MICROSTRUCTURE AND MECHANICAL PROPERTIES OF SIMULATED WELD HEAT AFFECTED ZONES IN X80 LINEPIPE STEEL

by

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Abstract

Low carbon micro-alloyed steels are used for linepipe applications as they provide a good combination of strength, toughness and weldability. An important part of the construction for long distance pipelines is the in-field joining of pipes. Owing to the complex thermal cycles during welding, the microstructures and mechanical properties of the base material are altered adjacent to the weld in the region known as the heat affected zone (HAZ), in particular, the regions, i) next to the fusion line (the coarse grain heat affected zone, CGHAZ) and ii) where the thermal fields from multi-pass welds overlap (for example: the intercritically reheated coarse grain heat affected zone, ICCGHAZ).

Using a Gleeble thermomechanical simulator, bulk microstructures, that were representative of the thermal conditions found in the CGHAZ and ICCGHAZ regions, were produced in two high strength low alloy steels. It was found that the cooling rate after the first weld pass had a large effect on the microstructure produced relevant to the CGHAZ. The second thermal excursion involves intercritical annealing of the initial microstructures (relevant to the ICCGHAZ). This produced a nearly continuous necklace of martensite along the prior austenite grain boundaries. The effects of i) the different morphologies of bainite and ii) the intercritical austenite fraction (which transforms to martensite-austenite (M/A) constituents during cooling) on the tensile and Charpy impact properties were systematically studied. The fine bainite microstructures formed at a cooling rate of 50°C/s were found to have the highest density of high angle grain boundaries resulting in the best combination of strength and ductile-brittle transition temperature. Upon intercritical annealing, the ductile-brittle transition temperature was significantly increased when a nearly continuous necklace of M/A formed on the prior austenite grain boundaries (for M/A \ge 10%). This work presents a systematic study on the effect of the fraction of M/A constituents on the tensile stress-strain response and the ductile-brittle transition behaviour. The conclusions from this work have the potential to provide guidelines to linepipe steel producers (in terms of chemistry) and pipeline constructors on the input of different welding parameters on the properties in the heat affected zone of the base pipe.

Lay Summary

The safe, efficient transportation of energy (natural gas and oil) over long distances is important for Canada and the rest of the world. However, there are concerns regarding the safe transmission without any spills, leaks or contamination. One area which requires careful analysis is the welding of steels during construction of pipelines. The strength and fracture properties of the steel adjacent to the weld is affected by the welding. In the present study, bulk samples, which resemble critical regions observed in actual welds, were produced experimentally in the laboratory. The strength and impact toughness of these structures were measured using mechanical tests and the properties were related to welding processes. The conclusions from this work can be used by steel producers to design alloys and by pipeline constructors to choose welding parameters for better strength and toughness upon welding.

Preface

The majority of this research work was conducted and completed at the department of Materials Engineering at The University of British Columbia, Vancouver by the author under the supervision of Dr. Warren Poole. This thesis is written by the author with discussion points and editing support from her supervisor Prof. Warren Poole.

- All the samples were machined at the UBC machine shop from sections of pipes provided by TC Energy and Evraz Inc. NA.
- The Gleeble experiments were conducted by the author with training from Dr. Thomas Garcin and Brian Tran.
- Some of the Charpy impact tests results in Chapter 5 and 6 are based on experiments conducted in Evraz NA R&D facility in Regina, Saskatchewan under supervision of Dr. Laurie Collins. The author was responsible for machining the notches on all samples grinded by the Evraz machine shop. The tests were conducted by Jason Szarkowicz and John Schmidt. The author designed the test temperatures and analyzed the data.
- All the metallography and microstructural analysis were conducted by the author at the electron microscopy facilities at the Materials Engineering department of UBC Vancouver.

A version of Chapter 5 and 6 has been published in a conference proceeding: M. Mandal, W.J. Poole, T. Garcin, M. Militzer, L. Collins, Mechanical behaviour of intercritically reheated coarse-grain heat affected zone in high strength linepipe steels, ASME: Materials and Joining, 2018 as part of the 12th International Pipeline Conference, Calgary 2018. All the co-authors were involved in the discussions held to write the conference paper as well as read and edited the manuscript.

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List of Symbols

A	Temperature dependent constant
A_0	Initial cross section area
a_i	Lattice parameter of phase <i>i</i>
В	Bain group
b	Burgers vector
d	Grain size
D	Diameter of precipitate
d_i	Diagonal length of indentation
d_p	Particle diameter
Ε	Young's modulus
е	Engineering strain
F	Applied load
fi	Volume fraction of phase <i>i</i>
G	Shear modulus
Н	High angle grain boundary density
Κ	Stress intensity factor
k_1	constant related to dislocation storage
k_2	constant related to annihilation
k_f	Petch coefficient for fracture
k_s	Scaling factor
k _y	Petch coefficient for yielding
l	Characteristic length scale

L_0	Initial gauge length
М	Taylor factor
Ms	Martensite start temperature
r_p	Plastic zone radius
S	Engineering stress
Т	Temperature
t	thickness
$T_{i\%}$	Temperature at i% transformation
V	Variants
v	Poisson's ratio
V(T)	atomic volume of the sample at temperature T
V_0	Initial volume
$V_i(T)$	atomic volume of phase i at temperature T
W	width
Wo	Initial width
Г	Normalised obstacle strength
α	Ferrite
γ	Austenite
ΔL	Change in length
ΔV	Change in volume
ΔW	Change in width
$\Delta \bar{g}$	Average misorientation of a point
3	True strain
\mathcal{E}_{f}	True strain at fracture

\mathcal{E}_p	plastic strain
ζ_c	atomic fraction of carbon
θ	Work hardening response
$ ho_{dis}$	Dislocation density
σ	True stress
σ_0	Chemistry dependent base strength
$\sigma_{boundary}$	Boundary strengthening
σ _{dis}	Dislocation strengthening
σ_{f}	True stress at fracture
σ_{GB}	Grain boundary strengthening
$\sigma_{\it ppt.}$	Precipitation strengthening
σ_{ss}	Solid solution strengthening
σ_y	Tensile yield stress
$ au_y$	Shear yield stress
φ	Notch angle

List of Abbreviations

API	American Petroleum Institute
APT	Atom Probe Tomography
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
BCC	Body Centred Cubic
CGHAZ	Coarse Grain Heat Affected Zone
СРР	Close Packed Plane
СТ	Compact Tension
СТЕ	Coefficient of Thermal Expansion
CTOD	Crack Tip Opening Displacement
CVN	Charpy V-Notch
DBTT	Ductile-Brittle Transition Temperature
DP	Dual Phase
DWTT	Drop-Weight Tear Test
EBSD	Electron Back-Scattered Diffraction
EPMA	Electron Probe Micro-Analysis
EQAD	EQuivalent Area Diameter
ERW	Electric Resistance Welding
FCC	Face Centred Cubic
FEGSEM	Field Emission Gun Scanning Electron Microscope
FEM	Finite Element Modelling
FGHAZ	Fine Grain Heat Affected Zone
GMAW	Gas Metal Arc Welding

