Nb}}^{\text{sol}}][X_C^{\text{sol}} + (X_N^0 - X_T^0)] \]  

(5-4)

The solubility product yields and equilibrium fraction of Nb in solution of 39 ppm. Relating the equilibrium fraction to the experimentally determined precipitation kinetics according to:

\[ X_{\text{Nb}}^{\text{sol}} = 204 \text{ ppm} - f_{\text{JMAK}}(204 \text{ ppm} - 39 \text{ ppm}) \]  

(5-5)

yields 93 ppm of Nb in solid solution after a holding time of 20 min at 900°C, see Figure 5-7b. Hence, the established thermal cycles for the X80 steel are designed to investigate the influence of Nb by comparison of approximately 200 and 100 ppm, i.e. all Nb and about half the Nb in solution. In the following the exact values of 204 and 93 ppm are used for further analysis as these are the values obtained from the measurements.

These results differ from the findings of Fazeli [135] which suggest that Nb is fully precipitated after 20 min holding at 900°C based on continuous cooling tests after varying holding times at 900°C. However, ageing tests are more suitable for the quantitative determination of Nb precipitation as dilatometry measurements might be influenced by decarburization for holding times longer than 20 min while the hardness is measured in the sample centre.
Figure 5-7: a) fraction of Nb precipitated in austenite during holding at 900°C as concluded from subsequent ageing tests at 570°C, error bars are omitted for clarity; b) calculated fraction of Nb in solution in the matrix during holding at 900°C

The error for the fraction precipitated obtained from ageing measurements shown in Figure 5-7 is expected to be in the range of ±0.2 based on the accuracy of the hardness measurements. Due to the indirect methods available to obtain the amount of Nb in solution, the accuracy of the absolute value for the amount of Nb in solution after 20 min is thus estimated to be approximately ±30 ppm.
Chapter 6: Austenite decomposition

6.1 Introduction

Austenite decomposition is strongly influenced by the prior austenite grain size, cooling rate and steel composition. In this chapter the austenite decomposition of X80 line pipe steel is described including the influence of the amount of Nb in solid solution. To study the effect of the austenite grain size on the $\gamma \rightarrow \alpha$ phase transformation three distinct austenite grain sizes within the limits that are relevant for the heat affected zone (HAZ) were selected for continuous cooling transformation tests. The cooling rates were chosen based on typical cooling times between 800 and 500°C ($t_{8-5}$) in the HAZ of girth welded pipelines [153].

To study the combined effect of Nb and Mo, the transformation kinetics of the Nb- and NbMo-steel were compared to the X80 steel at cooling rates of 3, 10 and 40°C/s at a prior austenite grain size between 22 and 26 µm depending on the steel composition.

6.2 Continuous cooling transformation (CCT) tests

The thermal cycles employed to systematically study the effects of Nb in solid solution, austenite grain size and cooling rate on austenite decomposition are shown in Figure 6-1. To study a wide range of austenite grain sizes and their influence on the austenite-to-ferrite or -bainite phase transformation austenite grain sizes of 5 µm, 26 µm, and 80 µm were selected for continuous cooling transformation tests in the X80 steel. For consistent reheat conditions,
all samples, including the samples reheated to obtain a grain size of 80 µm, were solutionized prior to reheating.

To evaluate the influence of Nb in solid solution on austenite decomposition, two sets of samples were prepared for each austenite grain size. After establishing the austenite grain size based on the peak temperatures shown in Figure 6-1 all samples were cooled to 900°C at a cooling rate of ≈120°C/s. The first set was then continuously cooled to room temperature at various cooling rates while the second set of samples was held at 900°C for 20 min to re-precipitate Nb prior to continuous cooling.

Figure 6-1: Thermal profiles for continuous cooling transformation tests to study the influence of austenite grain size and cooling rate at different amounts of Nb in solution in X80 steel
6.2.1 Influence of the prior austenite grain size (PAGS) on austenite decomposition

To compare the influence of the prior austenite grain size, Nb was kept in solution prior to cooling from 900°C to room temperature, resulting in 204 ppm Nb in solution. Figure 6-2 shows the corresponding transformation kinetics obtained from dilatation measurements for cooling at 30°C/s for prior austenite grain sizes of 5, 26, and 80 µm.

Transformation start and finish temperatures can be obtained from Figure 6-2. The transformation start temperature is determined by 5% transformed and the transformation finish temperature is defined as 95% transformed. A clear shift in the transformation start and finish temperature to lower temperatures can be observed with increasing PAGS. The smallest austenite grain size, i.e. 5µm, results in the highest transformation start temperature of 586°C due to the highest amount of favorable nucleation sites at austenite grain corners. With increasing PAGS transformation start shifts to 556°C and 536°C for 26 µm and 80 µm, respectively.

Figure 6-2: Transformation kinetics for continuous cooling at 30°C/s for several prior austenite grain sizes, i.e. 5 µm, 26 µm, and 80 µm. 204 ppm Nb in solid solution
The associated microstructures are shown in Figure 6-3. A shift from a mixture of a ferritic/bainitic microstructure formed from a PAGS of 5 µm to a fully bainitic microstructure for larger PAGSs is observed. The bainite morphology changes with decreasing transformation temperature and as a result of increasing austenite grain size from 26 µm to 80 µm. The obtained transformation products will be discussed in more detail below.

![Figure 6-3](image)

**Figure 6-3: CCT microstructures obtained for cooling at 30°C/s with 204 ppm Nb in solid solution and different prior austenite grain sizes of a) 5 µm; b) 26 µm; and c) 80 µm**

The CCT experiments were also carried out for cooling rates of 10, 60 and 100°C/s, consistently resulting in a decrease in transformation temperature with increasing PAGS. The influence of cooling rate on austenite decomposition will be described in the following section.
6.2.2 Influence of cooling rate on austenite decomposition

To study the influence of cooling rate on austenite decomposition continuous cooling was applied according to Figure 6-1 with varying cooling rates between 900°C and room temperature. Figure 6-4 shows the influence of cooling rate on transformation kinetics for a PAGS of 80 µm. With increasing cooling rate the transformation is shifted to lower temperatures for all investigated PAGSs while the temperature range between transformation start to finish increases with increasing cooling rate. The dependence of the transformation start temperature on the cooling rate decreases with increasing PAGS. For a grain size of 5 µm the transformation start temperature ($T_s$) is shifted by 135°C from 650°C at 10°C/s to 515°C at 100°C/s. When transforming from an intermediate PAGS of 26 µm $T_s$ is shifted by 115°C and for a large PAGS, i.e. 80 µm, the difference in $T_s$ decreases further to 75°C.

![Figure 6-4: Influence of cooling rate on transformation kinetics and microstructure for 80 µm PAGS and 204 ppm Nb in solid solution](image-url)
6.2.3 Influence of Nb in solid solution on austenite decomposition

To study the effect of Nb in solution on austenite decomposition samples were held at 900°C for 20 min prior to continuous cooling as shown in Figure 6-1 resulting in 93 ppm Nb in solution. When Nb re-precipitates prior to austenite decomposition, the transformation temperatures obtained for all investigated PAGSs and cooling rates are higher compared to those obtained when all Nb is in solution. With a PAGS of 5 µm austenite decomposition starts at temperatures of 600°C and higher for cooling rates up to 100°C/s when Nb is partially re-precipitated, i.e. when 93 ppm Nb is in solution. Increasing the cooling rate results in a shift of the transformation temperature to lower temperatures, however, the influence of cooling rate is reduced when less Nb is in solid solution, see Figure 6-5. Grey lines represent 93 ppm Nb in solution; black lines represent 204 ppm Nb in solution.

Figure 6-5: Influence of Nb in solution on transformation kinetics for a PAGS of 5 µm and cooling rates of 10°C/s and 100°C/s; black lines 204 ppm and grey lines 93 ppm Nb in solution

When all Nb is in solution, $T_s$ is shifted by more than 120°C when the cooling rates is increased from 10°C/s to 100°C/s, while the shift is reduced to 65°C when only 93 ppm Nb is in solution. Comparing the transformation start temperature at a cooling rate of 100°C/s, $T_s$ is shifted from 605°C when 93 ppm Nb is in solution to 515°C when 204 ppm Nb is in solution.
solution, leading to a shift from irregular ferrite containing isolated lath structures to a microstructure consisting to a large extend of bainite laths. At a cooling rate of 10°C/s the transformation start temperature is shifted from 680°C when 93 ppm Nb is solution to 640°C when all Nb is in solution.

A comparison of the transformation kinetics obtained from 26 µm with 93 and 204 ppm Nb in solution cooled at 30°C/s and 60°C/s, respectively, is shown in Figure 6-6. At both cooling rates the transformation temperature is shifted to lower temperatures by 55 to 60°C with increasing amount of Nb in solution. The micrographs showing the transformation products formed at 30°C/s illustrate a change in morphology due to the influence of Nb in solution and the associated shift in transformation temperature.

Figure 6-6: Influence of Nb in solution on transformation kinetics for a PAGS of 26 µm and cooling rates of 30°C/s and 60°C/s; black lines 204 ppm and grey lines 93 ppm Nb in solution. Micrographs are shown for 30°C/s.

Figure 6-7 shows the influence of Nb in solution on the transformation kinetics obtained from 80 µm PAGS cooled at 10°C/s and 100°C/s, respectively. Based on the observations above, a large austenite grain size, high cooling rate and Nb in solution shift the austenite decomposition to lower temperatures. Accordingly, the lowest transformation temperatures
in terms of transformation start (475°C) and finish temperature (360°C) are observed for 80 µm PAGS cooled at 100°C/s with 204 ppm Nb in solution. When Nb is partially precipitated prior to austenite decomposition transformation start is shifted up to 575°C even for a cooling rate of 100°C/s which is comparable to $T_s$ for cooling at 10°C/s when all Nb is in solution. In contrast to the transformation start the transformation finish temperature, however, is much lower in the case when Nb is partially precipitated and the sample is cooled at 100°C/s. The micrographs in Figure 6-7 show the transformation products resulting from 80 µm PAGS cooled at 100°C/s with 93 ppm Nb in solution and at 10°C/s with 204 ppm, respectively.

![Graph and micrographs](image)

**Figure 6-7: Influence of Nb in solution on transformation kinetics for a PAGS of 80 µm and cooling rates of 10°C/s and 100°C/s; black lines 204 ppm and grey lines 93 ppm Nb in solution. Micrographs show transformation products cooled at 100°C/s with 93 ppm Nb in solution and at 10°C/s with 204 ppm Nb in solution.**

Despite the similar transformation start temperatures, different morphologies are observed as the transformation finish temperature varies from 425°C when cooled at 10°C/s to 480°C when cooled at 100°C/s. This example shows that not only the transformation start temperature but the entire transformation temperature range is important for the microstructure evolution. However, in a first approximation, the transformation start
temperature yields consistent relations between the transformation kinetics and resultant microstructures which will be shown in the following sections as microstructural features discussed below will be related to the transformation start temperature.

6.2.4 The influence of Nb and Mo on transformation kinetics

The combined influence of Nb and Mo was studied based on a comparison of the X80 steel with the Nb- and NbMo-steels. Following the reheat strategy applied to the X80 steel shown in Figure 6-1, the Nb- and NbMo-steels were solutionized by heating at 10°C/s to 1300°C where they were soaked for 7s prior to He-quenching to room temperature. The Nb-steel was reheated at 100°C/s to 1200°C and held for 0.5 s to obtain an austenite grain size of 23 µm, while the NbMo-steel was reheated at 100°C/s to 1185°C and held for 0.5 s yielding an austenite grain size of 22 µm before CCT tests were carried out at 3°C/s, 10°C/s and 40°C/s. The resultant microstructures and transformation kinetics are compared to the X80 steel transformed from a prior austenite grain size of 26 µm. Figure 6-8 shows the transformation kinetics for cooling rates of 3°C/s, 10°C/s and 40°C/s. The Nb-steel consistently shows the highest transformation start and finish temperatures while the onset of transformation is delayed to lower temperatures in the NbMo-steel and further in the X80 line pipe steel.

![Figure 6-8: Experimental continuous cooling transformation kinetics for Nb-, NbMo-, and X80 steels cooled at 3°C/s, 10°C/s, and 40°C/s with all Nb in solution](image-url)
Figure 6-9 shows the transformation start temperature obtained at 5% transformed. Nb is fully dissolved and the Nb-steel contains the highest amount of Nb (0.06 wt. %) among the investigated steels. As the Nb contents in the other two steels are lower than that in the Nb-steel the shift to lower transformation start temperatures can be clearly attributed to the addition of Mo. Comparing the NbMo-steel with the X80 line pipe steel, both containing Nb and Mo, the transformation start is further shifted to lower temperatures in the X80. While the Nb content is higher in the NbMo-steel, X80 contains a higher amount of Mo which leads to the additional delay of the transformation start. The transformation temperature difference increases with increasing cooling rate.