GND	Geometrically Necessary Dislocations
HAGB	High Angle Grain Boundaries
HAZ	Heat Affected Zone
HSLA	High Strength Low Alloy
ICCGHAZ	Inter-Critically reheated Coarse Grain Heat Affected Zone
ICHAZ	Inter-Critical Heat Affected Zone
IF	Interstitial Free
IPF	Inverse Pole Figure
IQ	Image Quality
KAM	Kernel Average Misorientation
KS OR	Kurdjumov Sachs Orientation Relationship
LAGB	Low Angle Grain Boundaries
LSE	Lower Shelf Energy
LUMet	Laser Ultrasonics in Metallurgy
M/A	Martensite / Austenite
NSERC	Natural Sciences and Engineering Research Council
NW	Nishiyama Wassermann
PAG	Prior Austenite Grain
PAGB	Prior Austenite Grain Boundary
SAW	Submerged Arc Welding
SCHAZ	Sub-Critical Heat Affected Zone
SEB	Single Edge Bend
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
ТМСР	Thermo-Mechanically Controlled Processing

- TRIP TRansformation Induced Plasticity
- USE Upper Shelf Energy
- UTS Ultimate Tensile Stress
- YS Yield Stress

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Dedicated to my parents

Chapter 1: Introduction

Pipelines to transport liquids (e.g. bitumen and refined oil) and natural gas are an integral part of the North American energy landscape. According to Natural Resources Canada, the oil and gas sector contributes an average of \$19 billion in royalties, taxes and fees each year to the government and also constitutes nearly 8 percent of Canada's gross domestic product [1]. Some major crude oil pipelines currently operating in Canada are Enbridge mainline (from Alberta to Wisconsin carrying 2.5 million barrels/day), TC Energy Keystone (from Alberta to Illinois carrying 0.6 million barrels/day), the government of Canada's Trans Mountain pipeline (from Alberta to British Columbia carrying 0.3 million barrels/day) and TC Energy mainline (from Alberta to Quebec) transporting natural gas of 445 million cubic metres/day. On the one hand, there is rising demand for natural gas and crude oil in Canada. A natural gas pipeline is currently being built to the new liquefied natural gas (LNG) terminal at Kitimat in northern British Columbia to keep up with the demand. On the other hand, there are concerns regarding the safe transmission of oil and natural gas from reserves to refineries and distribution centers without any spills, leaks or contamination.

There is a trend towards using pipelines of larger diameter and/or increasing the operation pressure of the pipeline to improve the efficiency of the system. This leads to using higher strength linepipe steel grades so that less material is required thereby lowering material and transportation costs. High strength low alloy steels (HSLA) have been used as a popular material for producing linepipe grades due to its good combination of strength, toughness and the cost effectiveness [2]. In addition, the pipelines operate in extreme environments such as the Arctic where permafrost, frost heave and thaw settlement lead to axial strains in the pipelines as well temperature fluctuations from -60°C to 40°C. Therefore, it is of interest to understand the mechanical behaviour, (i.e. the yield behaviour, the work hardening response and the ductile to brittle transition temperature) for these steels over a wide range of temperature. Construction of pipelines involves: i) roll forming and joining of linepipe steel plates using submerged arc welding (SAW) and ii) in-field girth welding to join the pipes to construct long distance pipelines using gas metal arc welding (GMAW). Girth welding involves the deposition of weld metal in the joints using a single or dual weld torch and automized welding machines. The strength of weld metal can be controlled by the choice of the filler metal and significant research effort has already been given to improve the strength of the weld metal. However, welding the linepipe steels also involves both melting of the base steel at the fusion zone and heating of the steel to high temperature adjacent to the weld pool. This region is known as the heat affected zone (HAZ). The heat affected zones of the SAW and GMAW weld undergo different thermal profiles based on the heat input and number of weld passes.

The HAZ is of interest since the microstructure and mechanical properties are altered in this region as compared to the base metal owing to the complex thermal profile. In particular, the austenite (γ) to ferrite (α) phase transformation during cooling assumes a critical role in determining microstructures and resulting properties. Further, multi-pass welding leads to overlap of the heat affected zone from the different passes. The situation is further complicated when one considers cases of peak temperatures in the intercritical region or for multi-pass welding where, e.g. two peak temperatures can result that both lead to complete or partial austenitization. This leads to a highly complex spatially resolved microstructure.

The HAZ of actual welds possess a graded microstructure which varies within the HAZ. Thus, characterization and testing of the heat affected zones of actual welds is challenging. To address this problem, some research has been done to simulate the HAZ by applying a similar thermal treatment on a bulk sample using a thermal simulator.

The regions of particular concern in the heat affected zone are: i) the coarse grain heat affected zone (CGHAZ): a region which is heated to temperatures above 1300°C during the first pass resulting in austenite with a coarse grain size before cooling to form ferritic or bainitic microstructures and ii) the intercritically reheated coarse grain heat affected zone (ICCGHAZ): the region where the CGHAZ is

exposed to a second thermal excursion into the intercritical region during a subsequent weld pass and upon cooling form a nearly continuous network of martensite/retained austenite (M/A) constituents on the prior austenite grain boundaries in a bainitic matrix.

While there is a large amount of literature on the weld heat affected zone, there are competing and conflicting reports on the effect of the different microstructures in the CGHAZ and the ICCGHAZ on the mechanical properties of the HAZ due to their complexity. The research proposed here will systematically examine the relevant microstructures formed in the CGHAZ and ICCGHAZ during industrial welding scenarios for girth welds by producing bulk samples and will investigate their tensile and Charpy impact properties.

This work is part of a larger ongoing project between TC Energy, Evraz NA and The University of British Columbia Vancouver. In this project, Gaudet [3] and Kulakov [4] experimentally measured the thermal profiles of GMAW and SAW, Reichert [5] and Robinson [6] investigated the kinetics of austenite grain growth and austenite decomposition and Gaudet [3] examined the tensile properties of the various austenite decomposition products from sections of X80 grade linepipe steel originally developed and supplied by TC Energy and Evraz NA. The conclusions from this work have the potential to provide guidelines to linepipe steel producers (in terms of chemistry) and pipeline constructors on the input of different welding parameters on the properties in the heat affected zone of the base pipe.

Chapter 2: Literature Review

2.1 Linepipe steels

Micro-alloyed low carbon steels are well suited to meet the requirements of oil and gas pipeline industry for transmission of liquids and gases. High toughness can be attained in these steels by reducing the carbon content. The resultant loss in strength can be compensated by addition of alloying elements which i) refine the grain size and contribute towards grain boundary strengthening; and ii) form precipitates from microalloying additions such as niobium, titanium, vanadium to provide precipitation strengthening. These alloys have low carbon contents (between 0.03 - 0.1 wt.%), with an amount of manganese up to 2 wt.% [7]. Niobium, vanadium and titanium were initially added individually, in amounts as low as 0.005 - 0.010 wt.% in early steels, but later in combination as the strengths increased and the metallurgical approach became more refined [7].

2.1.1 Grades of linepipe steel

The first reported use of microalloying in linepipe steels occurred in Europe (Mannesmann) for an American Petroleum Institute (API) Grade X52 vanadium steel in 1952 followed by X56 and X60 in 1953 and 1962, respectively [8,9]. The number next to the letter X denotes the yield strength requirement in thousands of pounds per square inch or ksi. There has been a steady increase in available yield strengths from 52 ksi in the 1950s to as high as 120 ksi today using thermomechanical controlled processing [10,11]. Using higher strength steels means less material being required thereby lowering the weight, transportation and material costs. These steels are also required to retain acceptable mechanical properties over the range of the temperature of their use i.e. from -60°C to +40°C. However, despite the considerable amount of research, steels with strengths above 80 ksi are yet to see significant commercial service in pipelines, even though they have been incorporated into the latest revisions of international specifications [12,13]. Today's pipeline designs consider all aspects of a steel's performance, including mechanical properties (strength, fatigue and toughness), ease of fabrication (weldability, bendability) and environmental degradation (stress

corrosion cracking and resistance to sour hydrocarbons containing H₂S and CO₂). All these considerations must be balanced with economic considerations during the selection of chemistry and processing routes.

2.1.2 Overview of linepipe steel chemistry

The properties of steels depend on their microstructure which is controlled by the chemistry and the processing route. Typically, the most effective way to simultaneously improve the strength and toughness of a steel is by grain refinement due to small addition of Nb, Ti and V [7]. Carbon is one of the major alloying elements for strengthening of steels, but the use of carbon is limited due to its detrimental effect on weldability, formability and toughness. The highest strength grades for pipelines typically have carbon contents in the range of 0.03 - 0.06 wt.%. Carbon has different solubilities in ferrite and austenite due to differences in their crystal structure. Therefore, it has the potential to form carbon-enriched phases upon fast or non-equilibrium cooling. In linepipe steels, chemistry is often designed using a carbon equivalent. The carbon equivalent (CE), most commonly used to assess weldability in low carbon steels, is the one used by the American Welding Society (AWS):

$$CE = C + \frac{Mn+Si}{6} + \frac{Cr+Mo+V}{5} + \frac{Cu+Ni}{15}$$
(2.1)

where the elements are in wt.%. Higher CE values indicate high hardenability i.e. a higher potential for martensite formation which is not typically desired due to the low toughness of martensite. AWS suggests that CE should be maintained below 0.5% to avoid brittle failure [14].

Niobium is typically added to linepipe steels in the range of 0.03 – 0.09 wt.%. Nb is widely known to retard the kinetics of austenite recrystallization and grain growth during hot-rolling due to solute drag effect on the migrating boundaries [15] and also by pinning the austenite grain boundaries by precipitates [7,16]. Either mechanism results in a pancaked austenite which promotes the formation of fine grain transformation products. Further, NbC and Nb(C,N) precipitates may form in ferrite after austenite decomposition, contributing to precipitation strengthening [17,18].

Titanium is usually added in the range of 0.001 – 0.0015 wt.% to promote formation of TiN precipitates which are stable up to the melting temperature of the steel. The TiN precipitates can be used to limit austenite grain growth by Zener pinning during reheating of the steel, either for hot rolling or during welding [19]. However, coarse TiN particles above 500 nm can degrade the impact toughness by acting as crack initiation sites [20,21]. The appropriate Ti addition is made depending on the nitrogen content, for example steels produced by an electric arc furnace typically have higher nitrogen contents compared to integrated steel production by a basic oxygen furnace. The Ti/N stoichiometric ratio is usually maintained below 3.42 to avoid large TiN to form in the melt pool [20].

Vanadium, added in the range of 0 - 0.1 wt.%, is a carbide and carbonitride former, contributing towards precipitation strengthening. It has a lesser effect compared to Nb in delaying austenite recrystallization [22,23], but can lead to substantial precipitation strengthening in ferrite [24,25].

Manganese is usually maintained between 1.4 - 1.9 wt.% and it lowers the eutectoid composition and temperature leading to the formation of a three-phase region i.e. ferrite-cementite-austenite in the phase diagram. Moreover, being an austenite-stabilizer, it opens the austenite field thereby narrowing the range of the intercritical temperatures. Mn also forms manganese sulphides (MnS), thereby eliminating the formation of iron sulphides which are detrimental to toughness and lead to hot shortness (i.e. a loss of ductility at hot rolling temperatures) [26,27].

Molybdenum additions between 0 - 0.3 wt.% suppress the formation of pearlite or polygonal ferrite and promotes the formation of irregular ferrite and bainitic microstructures during continuous cooling by reducing the austenite to ferrite transformation temperature [28,29]. Mo also precipitates in form of carbides in ferrite.

2.1.3 **Processing of linepipe steels**

2.1.3.1 Thermomechanical processing

Numerous processing routes are employed by different steel plants to produce linepipe steel grades with similar microstructures and properties. However, the basic philosophy behind the thermomechanically controlled processing schedule, widely known as TMCP route, is as follows:

- *Slab reheating*: Continuous cast slabs are reheated for complete austenitization and elimination of inhomogeneity of the cast structure. Reheating also reduces the flow stress for subsequent deformation and dissolves the majority of micro-alloy precipitates such as Nb(C,N), V(C,N), TiC etc. to achieve the maximum benefit of microalloying [7,30]. Austenite grain growth is also controlled in this step by careful design of TiN precipitates.
- *Rough rolling*: Austenite (γ) grain refinement through static and dynamic recrystallization of γ grains are obtained by applying heavy deformation in multiple passes above the γ-recrystallization temperature [30].
- *Finish rolling*: Further deformations are applied on the strips or plates in the temperature range, above the inter-critical region, where no recrystallization of austenite is possible, thereby forming pancaked austenite structures [7,30].
- *Controlled cooling and coiling*: Controlled cooling is applied on the strips or plates using accelerated water-cooling methods on the run-out table. The cooling rates control the austenite decomposition products which may or may not be complete prior to coiling. The cooling stop temperature for plates determines how much Nb is precipitated and how much solute Nb remains dissolved in the hot-rolled coils.