Figure 6-9: Experimentally measured transformation start temperature for Nb-, NbMo-, and X80 steel

Comparing these results to the CCT study carried out for the X80 steel showing the influence of Nb in and out of solution at a constant Mo level suggests that the effect of Mo outweighs the influence of Nb. The available data indicate that more than 0.06 wt. % Nb would be needed in order to control the transformation start temperature in the presence of Mo. With
the given amount of Nb in solution, however, it cannot be concluded if it is possible for Nb to mask the effect of Mo and how much Nb would be required.

The findings of the present study are consistent with the investigation carried out by Isasti et al. [97] who compared the continuous cooling transformation behavior of five steels with a base chemistry of 0.05C-1.60Mn-0.05Si-0.03Al-0.05N (in wt. %) and varying levels of Nb (0.03 and 0.06 wt. %) and Mo (0.01 and 0.31 wt. %). Their study includes a solutionizing treatment at 1250°C for 5 min, followed by quenching and reheating to 1050°C for 5 min yielding austenite grain sizes of 12 to 19 µm. A comparison of the 0.06Nb-steel and the 0.06Nb0.31Mo-steel shows a shift to lower transformation temperatures for the NbMo-steel. The reported CCT diagram shows an increasing delay of the transformation start temperature with increasing cooling rate for cooling rates of 2°C/s, 10°C/s and 50°C/s, respectively, which is in accordance with the observations presented in Figure 6-9. Further the comparison of the transformation behaviour in the plain carbon steel with the 0.03Nb- and 0.06Nb-steels indicates that for cooling rates of 2°C/s and higher, the transformation start is shifted the lower temperatures in the Nb-steels but this shift is essentially the same for both Nb steels, i.e. there is no marked effect of the additional Nb content in the 0.06Nb-steel compared to the 0.03Nb-steel on the transformation behaviour suggesting that a saturation level is approached in terms of the amount of Nb. This conclusion applies to transformation from undeformed austenite which is of relevance for the HAZ. Isasti et al. extended their studies also to CCT from deformed austenite where a clear effect of Nb on increasing transformation temperatures is observed that can be attributed to the promotion of strain accumulation in austenite and subsequent acceleration of austenite decomposition with increased Nb microalloying.
6.3 Transformation products

6.3.1 Introduction

In the following the transformation products obtained from CCT studies of the X80 steel will be described. The microstructures obtained from the described CCT tests vary with transformation temperature. At higher temperatures ferritic microstructures are formed while lathy bainitic structures form at lower transformation temperatures. The microstructures formed in intermediate temperature ranges consist of mixtures of ferrite and bainite with gradually changing morphologies. In addition, a carbon-rich second phase comprised of martensite and retained austenite (M/A) is observed.

6.3.2 Microstructure characterization and classification

While most samples show a mixture of ferritic or bainitic microstructures with varying morphology, three distinct microstructure types were identified: irregular ferrite, upper bainite, and lower bainite. Figure 6-10a shows a ferritic microstructure formed from a prior austenite grain size of 5 µm at a cooling rate of 10°C/s with Nb partially precipitated. This case has, with 670°C, the highest transformation start temperature observed in this study. While some grains are nearly equiaxed the majority of grains show an irregular shape. Little to no substructure is observed within the grains and second phase constituents are dispersed throughout the microstructure. This microstructure type is categorized as irregular ferrite. Figure 6-10b highlights the second phase, i.e. martensite/austenite, etched with LePera reagent. The island-like constituents vary in shape from equiaxed to elongated particles within the irregular ferrite microstructure.

At lower transformation temperatures upper bainite forms. Figure 6-10c shows an example of upper bainite formed at 10°C/s from an intermediate austenite grain size of 26 µm with 204 ppm Nb in solution. Prior austenite grain boundaries (PAGBs) are preserved and are often decorated with M/A, Figure 6-10d. Elongated M/A constituents form a necklace...
structure along PAGBs and additional M/A is found within the coarse packets of upper bainite.

Lower bainite forming at even lower temperatures is presented in Figure 6-10e. The shown example was cooled at 30°C/s from large austenite grains, i.e. 80 μm, with all Nb in solution. The microstructure consists of fine bainite laths. The prior austenite grain structure is retained as bainite packets do not extend across PAGBs. Figure 6-10f shows fine M/A constituents contained in lower bainite. M/A is mostly found between bainite laths or along prior austenite grain boundaries.
Figure 6-10: Microstructures obtained during CCT tests. Left: Nital-etch; right: LePera-etch.
a) & b) irregular ferrite (5µm austenite grain size, cooled at 10°C/s, 93 ppm Nb in solution),
c) & d) upper bainite (26 µm austenite grain size, cooled at 10°C/s, 204 ppm Nb in solution),
e) & f) lower bainite (80 µm austenite grain size, cooled at 30°C/s, 204 ppm Nb in solution)
6.3.3 Quantification of phase fractions

The phase fractions of all CCT samples were determined and three cases for each of the categories described above were selected from the CCT samples based on the prevailing microstructure constituent to investigate the characteristic features of each microstructure type and to identify the correlation between martensite/ austenite constituents and the matrix microstructure. An overview of the three samples selected for each microstructure type is given in Table 6-1 and Figure 6-11 shows the fractions of the transformation products of these cases based on optical micrographs to discriminate between ferritic and bainite transformation products. The phase quantification of the remaining cases is included in the appendix.

Table 6-1: Selected cases to investigate characteristics of irregular ferrite, upper and lower bainite and the dependence of martensite/ austenite on the surrounding matrix

<table>
<thead>
<tr>
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<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
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<th>g)</th>
<th>h)</th>
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<tbody>
<tr>
<td>PAGS [µm]</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>80</td>
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<td>CR [°C/s]</td>
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<td>60</td>
<td>30</td>
<td>30</td>
<td>60</td>
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<tr>
<td>Nb sol. [ppm]</td>
<td>93</td>
<td>93</td>
<td>93</td>
<td>204</td>
<td>93</td>
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<td>204</td>
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</table>
Figure 6-11: Phase fractions of select CCT samples comprised of a distinct microstructure type, a)- c) irregular ferrite; d)- f) upper bainite; g)- i) lower bainite

Figure 6-12 shows the transformation start temperature of the nine cases listed in Table 6-1. A certain range of transformation start temperature can be attributed to each microstructure type. The austenite decomposition starts with the transformation of irregular ferrite at temperatures above 620ºC. Upper bainite starts to form in the temperature range of 585 to 600ºC. When the transformation is shifted to temperature ranges below 550 ºC lower bainite forms.
Figure 6-12: Transformation start temperature and prevailing microstructure type for three cases of irregular ferrite, upper and lower bainite, respectively

6.3.4 Martensite/ Austenite constituents

M/A is a carbon-rich constituent that depends on the matrix microstructure in terms of shape, size, and fraction. During the formation of irregular ferrite regions of retained austenite result from the rejection of carbon through the $\alpha/\gamma$ interface. As ferrite preferably nucleates from austenite grain boundaries and subsequently grows into the austenite grain the maximum carbon enrichment occurs within the centre of prior austenite grains resulting in blocky M/A islands. Prior austenite grain boundaries are not visible in the LePera etched micrographs. The maximum size in terms of area and maximum length of M/A particles is smaller in the ferritic microstructure than in upper or lower bainite. The M/A constituents are randomly distributed as illustrated in Figure 6-10b. The number density of M/A particles is constant throughout each sample, while the average particle size is larger for ferrite formed at a cooling rate of 10°C/s than for ferritic structures formed at higher cooling rates.

During the formation of upper bainite carbon is partitioned from bainitic ferrite and stabilizes the residual austenite resulting in a microstructure containing M/A particles dispersed in
bainitic ferrite. In addition, PAGBs are decorated with M/A particles building a necklace structure, Figure 6-10d. These particles form chains which consist of elongated particles with lengths of up to 15 µm or a combination of smaller particles. In this microstructure type the majority of elongated particles is located along PAGBs while the remaining particles inside prior austenite grains can be grouped into randomly distributed small spherical particles and less frequent elongated particles.

Lower transformation temperatures leading to lower bainite formation result in finer microstructural constituents and in an overall lower M/A fraction. The distribution of M/A constituents is less homogeneous in lower bainite and some areas appear to be clear of M/A under the optical microscope. PAGBs are partially decorated with M/A particles, Figure 6-10f, and particles with a maximum length of 10 µm are observed.

The area fraction of M/A constituents is shown in Figure 6-13 with respect to the transformation start temperature. Ferritic structures formed at temperatures between 670°C and 620°C yield M/A contents of 3 to 7 % whereas upper bainite accommodates the highest amount of M/A with 11 to 13 %. Lower bainite formed at temperatures below 550°C only allows for M/A fractions of approximately 2 %. The M/A content (in %) can be empirically related to the transformation start temperature, Ts, (in °C) by:

\[
M/A = 2 + 10.7 \cdot \exp\left(-\frac{(T_s - 586)^2}{648}\right) + \frac{3}{1 + \exp(-0.14T_s + 85.82)}
\]  

(6-1)
Figure 6-13: M/A content of X80 in relation to the transformation start temperature and empirical fit; measurements are based on LePera etched micrographs

An increase in the transformation start temperature results in larger M/A particles along PAGBs. The average particle size is obtained from the area of an ellipse fitted to each particle and the aspect ratio is the ratio of the major and minor axes. The size of M/A particles along PAGBs can be related to the transformation start temperature during continuous cooling as illustrated in Figure 6-14. For the selected cases the maximum average size of particles along PAGBs is 3.25 μm². The size increases by a factor of 4 from lower bainite formed at 508°C to upper bainite formed at 600°C.
The majority of M/A particles located inside prior austenite grains are small spherical particles, resulting in an average size between 0.5 and 1.2 µm$^2$ and an average aspect ratio of 2 for all investigated cases. The elongated shape of particles forming a necklace structure is expected to result in higher aspect ratios. However, the majority of M/A constituents is comprised of several smaller particles forming the necklace structures. The M/A constituents found along PAGBs show a slightly higher aspect ratio of 3 compared to the constituents inside grains. The small increase in aspect ratio might be due to limitations of the etching technique and the contrast based quantification as particles that appear as elongated in Figure 6-10 are often accounted for as several smaller particles due to varying contrast of the particles.
6.4 Discussion

Three microstructure types were identified within the transformation products obtained from CCT tests. These include irregular ferrite, upper bainite and lower bainite and are characterized based on their morphology observed with optical microscopy using different etching techniques. Varying amounts of martensite/austenite are contained in all microstructure types and the amount and shape of martensite/austenite is related to the surrounding microstructure. The occurrence of a prevailing microstructure type was linked to the transformation start temperature and an empirical relation of the amount of M/A as a function of the transformation start temperature is proposed.

The hardness was measured and the fraction of each microstructure constituent was determined for all CCT samples to create CCT diagrams. To correlate the phase fractions with the dilatation measurements, it was assumed that austenite transforms into one product phase at any time and that transformation of another phase initiates when the previous transformation finishes. The formation of transformation products was assumed to take place upon cooling in the following order: irregular ferrite (IR), upper bainite (UB), lower bainite (LB) and finally martensite. CCT diagrams are shown in Figure 6-15. Solid lines denote transformation start while dotted lines denote the end of transformation. For PAGSs of 26 µm and 80 µm several solid lines are displayed when various transformation products form subsequently during austenite decomposition. In the case of 5 µm PAGS the gradual change in transformation products is difficult to quantify based on optical micrographs. Thus, only the transformation start and finish temperatures are indicated in the CCT diagram without further distinction.
Figure 6-15: CCT diagrams for X80 for prior austenite grain sizes of 80µm, 26µm, and 5µm, respectively. Solid lines denote transformation start, dotted lines denote transformation finish; grey: 93 ppm Nb in solution, black: 204 ppm Nb in solution. Hardness values are included for each condition.

Comparing Nb in solution and partially precipitated, i.e. 204 ppm and 93 ppm in solution, respectively, the influence of Nb on the transformation start and finish temperature is marked by a clear shift to lower temperatures for all PAGSs and cooling rates. An exception is the
transformation form a small austenite grain size cooled at 3 and 10°C/s, respectively, where the transformation start temperature is not influenced by the amount of Nb in solution. The independence of the transformation start temperature at low cooling rates is in agreement with the findings of Isasti et al. [97] for the 0.03Nb- and 0.06Nb-steel described in section 2.4.2.