2.1.3.2 Forming and welding of pipes

Welding is an integral part of pipeline construction where coiled strips are formed spirally or longitudinally in factory facilities using sub-merged arc welding (SAW) or electric resistance welding (ERW) into individual pipes [20,31]. The pipes are transported to the field where the ends around the girth are welded usually by mechanized multi-pass gas metal arc welding (GMAW) to construct long distance pipelines [32]. A schematic of the process is shown in Figure 2.1.



Figure 2.1: Linepipe forming and welding in factory using electric resistance welding (ERW) or submerged arc welding (SAW) and girth welding in field using gas metal arc welding (GMAW) (*Adapted from* [33])

From the early 1960's gas metal arc welding (GMAW) was used in onshore gas pipeline construction for girth welding [32,34]. In GMAW process, an electric arc forms between the base metal and filler wire causing the melting and deposition of the filler metal in the weld. An inert gas such as argon or helium are used to shield the arc and molten pool during the process to protect from oxidation. The single wire mechanized GMAW process is currently the most widely used welding process for girth welding of large diameter transmission pipelines and there have been a number of recent welding procedure developments that have improved its productivity. Dual torch GMAW, where a second welding torch follows the first one within a certain distance depositing more weld metal is also done instead of single torch welding to increase the productivity and reduce the construction costs [35,36]. Continued development of GMAW with dual torch and tandem GMAW is leading to further increase in arc welding

productivity. In tandem GMAW, a single torch with two contact tips is used to feed two wires in a single weld pool [3,36].

Finally, submerged arc welding (SAW) is widely used in the production of linepipe due to economical reason as higher weld metal deposition rate can be achieved owing to faster weld speed [20]. In SAW, a protective gas shield and slag is generated using a blanket of powdered flux and it shields the arc between the base metal and the filler wire. However, a higher heat input is produced which results in a slower cooling of the joints and higher heat penetration in the material [35,36].

2.1.3.3 Weld temperature measurements

Heat-input, welding speed and pre-heat temperatures are some of the major parameters to predict the temperature distribution around a steel weld [35]. The heat input determines the peak temperature of the weld thermal cycle and the subsequent cooling rate in the heat affected zone (HAZ), i.e. higher heat input leads to a lower cooling rate. Analytical temperature models such as the Rosenthal equation can be used to calculate the temperature distribution around the weld in single torch welding, but significant approximations are required [35]. Real time temperature measurement using thermocouples is an alternate to study the complex thermal profile.

The Microstructure Engineering Group at UBC has experimentally measured the temperature profile for both GMAW and SAW using embedded thermocouples. Figure 2.2 shows an example from Gaudet [3] for a single pass GMAW. It was found that the average cooling rates in the temperature range for austenite decomposition are almost independent of the peak temperature. The common transformation start temperatures relevant to HAZ is between 600°C to 500°C (see Reichert and Robinson [5,6]). In this temperature range, Gaudet [3] calculated the cooling rate to be \sim 50°C/s. Figure 2.3 show the results from Kulakov [4,37] for submerged arc welds. In this case also, the cooling rate in the temperature range of 500 – 600°C was measured to be \sim 5°C/s. It is noted that these cooling rates are consistent with other results reported in the literature [3,37–41].



Figure 2.2: Temperature profile measured in a weld thermal cycle of a single torch GMAW for 0.25 kJ/mm heat input and 17 mm/s weld speed (*Reprinted with permission from author* [3])



Figure 2.3: Temperature profile measured by welding thermocouples at different distances away from the fusion line in a submerged arc weld for 2.5 kJ/mm heat input and 12.7 mm/s weld speed (*after* [4,37])

2.1.3.4 The heat affected zone

Welding of linepipe steels involves both melting of the steel and heating of the steel adjacent to the weld pool. The region of the welds outside the fusion zone is known as the heat affected zones (HAZ). While the base metal of state-of-the-art linepipe steels mainly consists of irregular ferrite or bainite, the microstructure in the HAZ is more complex and diverse depending on steel chemistry and the local cooling rate (which is inversely related to the heat input) [42–48]. The HAZ is categorized into four regions for a single pass weld: the coarse grain HAZ (CGHAZ) which is closest to the fusion line followed by the fine grain HAZ (FGHAZ), intercritical HAZ (ICHAZ), and subcritical HAZ (SCHAZ), as shown schematically in Figure 2.4 [36]. The CGHAZ is closest to the fusion zone where the temperature is high (~1350°C) such that austenite formation is complete and substantial grain growth occurs. It typically shows very large prior austenite grains owing to the high peak temperature of the welding pass. The FGHAZ forms when the region is fully austenite, but austenite grain growth is limited by low peak temperature. The ICHAZ is formed when the peak temperature is not high enough to facilitate complete austenitization, thus partial transformation into the $\alpha + \gamma$ phase field occurs followed by cooling to form transformation products. The SCHAZ is the region farthest away from the fusion zone where no austenite is formed but the base metal undergoes tempering and coarsening of carbides.

During multi-pass welding, a complex set of microstructures is formed in regions where the thermal fields from two weld passes overlap, i.e. the heat affected zones from a prior weld pass may undergo another thermal excursion and the overlap of different thermal fields occurs, as shown in Figure 2.5 [49]. Among all the zones, the most complex zone is the region where the CGHAZ from the first torch is reheated to the intercritical region i.e. $\alpha + \gamma$ phase field, resulting into partial austenitization. Austenite has been observed to form at the prior austenite grain boundaries producing necklace like structure which then transforms to martensite during cooling [50–52]. This region is referred to as the intercritically reheated coarse grain heat affected zone (ICCGHAZ) and there has been considerable interest to understand the effect of this region on the overall performance of the weld [38,40,43,46,50,53–58].



Figure 2.4: Schematic showing the relation between peak temperature, HAZ microstructure and Fe-C phase

diagram for a single torch weld, (adapted from [36])



Figure 2.5: Schematic of thermal profiles and corresponding HAZ during multi-pass welding (Adapted from

In investigations by Lee et al. [59], Davis and King [50,59], Li et al. [60], Bonnevie et al. [61], Li et al. [41,62], Mohseni et al. [46,57], Huda et al. [52,63], it is seen that the ICCGHAZ typically has higher amounts of martensite-austenite (M/A) constituents compared to CGHAZ. The literature has shown that that the CGHAZ [39,44,48,64–68] and ICCGHAZ [38,40,43,46,50,53–58] are important for the fracture behaviour at the welds. The next sections will review the relevant literature on the phase transformation and related mechanical properties for the HAZ.

2.2 Phase transformations

During weld thermal cycles, the heat affected zone reaches high temperatures where the base plate transforms to austenite (or partially transforms if the peak temperature is in the intercritical region) and then decomposes to various transformation products. The phase transformations in these regions can be divided in the following subsections.

2.2.1 Austenite formation

Austenite formation is a nucleation and growth process and as such the kinetics of austenite formation depends on heating rate and the initial state of the microstructure [69,70]. Increasing the heating rate shifts the austenite formation to higher temperatures for a given initial microstructure [69]. The final austenite grain structure depends on the kinetics of austenite formation as well as the peak temperature. In welding, austenite formation is of primary interest for microstructure evolution in the weld heat affected zones. The heating rates can be greater than 1000°C/s. The kinetics of austenite formation are usually investigated using the change in dimensions of the sample as ferrite/cementite transforms to austenite [71,72] and most recently using high energy in-situ X-ray diffraction [73,74]. As a general observation, for cases of complete austenitization the final microstructure is weakly dependent on process conditions since austenite grain growth determines the final microstructure as will be described in the next section.

2.2.2 Full austenitization followed by grain growth

The grain size of austenite plays a key role in controlling the subsequent austenite decomposition [6,19,75–77]. For example, a large austenite grain size shifts the austenite decomposition to lower temperature affecting the decomposition products. Microalloying elements such as Nb and Ti can be added to retard austenite grain growth due to formation of precipitates [7]. However, microalloying precipitates based on Nb (e.g. NbC, Nb(C,N)) undergo coarsening and dissolution above 1100°C resulting in a change of the pinning pressure at the austenite grain boundaries [19,76,78,79]. The investigation by Banerjee et al. [76] regarding the effect of heating rates up to 1000°C/s and various austenitizing temperatures up to 1350°C on the non-isothermal grain growth typical for the HAZ found that rapid dissolution of Nb-rich precipitates enables grain growth above the dissolution temperature and the austenite grain size depends primarily on the peak temperature and is only weakly dependent on the heating rate.

The measurement of austenite grain size is challenging since austenite is not stable at room temperature [80]. Metallographic techniques involve tempering of rapidly quenched microstructures. Segregation of S and P at the prior austenite grain boundaries allows them to be revealed upon subsequent etching. In the past two decades, in situ monitoring of austenite grain size evolution has been developed using laser ultrasonics. The attenuation of the ultrasonic waves has been carefully correlated with the austenite grain size making in situ grain size measurements possible [6,71,79].

2.2.3 Intercritical austenite formation

When the steel is heated to an inter-critical temperature, i.e. between Ae₁ and Ae₃, a mixture of austenite and ferrite is produced, i.e. relevant to the ICCGHAZ shown in Figure 2.5. The favorable sites for austenite nucleation are the carbon enriched regions and prior austenite grain boundaries. A necklace structure of austenite along the prior austenite grain boundaries is commonly observed [71,81,82]. The kinetics of austenite formation depends on both carbon diffusion and interface mobility where the substitutional elements slow down interface migration by solute drag [83]. There is also some limited redistribution of the substitutional elements such as Mn.

2.2.3.1 Effect of initial microstructures and heating rate on intercritical austenite formation

The effect of the initial microstructure on austenite formation has mostly been studied for coldrolled ferrite-pearlite microstructures [69,70,73,81,83–86]. The interaction between ferrite recrystallization and austenite formation not only affects the kinetics of austenite formation but also the spatial distribution and morphology of austenite [81]. For martensitic/bainitic initial microstructures, the temperature of austenite formation is thought to be only weakly affected by the initial microstructures [71,87]. However, Garcin et al. [71] observed that a smaller austenite grain size was obtained when transforming from a fine bainite microstructure as compared to coarse bainite. This behaviour indicates some recovery of the initial bainite/martensite and the cementite particles serve as new nucleation site for austenite. At higher heating rates, a finer and more heterogenous austenite structure forms due to the activation of more nucleation sites in the initial microstructure [81,88,89].

2.2.3.2 Tempering of initial structure during intercritical annealing

In cases where the initial microstructure is bainite or martensite, tempering of the untransformed structure can occur. Relatively little is known about possible tempering effects in linepipe steels. However, general observations suggest that precipitation and/or growth of carbides and recovery of dislocation structures will probably occur [90]. The early study of Irvine and Pickering [91] showed that annealing of a low carbon steel with a bainitic microstructure at a temperature of ~700°C produced a slight recovery and not much change in the morphology of the bainitic ferrite or the number density of carbide particles. However, it has been found from a recent study by Zhou et al. [92] that tempering of a granular bainitic structure at 600 °C for 2 hours resulted in an increase in strength due to precipitation of microalloying carbides and a significant decline in toughness. Given the limited and conflicting results in the literature, it is challenging to make predictions for particular cases, i.e. each must be considered on a case by case basis.

2.2.3.3 Characterization of austenite formation

The fraction of austenite formed during intercritical annealing is most commonly measured using a dilatometer attached to the sample during the thermal cycle which measures the dimensional changes associated with the ferrite to austenite phase transformation and thermal expansion/contraction [72,93,94]. It is common to use the lever rule to analyze dilation data in order to characterize the transformation behaviour. However, the lever rule analysis assumes that the concentration of carbon in austenite remains constant (at the bulk composition) at all stages of the transformation, while in reality, the local carbon concentration in austenite gradually decreases and this affects the thermal expansion. As a result of this, the lever rule analysis systematically underestimates austenite fraction in the beginning of austenite formation, but yields more accurate results in the later stages [94,95]. Kop et al. [95] have addressed this short coming by calculating the fraction transformed on the basis of lattice constants of ferrite and austenite considering the effect of carbon on the lattice parameter of austenite.

The carbon concentration of the austenite formed during intercritical annealing is a function of the amount of austenite formed and the overall carbon concentration of the steel. The relative amount of austenite formed at a particular intercritical temperature is also dependent on the overall concentration of the steel, as defined by the phase diagram [82]. The carbon concentration of austenite deceases as the fraction of austenite increases and reaches the bulk carbon concentration for the steel when 100% austenite is formed.

2.2.4 Austenite decomposition

2.2.4.1 Decomposition products upon continuous cooling from 100% austenite

The formation of different phases in linepipe steels after either hot rolling or a weld pass depends on many factors including the austenite grain size, the state of microalloying elements (precipitated or in solid solution), the conditioning of austenite (i.e. pancaked unrecrystallized grains during hot rolling) and the cooling rate. The common microstructures found upon continuous cooling are irregular ferrite and/or bainite along with some martensite/retained austenite (M/A) constituents (i.e. typically < 10%) [5].

Irregular ferrite

Ferrite mainly nucleates heterogeneously at grain boundaries at sufficiently slow cooling rates (<10°C/s) depending on the austenite grain size and whether Nb is in solution or precipitated. The nonequiaxed fashion of growth is attributed to the growing ferrite which can no longer maintain the planar interface with the carbon enriched austenite [82]. Both short range carbon-diffusion and interface reactions such as Nb solute drag play a major role in the rate controlling mechanism [29,96,97]. At larger undercooling, the increased tendencies of the ferrite to grow from the grain boundaries as plates promote the formation of Widmanstatten ferrite. With larger undercooling and a decrease in the transformation temperature, there is an increase in the dislocation density as well as some grain refinement due to activation of further nucleation sites resulting in some strengthening relative to polygonal ferrite [82].