A number of CCT diagrams of Nb/Mo-microalloyed steels can be found in the literature and the shift to lower transformation temperatures caused by Nb is commonly confirmed. The influence of Nb is generally studied by the comparison of several steel chemistries with varying amounts of Nb. While many studies include a solutionizing treatment to ensure all Nb is in solution, the literature review has not shown any studies where the Nb content in solution is varied for a given steel composition as it is the case here. The approach applied here allows to account for all possible scenarios that might emerge from multi-pass welding procedures. While the austenite grain size and amount of Nb in solution are usually linked through the thermal profile resulting in large austenite grains and Nb dissolution close to the fusion zone and smaller austenite grain sizes further away from the fusion zone where Nb mostly remains precipitated, the overlapping of several welding passes can result in different austenite conditions. The current study contributes systematic information on the transformation products to be expected in the HAZ based on the independent variation of austenite grain size, Nb in solution and cooling rate.

A study by Lee et al. [154] from the late 1980s aimed to increase the information on transformation products formed under continuous cooling conditions from undeformed austenite in low-carbon line pipe steel for Artic applications containing 0.052C-0.21Si-1.99Mn-0.059Nb-0.31Mo (in wt. %). The thermal cycle applied in their study (10 min holding at 1200°C) suggests that all Nb is in solution and a CCT diagram is constructed based on optical microscopy of the matrix microstructure while SEM and TEM images were used to study the second phases. The observed transformation products are grouped into four categories with similar features as the microstructures in the X80 steel of the current study.
The transformation start temperatures reported by Lee et al. also agree well with the current findings. The transformation start temperature in their study varies from 600°C at 6°C/s to 530°C at 140°C/s which is comparable to the transformation temperatures shown in Figure 6-15.

A more recent study by Xiao et al. [89] shows a CCT diagram for a line pipe steel containing 0.025C-0.24Si-1.56Mn-0.039Nb-0.32Mo (in wt. %). The transformation products are grouped into three categories based on the cooling rate. The transformation products reported for cooling rates of 0.1°C/s to 10°C/s correspond to the irregular ferrite described in section 6.3.2 while the transformation products for cooling rates of 10°C/s - 50°C/s and 50°C/s-100°C/s, respectively, are described as bainitic transformation products with changing morphological features of the matrix and second phase. Similar to the transformation products, the reported transformation start temperatures varying from 700°C at 0.1°C/s to 590°C at 100°C/s and transformation finish temperatures ranging from 400 to 500°C are in close agreement to the current study.

Although the described microstructural features and transformation temperatures reported in the literature agree well with the CCT diagrams of the investigated X80 steel, each study uses a different nomenclature to describe the complex transformation products. Several classification schemes have been proposed, with the most prominent ones being those of Bramfitt and Speer [155] and the ISIJ Bainite Committee [156]. However, a consistent labelling has not been established to date which urges for more quantitative descriptions of these complex transformation products.
Chapter 7: Advanced microstructure characterization of complex transformation products

7.1 Introduction

To be able to predict the mechanical properties and performance of the heat affected zone, relevant microstructure characteristics need to be quantified that influence the properties. It was shown in chapter 6 that uncertainties arise from optical metallography based on the complexity of the microstructure constituents. Particularly challenging is the distinction between different types of bainitic transformation products as well as the quantification of small martensite/austenite constituents. Thus, electron backscatter diffraction (EBSD) analysis was used to distinguish in detail the microstructure parameters that change depending on the transformation products obtained from the continuous cooling transformation tests described in chapter 6. Additional samples were prepared to obtain a polygonal ferritic microstructure in the X80 steel and to characterize the microstructure of different X80 samples previously investigated in terms of their tensile behaviour by Gaudet [149].

Four distinct microstructure types were investigated specifically to connect relevant microstructure parameters to the resulting tensile properties. The selected samples include polygonal ferrite, irregular ferrite, upper bainite and lower bainite. The microstructure
features will be quantitatively described here and a model to predict the tensile behavior based on these EBSD measurements will be presented in chapter 8.

7.2 Microstructure types

7.2.1 Overview

While the transformation products obtained from continuous cooling at cooling rates of 3°C/s or higher yield irregular ferrite as the first transformation product, an additional sample with 5 µm prior austenite grain size was held at 900°C for 20 min prior to cooling at 0.2°C/s to obtain polygonal ferrite as a benchmark microstructure for the establishing of structure-property relationships. The inverse pole figure maps of the microstructure types discussed in this chapter, i.e. polygonal ferrite, irregular ferrite, upper bainite and lower bainite are shown in Figure 7-1.

The inverse pole figure (IPF) map indicates the orientation of each point in the map in regard to the sample orientation which is defined in terms of rolling direction, normal and transverse direction. The color code is given for the standard triangle of the cubic symmetry showing which direction is parallel to the assigned sample direction:

- red: [001] direction parallel to the assigned sample direction
- green: [101] direction parallel to the assigned sample direction
- blue: [111] direction parallel to the assigned sample direction
Figure 7-1: Inverse polefigure maps of investigated microstructures. White areas represent second phase; grain boundaries >15° highlighted in black, grain boundaries <15° highlighted in grey; a) polygonal ferrite formed from 5 µm at 0.2°C/s, 93 ppm Nb; b) irregular ferrite formed from 5 µm at 50°C/s, 204 ppm Nb; c) upper bainite formed from 42 µm at 10°C/s, 93 ppm Nb; d) lower bainite formed from 42 µm at 50°C/s, 204 ppm Nb
Several samples were analyzed for each microstructure type and an overview of the austenite conditions leading to the transformation products described here is given in Table 7-1.

Table 7-1: Overview of X80 samples analyzed with EBSD

<table>
<thead>
<tr>
<th>Microstructure type</th>
<th>Nb in solution [ppm]</th>
<th>Grain size [µm]</th>
<th>Cooling rate [°C/s]</th>
<th>Tensile data available</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polygonal ferrite¹)</td>
<td>93</td>
<td>5</td>
<td>0.2</td>
<td>✓</td>
</tr>
<tr>
<td>Irregular ferrite¹)</td>
<td>93</td>
<td>5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Irregular ferrite²)</td>
<td>204</td>
<td>5</td>
<td>50</td>
<td>✓</td>
</tr>
<tr>
<td>Upper bainite²)</td>
<td>93</td>
<td>42</td>
<td>10</td>
<td>✓</td>
</tr>
<tr>
<td>Upper bainite/ lower bainite²)</td>
<td>93</td>
<td>42</td>
<td>50</td>
<td>✓</td>
</tr>
<tr>
<td>Upper bainite²)</td>
<td>204</td>
<td>42</td>
<td>10</td>
<td>✓</td>
</tr>
<tr>
<td>Upper bainite¹)</td>
<td>204</td>
<td>26</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Lower bainite²)</td>
<td>204</td>
<td>42</td>
<td>50</td>
<td>✓</td>
</tr>
<tr>
<td>Lower bainite¹)</td>
<td>204</td>
<td>26</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Lower bainite¹)</td>
<td>204</td>
<td>80</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

¹) Samples were heat treated according to Figure 4-4

²) Samples were heat treated by Gaudet to obtain the stated austenite conditions [149]

7.2.2 Polygonal ferrite

The inverse polefigure map of polygonal ferrite, see Figure 7-1a, shows that polygonal ferrite grains are separated by high angle grain boundaries (HAGB), which are represented in black. Only few low angle grain boundaries (LAGB), which are represented in grey, are observed. The uniform color within a given ferrite grain indicates the absence of orientation gradients.
within the grains. The white areas were identified as pearlite based on their morphology observed in the scanning electron microscope. The pearlite amounts to 4.5% within the investigated polygonal ferrite structure and is not considered in the further analysis. The sample does not contain any martensite/ austenite (M/A) constituents according to the procedures used to identify M/A (see chapter 4).

### 7.2.3 Irregular ferrite

Similar to observations made with optical microscopy EBSD analysis of irregular ferrite reveals irregularly shaped ferrite grains separated by high angle grain boundaries. Prior austenite grain boundaries cannot be distinguished from ferrite grain boundaries. Figure 7-1b also shows low angle grain boundaries delineated in grey, giving rise to substructures within irregular ferrite grains. It was shown in chapter 6 that M/A appears as islands in irregular ferrite dispersed throughout the microstructure. More detailed information on the second phase is obtained in terms of the mixture of austenite and martensite with EBSD. However, the amount of retained austenite (RA) might be underestimated due to the transformation of RA into martensite during sample preparation. Figure 7-2a shows the inverse pole figure map of irregular ferrite formed at 10°C/s from austenite with a grain size of 5 µm and Nb partially precipitated. Retained austenite is identified based on its FCC crystal structure and is outlined in Figure 7-2a. In the image quality (IQ) map shown in Figure 7-2b martensite constituents are outlined. The IQ map is a useful tool to visualize the distribution of image quality throughout the microstructure. The highest image quality (red, according to the legend) is observed within ferrite grains in the absence of substructure. Grain boundaries are distinguishable due to lower IQ values and appear green based on the provided color code. Martensite yields the lowest image quality and is clearly distinguished.
Figure 7-2: Irregular ferrite formed from 5 µm austenite grain size cooled at 10°C/s, 93 ppm Nb in solution; a) inverse pole figure map showing FCC phase outlined in black; b) image quality map showing martensite with low IQ outlined in black; c) combination of retained austenite (blue) and martensite (red)

A combination of RA and martensite displayed in Figure 7-2c illustrates the distribution of M/A in the irregular ferrite matrix. Although the overall fraction of martensite is higher than that of retained austenite, the M/A islands mostly consist of a mixture of austenite and martensite and are less frequently fully martensitic. More quantitative detail is given below.

7.2.4 Upper bainite

Optical microscopy revealed a high amount of substructure and martensite/austenite in upper bainite. Considering high and low angle grain boundaries using EBSD the microstructure is
comprised of a coarse network of high angle grain boundaries and a high amount of low angle grain boundaries, Figure 7-1c. Upper bainite contains the highest amount of M/A with more than 10% in all investigated samples. Figure 7-3 shows an inverse pole figure map of the M/A constituents contained in upper bainite. M/A constituents are found along prior austenite grain boundaries (PAGB) and within prior austenite grains. EBSD analysis shows that the constituents along PAGBs are mostly martensitic while retained austenite is predominantly found within prior austenite grains. Neighbouring retained austenite particles with a misorientation of 60° about the <111> axis indicate a twin relation of the austenite prior to the γ → α phase transformation.

Figure 7-3: Inverse pole figure map showing different types of M/A within the matrix of upper bainite formed from 42 µm austenite grain size cooled at 10°C/s, 93 ppm Nb in solution

Interconnected particles along PAGBs form necklace-like structures. Figure 7-4a shows the outline of M/A constituents forming a necklace structure along PAGBs highlighted in yellow. PAGBs are partially replaced by transformation products and cannot be consistently revealed by chemical etching methods. Based on the IPF map of the FCC phase regions of particular prior austenite grains can be identified and the prior austenite grain structure can be reconstructed in the IQ map of the BCC matrix as shown in Figure 7-4b. Based on image analysis 30% of these PAGBs are decorated with M/A.
Figure 7-4: a) inverse pole figure map of RA with highlighted location M/A along prior austenite grain boundaries in upper bainite formed from 42 µm austenite grain size cooled at 10°C/s, 93 ppm Nb in solution; b) image quality map with schematically drawn PAGBs in black and highlighted location of M/A along prior austenite grain boundaries in yellow

7.2.5 Lower bainite

Lower bainite comprises fine bainite laths which are mostly separated by HAGBs, while LAGBs are also present in the structure, Figure 7-1d. Depending on the orientation of bainite packets, grain boundaries parallel to the sample surface might not show up in the two-dimensional representation of EBSD maps. Figure 7-5 shows grain boundary maps of different samples comprising lower bainite. The first sample results form a prior austenite grain size of 26 µm and was cooled at 60°C/s, the second sample was cooled at 50°C/s from a prior austenite grain size of 42 µm (same as shown in Figure 7-1d) and the third sample was cooled at 30°C/s from a prior austenite grain size of 80 µm. LAGBs are shown in white, while HAGBs are divided into boundaries with a rotation angle of 15-50°, shown in black and boundaries with a rotation angle of 50-63°, shown in red. Bainite laths are separated by boundaries >50°, while prior austenite grain boundaries fall into the range of 15-50°.
Figure 7-5: High and low angle grain boundaries in lower bainite formed from different austenite grain sizes with Nb fully in solution; a) 26µm, cooled at 60°C/s; b) 42 µm, cooled at 50°C/s; c) 80µm, cooled at 30°C/s

The boundary rotation angle distribution of lower bainite is compared to that of upper bainite in Figure 7-6. Three samples are compared for each microstructure type. Misorientations below 5° are not included in the rotation angle distribution. The maximum rotation angle is given by the cubic symmetry and is 63°. Lower bainite shows LAGBs with a decreasing number fraction from 5° to 10° and no boundaries with rotation angles between 10° and 30°. Small peaks are found around 30°, 35°, and 45° followed by a subsequent increase in number fraction with a plateau between 50° and 55° and a strong peak at 60°. Upper bainite shows a high number fraction between 5° and 10° and a decrease between 10° and 20° with subsequent peaks at 30°, 35°, and 44°. The number fraction increases between 45° and 50° and further between 55° and 60° with a peak at 60°. Although the peaks are of varying intensity for different samples they appear at constant rotation angles.
Figure 7-6: Comparison of the boundary rotation angle distribution for three cases of 
a) lower bainite and b) upper bainite

The boundary rotation angle profile also contains information regarding the variant pairing of the respective transformation products as neighbouring variants are expected to follow certain misorientations given by their orientation relationship with the prior austenite. The differences shown in Figure 7-6 indicate that the variant pairing is different in upper and lower bainite and is utilized to distinguish between the two types of bainite. The quantitative description will be discussed below. Grain boundaries with a misorientation of 60° are known to have the lowest interface energy [157] and are favored at low transformation temperatures. Within a prior austenite grain these high misorientations can only be achieved by the adjacent formation of variants belonging to different Bain groups.