Bainite

As austenite is undercooled further, the driving force for transformation is increased but the rate of diffusion is reduced. This leads to a complex interface motion leading to the formation of lath or plate like microstructure known as bainite. There are two competing theories for explaining the transformation mechanism of bainite. The first theory proposes a diffusion-controlled transformation, describing the growth of the subunits occurs through carbon diffusion with subsequent precipitation of cementite, i.e. these processes take place simultaneously during the transformation [98,99]. The second theory favors a displacive, diffusion-less transformation, where carbon diffuses after the transformation away from the supersaturated ferrite to the inter-lath regions or precipitates within the laths [90]. Both the theories agree upon the classification of bainite into upper and lower bainite nomenclature and the incomplete reaction phenomenon due to carbon-supersaturated untransformed or retained austenite. Upper bainite forms at higher temperatures, resulting in a series of parallel ferrite laths separated by continuous or semi-continuous layers of carbide [82,100]. Lower bainite forms at lower temperatures where ferrite takes the form of laths or plates with carbides distributed inside the laths.

Crystallography of bainitic microstructures

In last two decades, the crystallography of bainite has been researched in detail [47,48,100–107]. Bainite nucleates with a specific orientation relationship with the parent austenite. The orientation relationship (OR) is described by the misorientation between two crystallographic lattices and can be quantified by parallel planes and directions of parent and product phases [108]. Most experiments report the Kurdjumov-Sachs (KS) or Nishiyama-Wasserman (NW) orientation relationship of the transformation product with the parent austenite. Both the NW and the KS 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> γ direction within the {111} γ plane to be parallel to a <111> α direction within the {110} α plane. The NW OR only differs in the parallel directions, requiring a $<112>\gamma$ direction parallel to $<110>\alpha$. These orientation relationships can be useful to discriminate the types of bainite. Depending on austenite state and the cooling path different selections of the 24 KS variants may occur during the austenite decomposition [105,109]. The 24 variants according to KS orientation relationship and inter-variant misorientation characteristics are shown in Table 2.1. The 24 variants can be divided into four close packed crystallographic packets (CPP) groups, each of which contains laths with same parallel ferrite plates as the habit plane, e.g. V1 to V6 in CPP1 in Table 2.1. The KS variants can also be grouped according to three variants of the Bain correspondence, also known as Bain groups or blocks: B1 (V1/V4), B2 (V2/V5) and B3 (V3/V6). Thus, each Bain group may contain eight variants depending on variant selection, the variants with one Bain group or block are separated by low misorientation angles. Therefore, packets are a group of variants belonging to same CPP groups whereas blocks are variants belonging to same CPP groups and Bain groups. Adjacent Bain groups or blocks such as B1 and B3 or B2 and B3 are separated by high misorientation angles.

Table 2.1: Twenty-four variants according to KS orientation relationship and inter-variant misorientation

Var. No.	Plane Parallel	Direction Parallel	Close-packed Plane (CPP) Group	Bain Group / Correspondence	Misorientation from V1	Boundary Type
V1	(111),//(011) _a	[101],//[111],	CPP1	B1 / [001] _y	-	-
V2		[101],//[111],		B2 / [0,0,1] _y	60.00°/[111]	Block
V3		[01]], // []],		B3/[010],	60.00°/[011]	Block
V4		[011],//[111],		B1 / [001] _y	10.53°/[011]	Sub-block
V5		[110],//[111] _α		B2 / [0,0,1] _γ	60.00°/[011]	Block
V6		[110] _y // [111] _a		B3 / [010] _γ	49.47° / [011]	Block
V7	$(1\overline{1}1)_{y}/(011)_{\alpha}$	[101] _γ // [111] _α	CPP2	B2 / [0,0,1] _γ	49.47° / [111]	Packet
V8		$[10\overline{1}]_{y} // [\overline{1}1\overline{1}]_{\alpha}$		B1 / [001]γ	10.53° / [111]	Packet
V9		[110], // [111] _α		B3 / [010] _γ	50.51° / [10313]	Packet
V10		[110] _γ // [111] _α		B2 / [0,0,1] _γ	50.51° / [755]	Packet
V11		[011] _γ // [11] _α		B1 / [001]γ	14.88° / [1,5,13]	Packet
V12		$[011]_{\gamma} // [\overline{1}1\overline{1}]_{\alpha}$		B3 / [010] _γ	57.21° / [356]	Packet
V13	(111),//(011) _a	[011] _y // [111] _a	CPP3	B1 / [001] _γ	14.88° / [5131]	Packet
V14		$[0\overline{1}1]_{\gamma}$ // $[\overline{1}1\overline{1}]_{\alpha}$		B3 / [010] _γ	50.51° / [557]	Packet
V15		[Ī01] _γ // [ĪĪ1] _α		B2 / [0,0,1] _γ	57.21° / [625]	Packet
V16		$[\bar{1}01]_{y} // [\bar{1}1\bar{1}]_{\alpha}$		B1 / [001] _γ	20.61° / [11116]	Packet
V17		[0,1,1], // [111] _a		B3 / [010] _y	51.73° / [11611]	Packet
V18		$[0,1,1]_{y} // [\overline{1}1\overline{1}]_{\alpha}$		B2 / [0,0,1] _γ	47.11° / [241021]	Packet
V19	$(11\overline{1})_{y}/(011)_{\alpha}$	$[\bar{1}10]_{y} // [\bar{1}\bar{1}1]_{\alpha}$	CPP4	B3 / [010]γ	50.51° / [3 13 10]	Packet
V20		[110], // [111] _a		B2 / [0,0,1] _y	57.21° / [365]	Packet
V21		[0]]], // []]],		B1 / [001] _γ	20.61° / [301]	Packet
V22		$[0\overline{1}\overline{1}]_{y} // [\overline{1}1\overline{1}]_{a}$		B3 / [010] _y	47.11° / [10 21 24]	Packet
V23		$[0,1,1]_{y}$ // $[\overline{1}\overline{1}1]_{a}$		B2 / [0,0,1] _γ	57.21° / [256]]	Packet
V24		$[0,1,1]_{\gamma} // [\bar{1}1\bar{1}]_{\alpha}$		Β1 / [001] _γ	21.06° / [940]	Packet

characteristics [105](Reprinted with permission from Elsevier)

Extensive work on variant selection in bainite by several researchers [47,48,101,104,105,107] postulates that the austenite to ferrite transformation temperature plays the key role in the selection and distribution of the preferred orientations or variants. A schematic of variant selection in low temperature and high temperature bainite is shown in Figure 2.6. During transformation, the transformation strain is accommodated by plastic deformation of the austenite. At low transformation temperature, the plastic accommodation is difficult, thereby favoring the formation of group of laths with same variants and different Bain groups: for example variant pairing of V1 and V2 or formation of all six variants within one packet can accommodate more transformation strain [45,47]. Therefore, the density of high angle boundaries is higher in low temperature transformation products. The thickness of the bainitic subunits decreases at the lower transformation temperatures, as demonstrated by Singh et al. [110]. They also proposed that high undercooling increases the driving force causing more frequent nucleation and impingement, therefore restricted growth of subunits. At high transformation temperatures, the plastic strain accommodation is easier due to the lower flow stress of austenite, thereby, favoring the arrangements of

variants in Bain zones, with low misorientation angles between the variants forming sub-blocks. An example is upper bainite, also termed as granular bainite which exhibit a greater number of low angle misorientation and low amount of high angle misorientations [111].



Figure 2.6: Distribution of crystallographic orientations or variants in (a) low temperature bainite or lath bainite and (b) high temperature bainite or granular/upper bainite [45] (*Reprinted with permission from*

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Martensite / austenite constituents (M/A)

During the austenitic decomposition into bainite or irregular ferrite, the partitioning of carbon to the remaining austenite leads to the formation of the carbon enriched M/A constituents. For the low temperature bainite transformation (500 - 550°C), the study of Reichert [112] found that for similar steels which will be examined in the current work, fine M/A constituents with percentage area up to ~3 % are located within the bainite laths whereas for high temperature transformation (~580 - 600°C) products up to 12 % M/A constituents are reported both at the boundaries and within the laths [5,112]. A detailed analysis of the M/A constituent in a Nb-microalloyed steel by Shanmugam et al. [113] revealed alternatives layers of martensite and retained austenite within M/A constituents. Very recently, Takayama et al. [114] conducted three-dimensional EBSD coupled with TEM analysis suggesting that when the surrounding bainite variants have same growth direction. Blocky M/A forms when the surrounding bainite variants have different habit plane

or growth direction [114]. Reichert et al. [112] suggested that the M/A constituents located at the boundaries are elongated with an aspect ratio of \sim 3 whereas the M/A inside the grains are more spherical. However, the formation of M/A is governed by the stability of austenite which is controlled by the morphology of bainite.

Martensite

The martensitic transformation requires a very high driving force and occurs during rapid cooling from austenite at temperatures below the martensitic start temperature (M_s) and well below the Ae₃ temperature. Depending on carbon content, body-centred tetragonal or body-centred cubic martensite forms as thin plates or laths in order to minimize the misfit strain [115] by a large shear deformation of the facecentred austenite lattice without any diffusion of atoms. The orientation relationship leads to a characteristic lath morphology in low carbon steel [116,117]. Each plate is characteristically tilted with respect to its habit plane and the apparent homogeneous nature of this distortion is best described as an invariant plane strain [118]. The mechanical properties of martensitic steels are greatly affected by the microstructures. The strength of low-carbon steels with lath martensite structure increases as the packet size decreases [117]. In most cases, the packets are clearly recognized from the orientation analysis. However, within each packet, all six possible variants do not necessarily appear and the number of the variants seems to depend on the size of the packet [119]. The temperature at which martensite starts to form can be calculated with the aid of empirical equations derived from a large body of experimental data [120]:

$$M_{s}(^{\circ}C) = 539 - 423C - 30.4Mn - 17.7Ni - 12.1Cr - 7.5Mo$$
(2.2)

where the chemical composition is that of untransformed austenite in wt.%.

2.2.4.2 Austenite decomposition from the intercritical region

Intercritical annealing controls the volume fraction and chemical composition of ferrite and austenite prior to the cooling step. However, after intercritical annealing the phase fractions may change depending on the cooling path. The formation of ferrite can take place such that the austenite grains shrink by movement of existing austenite/ferrite phase boundaries. Such growth of existing ferrite without nucleation is known as epitaxial ferrite growth [89]. During the epitaxial growth of ferrite, carbon is rejected into surrounding austenite creating a concentration gradient. As soon as conditions necessary for bainite formation are achieved, it forms in the interior of the austenite particles, where carbon concentration is lower and austenite thermodynamically is less stable [121]. During cooling to room temperature, any remaining austenite is transformed into pearlite upon slow cooling and into martensite upon very fast cooling or bainite at intermediate cooling rates.

Intercritical M/A formation (relevant to ICCGHAZ)

The M/A constituents can be found after intercritical annealing for various scenarios relevant to the HAZ, but the region of most interest is when 5 - 20% austenite is formed. Austenite preferentially nucleates along the prior austenite grain boundaries and bainite lath boundaries, i.e. the regions with higher concentration of carbon. These austenite islands become further enriched in carbon due to the high diffusivity of carbon in ferrite and its high solubility in austenite. The carbon enrichment in austenite reduces the driving force for ferrite or bainite transformation during cooling. If the carbon enrichment is high enough (~1.4 wt.%), austenite can be stabilized until room temperature. However, the austenite typically has a gradient of carbon within it and as such some transforms to martensite leaving films of retained austenite adjacent to the martensite. The subsequent cooling results in new M/A constituents decorating the prior austenite grain boundaries in a connected necklace fashion [114,122].

2.2.4.3 Characterization of microstructures

Conventional metallography routes are used to characterize the ferrite microstructures but bainitic microstructures are widely characterized using the electron back-scattered diffraction (EBSD) technique. The use of EBSD allows to determine the orientations of different variants of bainite and the orientation relationship with the parent austenite [100,105–107]. EBSD also provides the angle of misorientations

between neighboring grains and sub-grains. Further, extensive work by Britton and Wilkinson [123,124] on measurements of residual elastic strain and lattice rotations using high resolution 3D-EBSD has also allowed for the estimation of geometrically necessary dislocation densities (GNDs) for well-defined cases.

The presence of martensite and its area fractions can be characterized by LePera's etch. This etch reveals martensite as bright white, bainite as black and ferrite as brown [125]. In general, the internal structure of martensite is too fine to be characterized using optical microscope, SEM or EBSD [5]. Transmission electron microscopy (TEM) can be used to resolve the internal martensite structure and to estimate the dislocation densities. However, recent literature has reported the mapping of M/A constituents using 3D EBSD along with TEM [48,114]. The composition of the M/A constituents can be estimated using electron probe micro analysis (EPMA) (although measuring carbon is not possible using EPMA) or atom probe tomography (APT).