7.3 Distinction between upper and lower bainite

Bainitic transformation products follow an orientation relationship with the parent austenite close to the Kurdjumov-Sachs orientation relationship (KS OR). Based on the FCC symmetry of the austenite, the KS OR yields 24 possible variants to fulfill \( \{111\}_\gamma//\{011\}_\alpha \) \( <101>\gamma//<111>\alpha \). The orientation of the transformation products formed from the same
austenite grain is therefore dictated by the 24 KS variants. To investigate the different variant selection in upper and lower bainite, regions representing a former austenite grain were identified based on the retained austenite and cropped from an EBSD map to study the existing variants. The (001) pole figure proved to be a useful tool to compare the experimentally observed orientations with the theoretical variants calculated according to the KS OR. The austenite orientation was obtained from the retained austenite.

The available EBSD system allows to measure misorientations in the range of 1°, however, the orientation of the observed transformation products varies from the ideal KS OR and the orientations do not appear as distinct points in the pole figure as it is known for martensite but rather form a continuous path between variants which makes it quite challenging to separate distinct bainite variants [157]. The 24 KS variants can be grouped based on their close packed planes or the direction of compression along the z–axis. The three Bain groups corresponding to the latter can be readily distinguished in the (001) pole figure of the BCC phase and are thus used for the differentiation of transformation products. The maximum misorientation within one Bain group amounts to 10° between variant 1 and 2 (Table 2-2 in chapter 2). Variants belonging to different Bain groups are divided by high angle grain boundaries.

The studied X80 steel shows a clear difference in variant selection for different bainitic structures. Based on the previous identification using optical microscopy described in chapter 6 samples comprising upper and lower bainite, respectively, were investigated and compared. Figure 7-7a shows an ESBD map of upper bainite highlighting a prior austenite grain which was cropped from the map. In the case of upper bainite M/A necklace structures help to distinguish prior austenite grains. Figure 7-7b shows the calculated 24 KS variants based on the orientation of the retained austenite and a comparison with the orientations obtained from EBSD is shown in Figure 7-7c.
Figure 7-7: a) EBSD map of upper bainite formed from 42 µm cooled at 10°C/s, 93 ppm Nb in solution; b) (001) pole figure including 24 calculated KS variants based on retained austenite of highlighted prior austenite grain; c) (001) pole figure showing comparison of calculated KS variants and experimentally observed variants; d) Bain map showing transformation products coloured according to their Bain group.

The experimentally observed orientations are coloured according to the three Bain groups. In the example above only two Bain groups are present (coloured in red and blue, respectively). The so-called Bain map of the prior austenite grain where orientations are coloured according to the Bain group they belong to is shown in Figure 7-7d. Based on the Bain map the area fraction covered by variants belonging to each Bain group can be determined. Upper bainite is now clearly identified by the dominance of one of the three Bain groups within in the variants formed from the same prior austenite grain.

Lower bainite, however, exhibits variants of all three Bain groups which leads to an increase in high angle grain boundaries. Figure 7-8a shows an EBSD map of lower bainite as well as the area of a prior austenite grain that was cropped. The calculated 24 KS variants are compared in Figure 7-8b & c. The Bain map of the prior austenite grain cropped from the
map is shown in Figure 7-8d. The separation of bainite laths belonging to different Bain groups based on the KS variants is apparent.

Figure 7-8 a) EBSD map of lower bainite formed from 42 µm cooled at 50ºC/s, 204 ppm Nb in solution; b) (001) pole figure including 24 calculated KS variants based on retained austenite of highlighted prior austenite grain; c) (001) pole figure showing comparison of calculated KS variants and experimentally observed variants; d) Bain map showing transformation products coloured according to their Bain group

7.4 Microstructure refinement

Due to the variant selection upper bainite contains a large number of LAGBs within the transformation products formed from one prior austenite grain as variants belong to the same Bain group. Lower bainite shows a much higher density of HAGBs due to highly intricate laths belonging to different Bain groups. While polygonal ferrite can be precisely characterized by means of a grain size separating equiaxed grains with a misorientation of more than 5° from their neighbours, more advanced characterization tools are needed to describe the more complex transformation products. As the matrix microstructure varies with decreasing transformation temperature, refinement in terms of high angle grain boundaries
is observed. Figure 7-9 illustrates the increase of high angle boundary density and quantitative values are compared in Table 7-2.

Figure 7-9: Grain boundary maps for different microstructure types; black: HAGBs >15°; red: outline of M/A constituents throughout the matrix; a) & d) irregular ferrite formed from 5 μm at 50°C/s, 204ppm Nb; b) & e) upper bainite formed from 42 μm at 10°C/s, 93 ppm Nb; c) & f) lower bainite formed from 42 μm at 50°C/s, 204 ppm Nb

Grain refinement can be quantified by means of the boundary line length per area. As matrix and second phase can only be quantified in separate EBSD data sets, HAGBs in the matrix are occasionally interrupted at the location of second phases. The upper row in Figure 7-9 shows the HAGBs (black) with gaps originating at the location of M/A constituents. The lower row shows the M/A perimeter outlined in red in addition to HAGBs. As martensite is randomly indexed it is not possible to measure a misorientation between martensite constituents and the surrounding matrix. It is assumed that second phase particles are enclosed by HAGBs and the perimeter of all M/A constituents is added to the HAGB line length for the quantification of grain refinement. The modified high angle grain boundary density, $H$, is calculated as HAGB line length including the M/A perimeter per area:
\[ H = \frac{(HAGB \ line \ length + MA \ perimeter)}{Area} \] (7-1)

The values of \( H \) are shown in Table 7-2. Despite the high amount of M/A and its contribution to the line length of high angle grain boundaries upper bainite shows a lower HAGB density than irregular ferrite and lower bainite which is an indication of the coarseness of the structure. The lowest HAGB density is measured for polygonal ferrite.

Table 7-2: Modified high angle grain boundary density including M/A:

<table>
<thead>
<tr>
<th></th>
<th>HAGB density ( H ) [( \mu m^{-1} )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polygonal ferrite</td>
<td>0.57</td>
</tr>
<tr>
<td>Irregular ferrite</td>
<td>1.22</td>
</tr>
<tr>
<td>Upper bainite</td>
<td>0.92</td>
</tr>
<tr>
<td>Lower bainite</td>
<td>1.85</td>
</tr>
</tbody>
</table>

7.5 Strain induced local misorientations

Geometrically necessary dislocations introduced during the formation of ferritic or bainitic transformation products in microalloyed steels cause small lattice rotations that can be detected with EBSD [158]. Several methods can be applied to evaluate the local variations of the lattice orientation caused by the residual strain surrounding geometrically necessary dislocations (GNDs) [159]. These methods are either based on grains or on individual pixels [160]. While grain based methods are most suitable for microstructures with well-defined grains such as polygonal ferrite, point based methods, where a kernel is defined by a point and its nearest neighbours, are found to be more suitable for the investigated transformation products in this study [161]. In particular, the kernel average misorientation is used. The KAM represents the average misorientation \( \Delta \bar{g} \) of a point in the middle of a kernel with all
its neighbours. The size of the kernel can be varied by choosing the n-th nearest neighbour environment. The KAM is then calculated according to equation (7-2):

$$KAM = \left( \Delta g(g_{\text{point}}, g_{\text{neighbour}}) \mid \Delta g < \Delta g_{\text{max}} \right)$$

(7-2)

where $\Delta g_{\text{max}}$ is the threshold for the maximum misorientation that is considered in the average. A maximum misorientation has to be selected to avoid unreasonably high KAM values at grain boundaries [160]. The presented microstructures show sub-grain boundaries in the range of 2-10°. Maximum KAM values of 2° and 5°, respectively, were compared. The average KAM value for a given sample did not change within this range while the obtained KAM maps give a better representation for a smaller threshold. Based on the KAM maps, a threshold of 3° was selected for the calculations. To account for the small step size of 50 nm higher-order neighbours can be selected. In this study the third nearest neighbours are considered, calculating the orientation gradient over 150 nm in a square grid.

Figure 7-10 shows the KAM maps of the investigated microstructures as well as the KAM distribution. A log normal fit was applied to the KAM distributions and the mean value is used to compare the KAM. Visual inspection of the KAM maps shows a clear shift to higher KAM values from polygonal ferrite to irregular ferrite, upper bainite and lower bainite which indicates an increasing misorientation gradient with decreasing transformation temperature. The mean KAM values of 0.43°, 0.48°, 0.62° and 0.70° for polygonal ferrite, irregular ferrite, upper and lower bainite, respectively, shows a consistent increase with decreasing transformation temperature. These values are in agreement with a study by Zaefferer et al. [161] where the KAM was used to distinguish between ferrite and bainite in a low-carbon steel.

In a study by Calcagnotto et al. [159] the KAM was used to reveal orientation gradients around martensite islands in a dual phase steel containing 24 and 38 vol. % martensite, respectively. The volume change caused by martensite formation induces plastic deformation
of the surrounding ferrite grains, thus creating a high density of unpinned dislocations in the vicinity of martensite. These orientation gradients were quantified by means of KAM and the density of geometrically necessary dislocations was calculated based on the KAM yielding dislocation densities of $1.0 \times 10^{-14} \text{m}^{-2}$ to $2.4 \times 10^{-14} \text{m}^{-2}$ for different martensite volume fractions.

Figure 7-10: Kernel average misorientation maps. a) polygonal ferrite formed from 5 µm at 0.2°C/s, 93 ppm Nb; b) irregular ferrite formed from 5 µm at 50°C/s, 204 ppm Nb; c) upper bainite formed from 42 µm at 10°C/s, 93 ppm Nb; d) lower bainite formed from 42 µm at 50°C/s, 204 ppm Nb; e) experimentally measured KAM distribution and fitted lognormal distribution (black lines)
7.6 Martensite/ Austenite

The overall amount of M/A varies based on the surrounding matrix and has been related to the transformation start temperature in chapter 6. Intermediate area fractions are found at higher transformation start temperatures when ferritic microstructures are formed. With decreasing transformation start temperature, the M/A area fraction initially increases and reaches a maximum when a fully upper bainitic microstructure is formed. At lower transformation temperatures promoting lower bainite formation the smallest M/A fractions are observed.

EBSD measurements allow for a more precise measurement of the M/A constituents especially in the case of very small particles. The sample comprising polygonal ferrite contains 4.5% pearlite but does not contain M/A. The remaining samples confirm the overall trend suggested based on optical microscopy. EBSD measurements yield intermediate M/A amounts of 6% for irregular ferrite, the highest amount for upper bainite with 11% and the lowest number for lower bainite with 4%. The results for irregular ferrite and upper bainite are in very good agreement with the findings based on optical microscopy. However, the amount of M/A in lower bainite is twice as high as high compared to the results from optical microscopy as small particles in the range of 200 nm can be captured with EBSD but not with light optical microscopy.

The amounts of martensite, RA and M/A measured with EBSD are shown in Figure 7-11. The results show a higher measured amount of martensite than austenite for all microstructure types. Most particles are either fully martensitic or a mixture of RA and martensite. However, the amount of RA might be underestimated due to the potential transformation of RA into martensite during sample preparation. The measured ratio of austenite to martensite is highest for upper bainite.
Different shapes and locations of M/A constituents are found depending on the matrix microstructure. The size and shape within prior austenite grains varies from small equiaxed particles to larger elongated particles. The aspect ratio, $AR$, is calculated as:

$$AR = 4\pi \frac{\text{Area}}{\text{Perimeter}^2} \quad (7-3)$$

where the area and perimeter result from image analysis of the EBSD maps of retained austenite and martensite, respectively. The aspect ratio varies between zero and one for elongated particles and spherical particles, respectively. As RA and martensite are separately quantified, the area fraction of M/A results from the addition of the austenite and martensite fractions. Table 7-3 lists the amount and aspect ratio of martensite and retained austenite for different microstructure types. A correlation between the size and aspect ratio is shown in Figure 7-12.
Table 7-3: Martensite and austenite area fractions based on EBSD measurement for irregular ferrite, upper and lower bainite

<table>
<thead>
<tr>
<th></th>
<th>M/A</th>
<th>AR</th>
<th>M/A</th>
<th>AR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irregular ferrite</td>
<td>0.30</td>
<td>0.93</td>
<td>5.8</td>
<td>0.51</td>
</tr>
<tr>
<td>Upper bainite</td>
<td>2.1</td>
<td>0.79</td>
<td>8.8</td>
<td>0.41</td>
</tr>
<tr>
<td>Lower bainite</td>
<td>0.13</td>
<td>0.75</td>
<td>3.6</td>
<td>0.62</td>
</tr>
</tbody>
</table>

The maximum size of retained austenite decreases from irregular ferrite to upper bainite and further to lower bainite. With increasing area fraction the particle size increases while bigger particles tend to be more elongated, i.e. have a lower aspect ratio, than smaller ones, see Figure 7-12.

Figure 7-12: Aspect ratio of martensite and austenite constituents as a function of the average size; measurements based on EBSD data
The highest aspect ratio of 0.93 is shown by blocky retained austenite constituents in irregular ferrite. Retained austenite generally shows a higher aspect ratio than martensite for all microstructures.

7.7 The influence of Nb and Mo on microstructural features

In the following the transformation products resulting from the comparison of the Nb-, NbMo-, and X80 steel are discussed. The microstructures acquired by EBSD are shown in Figure 7-13. Depending on the alloying content and cooling rate three different transformation products are observed. At 3°C/s a comparatively coarse irregular ferritic microstructure is found with increasing prominence of prior austenite grain boundaries in the order of Nb-, NbMo-, X80 steel. The Nb-steel shows microstructure refinement in terms of HAGBs and more irregularly shaped high angle grain boundaries (highlighted in black) are observed when cooled at 10°C/s. The X80 line pipe steel shows a typical upper bainitic microstructure with M/A decorating the prior austenite grain boundaries. The microstructure of the NbMo-steel cooled at 10°C/s is similar to that observed at 3°C/s, while the microstructure is refined and prior austenite grain boundaries are clearly visible (indicated with arrows). At 40°C/s all steels form lathy lower bainite.
Figure 7-13: Microstructures obtained at 3°C/s, 10°C/s and 40°C/s; a)-c) Nb-steel; d)-f) NbMo-steel; g)-i) X80. Grain boundaries >15° highlighted in black, grain boundaries <15° highlighted in white. Arrows indicate prior austenite grain boundaries.

The associated grain boundary rotation profiles for the Nb- and NbMo-steels, representing the grain boundary angle in the EBSD map, are shown in Figure 7-14. The misorientation profiles of the Nb-steel confirm that the same transformation products are formed at 3°C/s and 10°C/s. The profiles show a peak at misorientations below 10°, representing low angle grain boundaries (LAGB) and a broad peak between 50° and 60° indicative of the ferrite grain boundaries. In case of the NbMo-steel, the same peaks are observed for 3°C/s. At 10°C/s, additional sharp peaks are observed at 30°, 45°, 54° and 60°. According to the misorientation between different Kudjumov-Sachs (KS) variants given in table 2-2 the peaks
at misorientations of 45°, 54° and 60° are consistent with the misorientation of KS variants belonging to different Bain groups. However, there are no variants showing misorientations in the range between 21.1° and 47.1° in accordance with the exact KS-orientation relationship. The peak at 30° is assumed to be related to the preserved prior austenite grain boundaries which are especially prominent in the microstructure formed at 10°C/s which is in agreement with the observation for upper bainite in the X80 steel. The lower bainite formed at 40°C/s shows a strong peak at 60° with a shoulder at 54°. These peaks represent the high angle grain boundaries (HAGB) formed between adjacent variants belonging to different Bain groups.

![Graph showing distribution of boundary rotation angle for Nb- and NbMo-steel cooled at 3°C/s, 10°C/s, and 40°C/s](image)

**Figure 7-14: Distribution of boundary rotation angle for Nb- and NbMo-steel cooled at 3°C/s, 10°C/s, and 40°C/s**

The lath structure of lower bainite leads to an increase of the overall amount of HAGBs compared to irregular ferrite and upper bainite which is in agreement with the findings for X80 presented in chapter 6. The HAGB density can be related to the transformation start temperature. Figure 7-15 shows the increase in HAGB density with decreasing transformation start temperature for all three steel chemistries.
Figure 7-15: High angle grain boundary density as a function of the transformation start temperature for a) X80; b) NbMo-steel; and c) Nb-steel

The results for all steels are compared in Table 7-4. A strong effect of cooling rate on the HAGB density is observed, i.e. for all steels the HAGB density increases with cooling rate because of grain refinement with lower transformation temperatures. At a given cooling rate the HAGB density varies only slightly for the different steels.

Table 7-4: High angle grain boundary density including the contribution of M/A for Nb-, NbMo-, and X80 steel at various cooling rates

<table>
<thead>
<tr>
<th>Steel</th>
<th>3°C/s HAGB density, µm⁻¹</th>
<th>10°C/s HAGB density, µm⁻¹</th>
<th>40°C/s HAGB density, µm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>0.41</td>
<td>0.76</td>
<td>3.0</td>
</tr>
<tr>
<td>NbMo</td>
<td>0.73</td>
<td>0.78</td>
<td>2.4</td>
</tr>
<tr>
<td>X80</td>
<td>0.61</td>
<td>0.89</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Similar to the HAGB density the kernel average misorientation increases with decreasing transformation start temperature due to an increasing dislocation density at lower transformation temperatures. The KAM values presented in Figure 7-16a show a linearly increasing trend for the three samples cooled at 3°C/s. Transformation start temperatures between 650°C and 600°C yield KAM values of 0.38°, 0.42°, and 0.44° for Nb-steel, NbMo-
steel, and X80, respectively. A sharp transition to higher KAM values, consistently increasing with decreasing transformation start temperature in the range of 0.55° to 0.71° occurs for the transformation products resulting from 10°C/s and 40°C/s.

Figure 7-16b shows the M/A content as a function of the transformation start temperature. For the Nb-steel and the NbMo-steel the M/A content also increases with decreasing transformation start temperature while the X80 shows a constant M/A content between 5 and 5.5 % for all three cooling rates. The increase between 650°C and 580°C is in agreement with the previous results observed for X80 where the M/A content increases with decreasing transformation start temperature from irregular ferrite to upper bainite with a maximum M/A content around 600°C before the M/A content then decreases with further decreasing transformation temperature due to a transition from upper bainite to lower bainite.

Figure 7-16: a) Kernel average misorientation and b) M/A content for Nb-steel, NbMo-steel, and X80 as a function of the transformation start temperature
EBSD is an appropriate tool to quantify the complex microstructures in Nb/Mo-microalloyed steels. In particular, the orientation relationship with the prior austenite is used to discriminate between different transformation products, i.e. upper and lower bainite. Similar to the approach made by Takayama et al. [71] KS variants are grouped into three Bain groups to distinguish differences in variant selection. The categories proposed by Takayama et al., as mentioned in section 2.3.4, can be applied to the investigated steels in this study. Upper bainite compares well to the type I bainite defined by Takayama et al. while lower bainite corresponds to their type II bainite. You et al. [162] propose similar categories based on Bain groups for the HAZ transformation products observed in an X100 line pipe steel. They reconstruct several prior austenite grains based on the orientation of the transformation products. The transformation products in their study result from thermal cycles simulating different heat inputs during the second welding pass. While this approach produces microstructures relevant to particular welding scenarios the systematic thermal cycles applied in the current study allow for a more systematic understanding of the possible transformation products based on the austenite conditioning. The agreement of the classification of different bainitic transformation products based on Bain groups indicates that this approach is suitable to compare the complex transformation products of different microalloyed steels.

An advantage of the current study, arising from the separation of matrix and second phase for detailed EBSD analysis is the utilization of the retained austenite identified in all investigated samples to directly determine the 24 KS variants while most approaches found in literature apply complicated austenite reconstruction programs to study the orientation relationship between the parent austenite and its transformation products [71], [163], [164].

Further, microstructure refinement is quantified in terms of HAGB line length per area, including the contribution of martensite/austenite which is made possible by the independent characterization of the M/A constituents and the subsequent combination of M/A boundaries.
and the matrix in terms of HAGBs. The M/A area fractions measured with EBSD are in agreement with the results from optical microscopy while the amount found in lower bainite is twice as high. The small step size of 50 nm accounts for small constituents that are not observed at lower magnifications. The ratio of austenite to martensite is highest for upper bainite, however, RA might transform into martensite leading to an underestimation of the fraction of RA. The aspect ratio of RA and martensite is correlated to the particle size and shows that particles become increasingly elongated with increasing size.

The kernel average misorientation was measured over a range of 150 nm (based on the 3rd nearest neighbour). The comparison of the Nb-, NbMo- and X80 steel shows that these microstructural characteristics can be related to the transformation start temperature. For the X80 steel the KAM increases in the order of polygonal ferrite, irregular ferrite, upper bainite, and lower bainite. The KAM will be used to evaluate the increase in dislocation density for the different transformation products to establish a relation between the microstructure and the tensile properties which will be discussed in the following chapter.
Chapter 8: Modelling

8.1 Introduction

A model was created to describe the austenite decomposition of X80 based on the continuous cooling transformation (CCT) tests described in chapter 6. Three different sequences were observed during CCT tests and are considered in the model:

1. *Austenite decomposes fully into ferrite including M/A:*

   This is only observed for a small austenite grain size, i.e. 5µm and slow cooling up to 10°C/s when Nb is partially precipitated and 3°C/s when Nb is in solution.

2. *Austenite decomposition starts with ferrite and continues with bainite:*

   Initial ferrite formation followed by bainite is observed for 5µm at cooling rates of 30 - 60°C/s when Nb is precipitated and 30°C/s when Nb is in solution and for 26 µm at cooling rates up to 10°C/s when Nb is out of solution.

3. *Austenite decomposed fully into bainite including M/A:*

   The transformation starts with bainite at intermediate and large grain sizes. i.e. 26 µm and 80 µm, for a range of cooling rates between 10 and 100°C/s.
The model is designed to capture the effect of Nb in solid solution, prior austenite grain size and cooling rate. It consists of five sub-models including (i) ferrite start temperature, (ii) ferrite growth, (iii) ferrite/bainite transition temperature, (iv) bainite start temperature, (v) bainite growth kinetics.

Further, the relationship between the microstructure and the tensile behavior is quantified for the X80 steel based on tensile tests carried by Gaudet [149] and the quantitative microstructure description presented in chapter 7. A model is proposed to predict the yield strength, uniform elongation and ultimate tensile strength.

### 8.2 Modelling the austenite decomposition in X80

#### 8.2.1 Ferrite start

The model that is applied here was first introduced to calculate the ferrite start temperature during continuous cooling for a plain carbon steel by Militzer et al. [147] and was then extended to account for a solute-drag effect of Nb in solution [135]. Ferrite nucleation is considered to start at grain corners at a nucleation temperature $T_N$ and early growth of ferrite is assumed to be controlled by carbon diffusion in the surrounding austenite. Adopting a spherical growth geometry and considering steady-state growth, the growth rate of corner nucleated ferrite is given by:

$$\frac{dR_\alpha}{dT} = D_c \left( X_C^x - X_C^0 \right) \frac{1}{R_\alpha} \left( 1 + \frac{D_c \beta_1 X_{Nb}^{sol}}{R_\alpha} \right)^{-1}$$

(8-1)

where $R_\alpha$ is the radius of the corner nucleated ferrite grain, $D_c$ is the diffusion coefficient of carbon in austenite, $\beta_1$ is a parameter accounting for solute drag of Nb, $X_{Nb}^{sol}$ denotes the amount of Nb in solution and $X_C^0$ is the average carbon bulk concentration. $X_C^x$ and $X_C^y$ are the equilibrium atomic fractions of carbon in ferrite and austenite, respectively, calculated with Thermo-Calc using the TCFE7 database. Full equilibrium for all alloying elements is assumed. The carbon profile around the growing ferrite is a function of the radius, $R$, around the grain corner nucleated ferrite with a size of $R_\alpha (R>R_\alpha)$ [147]:

128
\[ X(R) = \left( X_C^\gamma - X_C^0 \right) \frac{R_x}{R} + X_C^0 \]  

(8-2)

Following the approach by Militzer et al. the transformation start temperature is associated with the cessation of ferrite nucleation. Nucleation cannot take place at those boundary areas which are already covered by ferrite or in the proximity of a growing ferrite grain, where the increase in carbon concentration leads to a reduction of the driving pressure for nucleation. Thus, ferrite nucleation is inhibited if a limiting carbon level \( X^* \) is reached at the austenite grain boundaries. The radius \( R^* \) to reach carbon levels of \( X_C > X_C^* \) is given by:

\[ R^* = \frac{X_C^\gamma - X_C^0}{X_C^* - X_C^0} R_a \]  

(8-3)

Nucleation site saturation occurs when the critical carbon concentration \( X^* \) is reached along the entire austenite grain boundaries, i.e.:

\[ R_a \geq \frac{X_C^* - X_C^0}{X_C^\gamma - X_C^0} \frac{d_x}{\sqrt{2}} \]  

(8-4)

The parameter \( X^* \) is related to the austenite grain size \( d_y \) by an empirical expression of the form \( X_C^*/X_C^0 = \lambda_1 + \frac{\lambda_2}{d_y} \) as proposed by Militzer et al. [120] and nucleation site saturation is considered to coincide with measurable ferrite start, i.e. 5% transformed.

The transformation start temperature \( T_s \) under continuous cooling conditions is then obtained by integrating equation (8-1) until condition (8-4) is reached. The adjustable parameters used to calculate the ferrite start temperature are given in Table 8-1.
Table 8-1: Fit parameters to calculate the ferrite start temperature of X80

<table>
<thead>
<tr>
<th>( T_N ) (°C)</th>
<th>( X_C^* / X_C^0 )</th>
<th>( \beta_1 ) (s. ( \mu m^{-1} ).at. ppm(^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 [135]</td>
<td>( 1.74 + 6.8/d_\gamma )</td>
<td>0.043</td>
</tr>
</tbody>
</table>

Although the investigated X80 steel forms irregular ferrite rather than polygonal ferrite the assumption of spherical ferrite nuclei is found to yield good agreement with the experimentally ferrite start temperature and the strong dependence on the austenite grain size observed in the CCT tests can be captured by the model.

If the formation of irregular ferrite is followed by bainite formation, the transition from ferrite to bainite is calculated based on the critical driving pressure for bainite formation. Based on the unified nucleation function proposed by Ali and Bhadeshia [148] providing the minimum driving pressure \( G_N \) necessary to obtain a significant nucleation rate for Widmanstätten ferrite or bainite in low-alloy steels, the critical driving pressure for bainite formation can be calculated as a function of the temperature. The free energy change as a function of the ferrite fraction is calculated with Thermo-Calc database TCFE7 accounting for the carbon enrichment of austenite with increasing ferrite fraction. A transition from ferrite to bainite occurs when the free energy of the system exceeds the driving pressure for bainite formation. The bainite transition temperature \( B_T \) for the investigated X80 steel is obtained from the comparison of the free energy as a function of the ferrite fraction and is given by:

\[
B_T = 640°C - 143f_a^{0.5} + 288f_a - 528f_a^2 + 646f_a^3 - 380f_a^4
\]  

(8-5)

8.2.2 Bainite start

When bainite starts without previous ferrite formation, the carbon content is invariant and hence does not influence the transformation start temperature. The bainite nucleation temperature \( B_N \) of 640°C is determined from the critical driving pressure and is independent of the cooling rate or
austenite grain size. Early growth of bainite laths is considered following nucleation to obtain a measurable amount of bainite, i.e. 5% transformed [121]. A lath geometry with constant area $A$ is assumed where only the length $l$ changes during early growth. Experimental CCT data indicate that the bainite start temperature $B_s$ is independent of the austenite grain size. The model therefore does not include the prior austenite grain size and $B_s$ is reached when 5% of the volume is occupied by bainite laths:

$$0.05 = \int N \, A \, dl$$

(8-6)

Here, $N$ is the number of laths per unit volume. To capture the length change, a linear growth velocity of bainite laths is assumed including a solute drag effect of Nb in solution [121]:

$$dl = \frac{l_1 + l'_2 T}{1 + \beta_2 X_{Nb}^{sol}} dt$$

(8-7)

where $X_{Nb}^{sol}$ is the atomic fraction of Nb in sol and $\beta_2$ is a constant accounting for solute drag of Nb. Assuming that $N$ and $A$ are constant, integration of equations (8-6) and (8-7) yields the bainite start temperature, $B_s$ at a constant cooling rate $\psi$:

$$0.05 = \int_{B_s}^{B_s^\prime} \frac{1}{\psi} \frac{l_1 + l'_2 T}{1 + \beta X_{Nb}^{sol}} dT$$

(8-8)

The adjustable parameters for the bainite start temperature are given in Table 8-2.

<table>
<thead>
<tr>
<th>$l'_1 (s^{-1})$</th>
<th>$l'_2 (s^{-1} C^{-1})$</th>
<th>$\beta_2 (at ppm^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>87.0</td>
<td>-0.132</td>
<td>104.0x10^8</td>
</tr>
</tbody>
</table>

Table 8-2: Fit parameters to calculate the bainite start temperature of X80
The model for the bainite start temperature provides good agreement with dilation measurements. Figure 8-1 compares the experimentally measured and calculated bainite start temperatures for Nb in and out of solution when no ferrite is formed. The shift to lower temperatures when Nb is in solution is well described while the influence of increasing cooling rate for cooling rates higher than 30°C/s is overpredicted by the model when Nb is partially precipitated, i.e. for 93 ppm Nb in solution.

![Figure 8-1: Model prediction and measured bainite start temperature for 26 and 80 µm prior austenite grain sizes considering 204 ppm (grey) and 93 ppm Nb in solution (black)](image)

8.2.3 Growth kinetics

Subsequent ferrite and bainite growth is described using the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model including additivity according to equation (2-4). Based on the CCT diagrams presented in chapter 6, the dilation data was divided into ferrite and bainite fractions. It is found that upper and lower bainite can be described with the same model parameters while a different set of parameters was established for ferrite. To describe ferrite growth kinetics para-equilibrium is assumed.
In the present model the experimental data can be best described using a JMAK exponent \( n \) of 1.1, which is close to the value of \( n=1 \) which has been reported in the previously developed models employing the JMAK equation for the austenite-to-ferrite transformation [120], [147]. The temperature dependent rate parameter \( b \) varies with the austenite grain size \( d_\gamma \) and the amount of Nb in solution and can be captured as follows:

\[
\ln b = b_1 T + \frac{b_2}{d_\gamma^m}
\]

(8-9)

A linear relation is assumed for the influence of Nb in solution as only two different amounts of Nb are considered here, see Table 8-3.

**Table 8-3: Fit parameter to calculate the austenite decomposition kinetics of X80**

<table>
<thead>
<tr>
<th>Ferrite growth</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_1 ) (°C(^-1))</td>
<td>( b_2 ) (µm(^m))</td>
<td>( m )</td>
</tr>
<tr>
<td>(-1.22\times10^{-4} \times X_{Nb}^M - 2.72\times10^{-4})</td>
<td>(7.48\times10^{-2} \times X_{Nb}^M + 1.83\times10^{-1})</td>
<td>(4.87\times10^{-4} \times X_{Nb}^M + 6.28\times10^{-4})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bainite growth subsequent to ferrite</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_1 ) (°C(^-1))</td>
<td>( b_2 ) (µm(^m))</td>
<td>( m )</td>
</tr>
<tr>
<td>(-1.07\times10^{-4} \times X_{Nb}^M - 1.95\times10^{-4})</td>
<td>(6.28\times10^{-2} \times X_{Nb}^M + 1.38\times10^{-1})</td>
<td>(3.32\times10^{-4} \times X_{Nb}^M + 8.95\times10^{-4})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bainite growth without previous ferrite</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_1 ) (°C(^-1))</td>
<td>( b_2 ) (µm(^m))</td>
<td>( m )</td>
</tr>
<tr>
<td>(-1.07\times10^{-4} \times X_{Nb}^M - 1.95\times10^{-4})</td>
<td>(4.88\times10^{-2} \times X_{Nb}^M + 9.92\times10^{-2})</td>
<td>(0)</td>
</tr>
</tbody>
</table>
When austenite transforms fully into ferrite, the ferrite fraction is normalized based on the M/A content. When austenite decomposition starts with ferrite and proceeds with bainite, the ferrite fraction is normalized at the bainite transition temperature while the bainite fraction is normalized based on the ferrite and M/A fractions.

If no ferrite is formed and austenite decomposition starts with bainite, the bainite growth kinetics are independent of the austenite grain size and the parameter $m$ reduces to zero, while the temperature dependent term $b_1$ is the same for bainite with or without preceding ferrite formation. The bainite fraction is then normalized based on the M/A content.

The accuracy of the model was evaluated based on comparing the calculated and experimentally observed temperatures for 50% transformed. An agreement of ±10°C (for most cases ±5°C) between the experimental and calculated temperatures is obtained with the model parameters listed in Table 8-3 for all possible sequences of ferrite and/ or bainite formation. Figure 8-2 shows a comparison of the transformation kinetics measured with dilatometry and the model prediction. The selected cases represent typical austenite conditions in the heat affected where large austenite grains and Nb dissolution are observed close to the fusion zone, while smaller grain sizes and less Nb in solution are observed close to the base metal due to lower peak temperatures. Intermediate grain sizes and varying amounts of Nb in solution are found in areas in between. For 5µm cooled at 10°C/s when Nb is partially precipitated, i.e. 93 ppm Nb in solution, the microstructure fully transforms into irregular ferrite. For 26µm cooled at 30°C/s the transformation starts with bainite. Although the bainite start temperature is overpredicted by the model when all Nb is in solution, the overall shift to lower transformation temperatures caused by the increase of Nb in solution from 93 ppm to 204 ppm is captured by the model. When transforming from an austenite grain size of 80 µm, the austenite decomposition starts with bainite for all investigated cases and a fully bainitic structure is formed, including M/A.
Examples of the experimentally determined phase fractions and the model predictions for 5 and 26 µm with 93 ppm Nb in solution are shown in Figure 8-3. The chosen examples include cases where the austenite decomposition starts with ferrite and continues with bainite. For larger grain sizes and 204 ppm Nb in solution the austenite decomposition mostly starts with bainite formation. A comparison of the model predictions and experimentally determined phase fractions for the remaining cases is shown in the appendix. For an austenite grain size of 5 µm the M/A content varies between 3 and 7% based on the experimentally determined phase fractions and between 5 and 12% based on the model predictions. A gradually decreasing amount of irregular ferrite with increasing cooling rate was observed experimentally. While the model predictions show the same trend, the change in the predicted phase fractions is less gradual. A fully ferritic microstructure, including M/A, is predicted for 3 and 10°C/s, while 70% bainite formation is predicted for 30°C/s and more than 80% of bainite formation is expected for cooling rates of 60 and 100°C/s.
Figure 8-3: Comparison for experimentally determined phase fractions and model prediction for continuous cooling at 3-100°C/s with 93 ppm Nb in solution; a), b) 5µm austenite grain size; b), d) 26 µm austenite grain size

The transformation products formed when transforming from an austenite grain size of 26 µm are mostly bainitic which is both observed experimentally and predicted by the model. For a cooling rate of 3°C/s the model predicts a fully ferritic microstructure containing 5% M/A while a small amount of bainite and an M/A amount of 12% was observed experimentally. During cooling at 10°C/s a small amount of ferrite, i.e. 5%, was observed experimentally which is also captured by
the model. For cooling rates between 30 – 100°C/s a fully bainitic microstructure including M/A is observed experimentally and predicted by the model.

The prediction of the M/A fraction shows opposite trends when comparing the experimentally measured amount and the model prediction, which is due to the calculation of the M/A fraction solely based on the transformation start temperature. While overall similar transformation products are formed at varying transformation temperatures between 600 and 550°C, the amount of M/A in the model is strongly temperature dependent.

8.2.4 Summary

The austenite decomposition model originally proposed by Militzer et al. [120] as part of a process model for hot strip rolling of various low-carbon microalloyed steels containing Nb-Ti-V was applied to the X80 line pipe steel and is capable to capture the influence of Nb in solution on the austenite decomposition in terms of transformation start temperature and growth kinetics of ferrite and bainite. A linear relation is assumed for the influence of Nb as only two different Nb contents were investigated. However, it is expected that the effect of Nb levels out above a certain amount of Nb in solution similar to the study by Isasti et al. [97], mentioned above, where the addition of 0.03 wt. % Nb to a plain carbon steel has a stronger effect on transformation kinetics than the additional increase of Nb in a steel containing 0.06 wt. % Nb with the same base composition.

A prior austenite grain size dependence is observed for the ferrite start temperature and growth kinetics which confirms the observations by Fazeli et al. [121]. The experimentally observed influence of the austenite grain size on the bainite start temperature is negligible and is not included in the model. The bainite start temperature is predicted based on the cooling rate and the amount of Nb in solution. Bainite growth is only grain size dependent in the case of preceding ferrite formation. When the austenite decomposition starts with bainite, the growth kinetics are grain size independent.
8.3 Structure-property relationships for X80

Based on the tensile data by Gaudet [149] and the microstructure parameters obtained from electron backscatter diffraction (EBSD) analysis the tensile behavior of the investigated X80 line pipe steel can be described. Three additional tensile tests were carried out according to the procedures established by Gaudet to include the tensile properties of polygonal ferrite as a benchmark. The experimental tensile data are shown in Table 8-4.

Table 8-4: Experimental tensile data of X80 line pipe steel used to develop structure-property relationships based on EBSD analysis

<table>
<thead>
<tr>
<th>Microstructure type</th>
<th>Yield strength 0.02% offset [MPa]</th>
<th>Uniform elongation</th>
<th>UTS [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polygonal ferrite (1)</td>
<td>370</td>
<td>0.16</td>
<td>633</td>
</tr>
<tr>
<td>Irregular ferrite (2)</td>
<td>500</td>
<td>0.09</td>
<td>725</td>
</tr>
<tr>
<td>Upper bainite (3)</td>
<td>540</td>
<td>0.06</td>
<td>692</td>
</tr>
<tr>
<td>Upper bainite (4)</td>
<td>450</td>
<td>0.08</td>
<td>632</td>
</tr>
<tr>
<td>Upper bainite/ lower bainite (5)</td>
<td>500</td>
<td>0.07</td>
<td>703</td>
</tr>
<tr>
<td>Lower bainite (6)</td>
<td>583</td>
<td>0.05</td>
<td>825</td>
</tr>
</tbody>
</table>

1) Heat treatments and tensile tests were carried out by Gaudet [149]

The work hardening behavior of the investigated X80 steel has previously been described using a dislocation evolution law proposed by Bouaziz [149], [165]. In a first step, the initial dislocation density has to be determined while subsequent dislocation strengthening is then calculated as a function of the strain. Here, the initial dislocation density is calculated based on the yield strength and the measured KAM values.
The yield strength (in MPa) is calculated considering the base strength of the material, \( \sigma_0 \), the grain size strengthening, \( \sigma_{H_A} \), as well as dislocation strengthening, \( \sigma_\rho \). A contribution to the yield strength due to precipitation strengthening is neglected. Based on the ageing observations described in section 5.4 hardening due to Mo precipitation was found to be negligible. Precipitation strengthening of NbCN is not expected as the applied cooling rates (>10\(^\circ\)C/s) do not allow for sufficient time for precipitation during cooling, while the NbCN precipitates formed at 900\(^\circ\)C are likely too coarse to contribute to the strength.

To calculate the yield strength accumulative strengthening is assumed according to:

\[
\sigma_{\text{yield}} = \sigma_0 + \sigma_{H_A} + \sigma_\rho
\]  

(8-10)

The base strength is calculated using the empirical relationship originally proposed for plain low-carbon steels by Choquet et al. \[166\]. While the Choquet equation includes a Hall-Patch type grain size contribution, only the chemistry depend term \( \sigma_0 \) is used for the current analysis:

\[
\sigma_0 = 63 + 23Mn + 53Si + 700 \ P
\]  

(8-11)

where the concentrations are given in wt. %. The Hall-Patch equation considering the grain size in terms of an equivalent area diameter is not appropriate when dealing with the complex ferrite-bainite microstructures of the investigated steel. Instead, the inverse of the high angle grain boundary line length per area (as described in chapter 7, equation (7-1)) is defined as effective grain size, \( H_A \) (in mm), and is used to calculate the strengthening contribution of the observed microstructure refinement caused by increasing high angle grain boundary density. This approach also accounts for martensite/austenite (M/A) which is included in \( H_A \):

\[
\sigma_{H_A} = c_1 H_A^{-1/2}
\]  

(8-12)

A coarse structure such as polygonal ferrite yields a high effective grain size \( H_A \), while the smallest value is observed for lower bainite due to fine bainite laths throughout the structure. To determine
the parameter $c_1$ it is assumed that polygonal ferrite contains the minimum amount of dislocations leading to a negligible dislocation strengthening contribution. Subtracting the base strength from the experimentally measured yield strength then yields the parameter $c_1$ which is found to be 10.3 MPa mm$^{0.5}$. The dislocation density in polycrystalline materials varies from $10^{10}$ m$^{-2}$ in well-annealed crystals to about $10^{14}$ - $10^{15}$ m$^{-2}$ in heavily deformed materials [167]. Dislocation strengthening is given by the Taylor relation [168], [169] according to:

$$\sigma_\rho = \alpha M G \sqrt{\rho}$$  \hspace{1cm} (8-13)

where $\alpha$ is a temperature dependent constant, $M$ is the Taylor factor, $G=76923$ MPa is the shear modulus, $b=2.56 \times 10^{-10}$ is the magnitude of the Burgers vector, and $\rho$ is the dislocation density (in m$^{-2}$). The constants $\alpha=0.3$ and $M=3.06$ are adopted from a previous study on the investigated X80 [149]. With a minimum dislocation density, i.e. $10^{10}$ m$^{-2}$, the dislocation strengthening of polygonal ferrite amounts to 1.8 MPa, which is within the accuracy of yield strength measurements.

Based on the assumptions made by Kubin and Mortensen [170] the kernel average misorientation has been used by several researchers, e.g. [115], [159], [171], to relate the dislocation density to the local misorientation gradients within the microstructure using:

$$\rho = \frac{2\nu}{ub}$$  \hspace{1cm} (8-14)

where the twist angle $\nu$ is replaced by KAM (in rad), the unit length $u$ is associated to the Kernel parameter as 1.86 times the step size [171] and $b$ is the Burgers vector. However, it is found that this approach overestimates the dislocation density of bainite [115]. For the KAM values measured in this study, equation (8-14) yields dislocation densities of $6.9 \times 10^{14}$ m$^{-2}$ - $1.0 \times 10^{15}$ m$^{-2}$ which is in the order of strongly deformed polycrystals and therefore higher than the dislocation densities expected from the $\gamma$-to-$\alpha$ transformation.
Using equation (8-10), the initial dislocation density is used as a fit parameter to match the experimentally measured yield strength. Based on the yield strength, a dislocation density of 4x10^{11} m^{-2} is estimated for irregular ferrite based on a measured KAM value of 0.48°. This value is in agreement with the expected range of dislocation densities in undeformed material [167].

Lower bainite contains the highest dislocation density among the investigated microstructures and also shows the highest KAM value. Based on the experimental yield strength and the relative increase of KAM among the investigated microstructures, see Table 8-5, a dislocation density of 8x10^{12} m^{-2} for lower bainite yields good agreement of the calculated and experimentally measured yield strength (i.e. within 5%). The dislocation density of 8x10^{12} m^{-2} falls into an intermediate range of the values given above for undeformed and highly deformed polycrystals [167]. An empirical expression is established to describe the dislocation density (in m^{-2}) of different transformation products based on the measured KAM values according to:

\[
\rho = 3.4 \times 10^{13} m^{-2} \times KAM - 1.6 \times 10^{13} m^{-2}
\]  

(8-15)

Using the initial dislocation density based on the KAM measurements and the yield strength, the work hardening behavior up to the ultimate tensile strength can be predicted. The evolution of the dislocation density is calculated according to the approach proposed by Bouaziz [165]:

\[
\frac{d\rho}{d\varepsilon} = M \left( \frac{k}{\rho} \sqrt{\rho} \exp \left( -\frac{\zeta}{\sqrt{\rho}} \right) \right)
\]  

(8-16)

where \( k \) is a constant describing the dislocation storage, \( \zeta \) is a characteristic length scale capturing the distance for dynamic recovery and \( M \) is the Taylor factor. The work hardening rate decreases with increasing stress and necking is defined by the Considère-criterion, which is fulfilled when the work hardening rate equals the true stress:

\[
\sigma_{true} = \frac{d\sigma_{true}}{d\varepsilon_{true}}
\]  

(8-17)
Table 8-5: EBSD measurements of microstructure features and resulting strength contribution

<table>
<thead>
<tr>
<th>Microstructure Feature</th>
<th>EBSD Measurements</th>
<th>Strength Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_A$, mm</td>
<td>KAM</td>
</tr>
<tr>
<td>Polygonal ferrite (1)</td>
<td>$1.7 \times 10^{-3}$</td>
<td>0.42</td>
</tr>
<tr>
<td>Irregular ferrite (2)</td>
<td>$8.2 \times 10^{-4}$</td>
<td>0.48</td>
</tr>
<tr>
<td>Upper bainite (4)</td>
<td>$7.0 \times 10^{-4}$</td>
<td>0.62</td>
</tr>
<tr>
<td>Upper bainite (3)</td>
<td>$1.1 \times 10^{-3}$</td>
<td>0.62</td>
</tr>
<tr>
<td>Mix upper &amp; lower bainite (5)</td>
<td>$8.6 \times 10^{-4}$</td>
<td>0.62</td>
</tr>
<tr>
<td>Lower bainite (6)</td>
<td>$5.4 \times 10^{-4}$</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Raeisinia et al. [172] investigated the effect of grain size distributions on the tensile behavior of a number of polycrystals with grain sizes between 500 nm and 50 µm. For polycrystals with varying mean grain sizes where all grains have the same size, they found that as the average grain size increases the yield strength decreases but the work hardening capability of the polycrystals increases. Plastic deformation is assumed to only occur by dislocation-based crystallographic slip and that the evolution of the threshold stress of each slip system is grain size dependent.

Similarly, a higher workhardening rate is observed for polygonal ferrite, with the largest effective grain size in this study, compared to lower bainite with the smallest effective grain size. An empirical approach is proposed here to link this grain size dependence of the work hardening to dynamic recovery, relating the dynamic recovery parameter $\zeta$ to the effective grain size $H_A$, see Figure 8-4. This approach captures the experimentally observed change in work hardening rate for the investigated cases.
Polygonal ferrite was used as a benchmark to obtain the best fit to describe the tensile behavior of X80 in terms of yield strength, ultimate tensile strength and uniform elongation yielding the two adjustable parameters $k=0.265$ and the dynamic recovery rate $\xi$ which is described as:

$$\xi = c_2 H_A^{-1/3}$$  \hfill (8-18)

with $c_2=2.4\times10^{-7} mm^{-1/3}$.

The experimental and calculated true stress-true strain curves are shown in Figure 8-5. Good agreement is obtained for irregular ferrite in terms of yield strength and ultimate tensile strength (UTS). The uniform elongation, however, is over predicted by the model. While the work hardening rate compares well to the experiments in the plastic region, the model does not account for the elastic-plastic transition. At low strains the work hardening rate is very high leading to a

\[\text{Figure 8-4: Empirical correlation between the effective grain size and the dynamic recovery parameter describing the work hardening of X80}\]
steep slope which is not captured by the model therefore resulting in an overestimation of the uniform elongation.

A similar trend is observed for lower bainite. While the yield stress is in good agreement, the work hardening rate is strongly underestimated at low strains while the uniform elongation is overpredicted. Due to the low work hardening rate of lower bainite in the plastic region, the estimation of the UTS is nevertheless within 5% of the experimental results.

The only exception where the model does not predict accurately the work hardening rate and UTS is upper bainite. Although, the calculated UTS of 720 MPa lies within 3% of the experimental value in case (4), see Figure 8-5, the plastic part of the stress strain curves is not captured properly leading to a predicted UTS up to 10% higher than the experimentally measured value in case (3) and (5).

These discrepancies might result from the high amount of M/A that are typically found in upper bainite and in particular the retained austenite which might transform into martensite under stress leading to a transformation induced plasticity (TRIP) effect. Further, a high amount of M/A decorates prior austenite grain boundaries in upper bainite. These necklaces might weaken the material substantially while smaller M/A constituents within the structure can strengthen the material similar to the dual phase structure of a composite material. The current model does not account for these effect of M/A, however, including additional considerations for M/A contents >10% might mitigate the overestimation of the UTS in upper bainite.

Figure 8-6a shows the experimentally measured yield strength using the 0.2% offset method and the calculated yield strength. Good agreement with the experimental measurements is obtained. The calculated values lie within 5% scatter bands (dashed lines) for all microstructures. A conversion of UTS into the engineering stress is carried out to compare the results to the experimentally observed UTS, see Figure 8-6b.
Figure 8-5: Experimental and calculated stress strain curves for various X80 microstructures
Figure 8-6: a) Comparison of model prediction and experimentally measured yield stress of X80; b) Comparison of model prediction and experimentally measured ultimate tensile strength; dotted lines indicate 5% deviation

The predicted UTS is within 5% of the experimentally measured UTS for polygonal ferrite (1), irregular ferrite (2) and lower bainite (6) as well as for one case of upper bainite (4) while the UTS is overpredicted for the second case of upper bainite (3) and the mixed microstructure containing upper and lower bainite (5).

8.3.1 Discussion

A unified model is proposed to connect the obtained microstructures to the resulting tensile properties and to predict the tensile behavior of ferritic and bainitic microstructures in X80 steel in terms of yield strength, uniform elongation and ultimate tensile strength. Similar to approaches found in literature, e.g. [114], [115], [173], [174], the accumulative strengthening contribution of steel chemistry, grain size contribution and dislocation strengthening is considered to determine the yield strength. In a similar approach by Isasti et al. [171], [175] a combination of EBSD analysis and optical microscopy is used to establish structure-property relationships for Nb/Mo-microalloyed steels. In their study, the dislocation density is calculated based on the KAM
following the assumptions of Kubin and Mortensen [170] leading to dislocation densities in the range of $3.5 \times 10^{14} - 6 \times 10^{14}$ m$^{-2}$. The grain size contribution in their study includes grain boundaries with misorientation angles $>2^\circ$ and two different trends are observed depending on whether the steel is microalloyed with Nb or with both Nb and Mo. For the NbMo-steels, a fine substructure is observed, with unit sizes ranging from 3 to 4 µm considering grain boundaries $>2^\circ$ and a sharp increase in yield strength is measured as the unit size decreases. However, there is no clear dependence of yield strength on low angle unit sizes in the Nb-steels. A strengthening contribution of martensite/ austenite is considered in their model based on the M/A fraction determined from LePera etched micrographs.

In the current study, four distinct microstructures, i.e. polygonal ferrite, irregular ferrite, upper and lower bainite have been used to establish structure-property relationships and microstructural features are quantified with electron backscatter diffraction. However, the EBSD analysis does not require the distinction of different transformation products which is often challenging considering the complex transformation products of line pipe steels and the same set of fit parameters is used for all microstructure types. The proposed model uses an empirical relation between the KAM and dislocation density which is scaled with the experimentally measured yield strength. The obtained dislocation densities are lower than those predicted by Isasti et al. [171] or Iza-Mendia and Gutiérrez [115]. Iza-Mendia and Gutiérrez divide boundaries into three categories including low angle boundaries with a misorientation $<2^\circ$, medium angle boundaries with misorientations between 2 – 15° and high angle boundaries with misorientations $>15^\circ$. The first category is assumed to contribute to the overall dislocation density while, medium and high angle boundaries are considered for grain size strengthening.

The comparatively low dislocation density in the current study on X80 leads to a reduced contribution of dislocation strengthening, therefore increasing the grain size contribution to the yield strength. The EBSD analysis presented in chapter 7 replaces the need for optical microscopy for the quantification of martensite/ austenite and allows for the inclusion of M/A in the effective grain size. This new approach is necessary to capture the grain boundary network in the
investigated microstructures due to the high amount of M/A throughout the microstructure, often intersecting with grain boundaries. The proposed high angle grain boundary density is a versatile measure to capture a wide range of microstructures with varying morphologies and can be extended to include low angle grain boundaries.

The model prediction for the yield strength shows very good agreement with the experiments and is within 5% of the experimentally measured yield strength at 0.2% offset strain for all microstructure types. Although the uniform elongation is overestimated for irregular ferrite and bainite by the model due to the very steep slope of the work hardening rate in the elastic-plastic transition region, the predicted ultimate tensile strengths are also within 5% of the experimental data with exception of upper bainite. The high amount of M/A (>10%) contained in upper bainite is assumed to be the main reason for the discrepancy between model and experiments for upper bainite.
Chapter 9: Conclusions and future work

9.1 Conclusions

The current study contributes systematic information on the transformation products to be expected in the heat affected zone of microalloyed steels based on the independent variation of austenite grain size, Nb in solution and cooling rate. The effect of varying amounts of Nb in solution on austenite decomposition in the investigated X80 line pipe steel containing 0.06C- 0.034Nb- 0.24Mo- 0.012Ti- 0.0005N (in wt. %) is quantified and the applied phenomenological model is capable of capturing the experimentally obtained transformation kinetics as a function of the prior austenite grain size, the amount of Nb in solution and the cooling rate.

Despite the limitation of the available methods to estimate the amount of Nb in solid solution, the precipitation kinetics of Nb in austenite at 900°C can be inferred from ageing experiments in ferrite to provide estimates for the amounts of Nb in solution for varying holding times at 900°C. The effect of Nb considered in the austenite decomposition model is obtained from the linearization between two distinct amounts of Nb. This simple approach is suitable to account for the influence of Nb on the austenite decomposition in the investigated conditions. However, it is expected that the influence of Nb in solution approaches a limiting level beyond which there will be no additional effect on the transformation kinetics.
The electron backscatter diffraction (EBSD) analysis of complex transformation products is advanced by a novel definition of the effective grain size considering the combined line length of high angle grain boundaries and the boundaries of martensite/ austenite (M/A) constituents per area. The kernel average misorientation obtained from EBSD is used to determine the dislocation density. This approach provides the linkage of microstructure and tensile properties, i.e. the contribution of microstructural refinement and dislocation strengthening.

In addition to the quantification of microstructural features used to establish structure-property relationships, the EBSD analysis shows that the applied approach using the orientation of the transformation products relative to the retained austenite within the microstructure is a suitable method to distinguish between upper and lower bainite. A comparison with the literature (e.g. [71], [176]) shows that this approach can be applied to line pipe steels with varying compositions and is less subjective than the distinction based on optical microscopy. Furthermore, the separate analysis of matrix and martensite/austenite constituents based on ESBD data improves the quantification of M/A in terms of content, size and aspect ratio and yields more accurate results than the interpretation of LePera etched micrographs.

A model is proposed to predict the tensile properties of the investigated X80 steel in terms of yield strength, uniform elongation and ultimate tensile strength (UTS) based on microstructural features quantified with EBSD. In terms of yield strength and UTS the model is in good agreement with the experimental data for polygonal ferrite, irregular ferrite and lower bainite, while the uniform elongation is overestimated for irregular ferrite and lower bainite. In the case of upper bainite, the model does not capture the influence of the high MA/ content (>10%). Overall, the model shows that the proposed high angle grain boundary density, including martensite/austenite constituents, is a reasonable measure of grain refinement observed in the investigated steel.
9.2 Suggestion for future work

Based on the results of the presented work, several suggestions for future work arise:

- A detailed study with strategically changing amounts of Nb and Mo at a constant base composition in terms of C and Mn will be useful to quantify the combined effect of Nb and Mo on the austenite decomposition in more detail. These experimental studies will permit to extend the austenite decomposition model by including the effect of Mo and a more precise description of the effect of Nb in solution, i.e. considering more than two specific amounts of Nb in solution, on the transformation kinetics.

- Further, it is critical to extend the austenite decomposition model to predict the effective grain size and dislocation density of the transformation products as a function of austenite grain size, cooling rate, and the amounts of Mo and Nb in solution. This will enable the combination of the transformation model with structure-property relationships to predict the resulting mechanical properties.

- The proposed structure-property model to predict the tensile behaviour of X80 should be extended to account for larger amounts of M/A (i.e. M/A >10%). The transformation of retained austenite to martensite as well as the specific arrangements of M/A forming necklaces around prior austenite grain boundaries suggests that M/A should be accounted for to obtain a better prediction of the uniform elongation. 3D EBSD analysis would be a useful tool to obtain more information on the shape of M/A constituents, especially of necklace structures.

- To further employ laser ultrasonics for metallurgy (LUMet) for the design of complex thermal cycles for CCT studies of the investigated steels, the LUMet grain size measurements in the solutionized samples need to be further investigated in the temperature of 900 - 1100°C to clarify the apparent decrease in attenuation attributed to grain scattering.
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Appendix A

A1 - EBSD parameters

The parameters for data collection using the OIM Data Collection software 6.0 are shown below.

The classic Hough transform was applied using a 9x9 convolution mask. The minimum peak magnitude, representing the band contrast was set to 5 and the minimum peak distance in pixels was set to 25. The number of bands detected from each pattern was set to a minimum of 4 and a maximum of 11 bands. A bin size of 8x8 was used with a binned pattern size of 96. The angular spacing of the Hough transform was set to 1°, excluding misorientations between bands <1°.
In the post-processing software, a grain was defined by a tolerance angle of 5° and had to contain at least 4 pixels. The minimum confidence index was 0 for the martensite and austenite data set and 0.2 for the matrix data set.

![Grain Size window with settings]

- **Grain Tolerance Angle**: 5°
- **Minimum Grain Size**: 4 pixels
- **Minimum Confidence Index**: 0.2

Min CI = 0 for martensite & austenite
Min CI = 0.2 for matrix
Appendix B

B1- Comparison of experimentally measured phase fractions and model prediction for 5 µm austenite grain size

The comparison of the experimentally measured and predicted phase fractions for a prior austenite grain size of 5 µm and 93 ppm Nb in solution is described in detail in section 8.2.3. The quantification of transformation products formed from a prior austenite grain size of 5 µm when all Nb is in solution (i.e. 204 ppm) is difficult based on optical micrographs due to a gradual change
of ferritic/bainitic transformation products. Comparing the model predictions, showing a decreasing amount of irregular ferrite when 204 ppm Nb is in solution, to the observation made for the transformation products formed with 93 ppm Nb in solution is in agreement with the overall observations. The predicted amount of M/A based on the ferrite and bainite start temperature compares well with the experimentally measured amount for both cases, i.e. when the transformation is predicted to start with ferrite or bainite.
B-2 Comparison of experimentally measured phase fractions and model prediction for 26 µm austenite grain size

Figure B2: Experimentally measured phase fractions based on optical metallography and model predictions for 26 µm prior austenite grain size; a), b) 93 ppm Nb in solution; c), d) 204 ppm Nb in solution

The comparison of the experimentally measured and predicted phase fractions for a prior austenite grain size of 26 µm and 93 ppm Nb in solution is described in detail in section 8.2.3. When all Nb is in solution (i.e. 204 ppm) the experimentally observed transformation products are fully bainitic for all investigated cooling rates between 3 and 100°C/s. At a cooling rate of 3°C/s the model predicts that austenite decomposition starts with ferrite formation. Although ferrite is not quantified experimentally, it is possible that austenite decomposition starts with ferrite formation
while the amount of irregular ferrite is too low small to be quantified due to the complexity of the transformation products.
B-3 Comparison of experimentally measured phase fractions and model prediction for 80 µm austenite grain size

For a prior austenite grain size of 80 µm austenite decomposition results in fully bainitic transformation products including M/A. As the M/A fraction is predicted as a function of the transformation start temperature, the prediction of the bainite start temperature directly influences the predicted M/A content. The bainite start model slightly overpredicts the transformation start temperature when all Nb is in solution, i.e. 204 ppm, leading to a higher M/A content compared to the experimentally measured fractions. However, the EBSD analysis presented in chapter 7 has
shown a higher M/A content for lower bainite compared to the amount measured based on LePera micrographs.