2.2.4.4 Relevance to the HAZ microstructures

Coarse grain heat affected zones (CGHAZ)

The CGHAZ is characterized by coarse austenite grains formed during the weld pass. Adjacent to the fusion zone, the local temperature is just below the melting temperature (~1450°C) depending on the detailed chemistry. The temperature history is highly non-isothermal and depends primarily on the heat input and pre-heat temperature. The basic metallurgical processes involved are non-isothermal grain growth (including dissolution of microalloying precipitates) [76,78,79] followed by decomposition of austenite [68,126,127]. The average austenite grain size is relatively large 40 - 80 μ m [6,79,128] with the niobium carbonitrides dissolved [6,68,128], but TiN mostly remains stable.

The decomposition of austenite is dependent on the austenitic microstructure produced during the thermal cycle, i.e. the austenite grain size, the state of microalloying elements (either precipitated or in solid solution) and the cooling rate. As described in Section 2.1.3 on weld trial measurements, the cooling rates in the temperature range where austenite decomposition begins vary between 5 - 50°C/s [3,37–41]. The resulting microstructures are typically bainitic due to the large grain size, the effect of niobium solute drag

on depressing the transformation start temperature and the relatively high cooling rate [5,129]. Further, there is a transition in the bainitic microstructures as cooling rate increases i.e. at low cooling rate resulting in higher transformation temperatures, bainite forms with predominately one Bain group while at lower transformation temperature, all 24 KS orientations of bainite are observed (multiple Bain groups) [45,47,101,104,105,130].

M/A constituents with different fractions and morphologies are found in the CGHAZ and this is determined by the stability of retained austenite during the austenite to bainite transformation. Terasaki and Komizo [131] 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 Bain group. Both elongated and equiaxed M/A of about 4 - 6% by area are reported for medium to high heat input CGHAZ by Lambert-Perlade [65]. Reichert et al. [112] suggested that the M/A constituents located at the boundaries are elongated with an aspect ratio of ~ 3 whereas the M/A inside the grains are more spherical. The mean size of M/A in the CGHAZ varies from $0.3 - 1 \mu m$ in the low temperature bainite and $1 - 3 \mu m$ in the high temperature bainite [40,52,107].

The CGHAZ has been widely considered as a potential region of low toughness and increased ductile-brittle transition temperature by several researchers [23,44,45,58]. M/A constituents in bainitic structures are theorized to act as cleavage crack nucleation sites [46,52,57,65,132,133]. However, Li and Baker [53] noted that M/A constituents may also act as crack deflection sites. Further, the distribution of M/A is crucial: M/A can be present as isolated islands, films or necklace structure [134] and morphology is thought to be important for fracture [61]. Further, Subramanian et al. argued that at higher cooling rates i.e. lower transformation temperatures, the bainitic transformation occurs by formation of different Bain groups with high angle boundaries between the variants resulting in an increase in toughness, essentially due to a dramatic refinement in the microstructure [5,41,45,104,105]. On the other hand, Hutchinson et al. [48] recently reported very different behaviour for toughness in two steels which have similar strength levels (a V-Nb and Nb based steel) suggesting the complexity of the problem. However, it is generally

understood that the high temperature decomposition products i.e. upper bainite or granular bainite microstructures and M/A constituents in the CGHAZ are more prone to low toughness [113,132,135].

Intercritically reheated Coarse grain heat affected zones (CGHAZ)

It has been reported that approximately 2 - 20% M/A constituents are found in ICCGHAZ of linepipe steels and the M/A constituents are arranged in a nearly continuous necklace fashion at the prior austenite grain boundaries constituents [41,43,47,50,54,62,136,137]. The area fraction of M/A increases with an increase in the intercritical temperature [50]. For a X100 steel containing Fe–0.07C–0.25Si–1.94Mn–0.081Nb–0.28Cr–0.26Mo–0.014Ti, the intercritical M/A particles were found to be notably enriched with C-0.49 wt.% and Mn-2.3 wt.% with using atom probe tomography [138], however the fraction of M/A was not reported. Li and Baker [53] reported four different morphologies of M/A particles including blocky particles, also described as islands, 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.

However, crystallographic studies of the M/A constituents formed after intercritical annealing has not been studied in detail due to the microstructural complexity. Both lath and twinned martensite are reportedly present in the M/A [139–141]. Lambert-Perlade et al. [141] reported that martensite constitute the majority of the M/A and are surrounded by retained austenite at periphery in simulated ICCGHAZ. Recently, Li et al. [62] confirmed that the grain boundary M/A constituents are lath martensite in majority (87%) with a near KS orientation relationship with the neighboring retained austenite.

2.3 Mechanical properties

A wide range of mechanical tests have been used to evaluate the performance of linepipe steels including the weld HAZ. The mechanical properties of the different microstructures relevant to as-rolled products and HAZ will be considered in this section. In order to evaluate the mechanical properties, the complex interaction of different phases during deformation will be considered.

2.3.1 Yield strength

The yield strength of steels used in linepipe applications derives from a combination of strengthening contributions i.e.

$$\sigma_y = \sigma_0 + \sigma_{SS} + \sigma_{GB} + \sigma_{ppt.} + \sigma_{dis}$$
(2.3)

where, σ_0 is the intrinsic strength of ferrite due to lattice friction stress, σ_{SS} is the contribution from solid solution strengthening, σ_{GB} is the grain boundary strengthening, σ_{ppt} is the contribution from precipitates and σ_{dis} is related to the dislocation strengthening. However, some researchers have suggested that different addition laws are appropriate [142,143]. For example, Charleux et al. [142] used:

$$\sigma_y = \sigma_0 + \sigma_{SS} + \sigma_{GB} + \left(\sigma_{ppt.}^2 + \sigma_{dis}^2\right)^{1/2}$$
(2.4)

by considering that precipitation and dislocation strengthening arise from obstacles of similar strength and density to dislocation motion.

The lattice friction stress or Peierls-Nabarro stress is determined from the crystal structure, slip systems and dislocation mobility and depends on the temperature and strain rate. Leslie [144] has reported the temperature dependence of yield stress in interstitial free steel and the temperature dependence of hardness for an Fe-Co martensite as shown in Figure 2.7.



Figure 2.7: The temperature dependence of yield stress, flow stress and hardness in Fe-3 Co, tested at a strain rate of 2.5 x 10⁻⁴ s⁻¹ for a grain size ASTM # 4-5 (*reprinted from Leslie* [144])

According to Leslie [144], the large temperature dependence of the yield stress below 300 K has been attributed to: i) interstitial impurities, ii) the temperature dependence of the Peierls-Nabarro stress and iii) thermally-activated sessile-glissile transformations of screw dislocations. Winkler et al. [145] also reported decrease in strength at elevated temperatures (150°C and 300°C) for HSLA and dual phase steel and attributed it towards a combination of carbon content, thermal softening and dynamic strain aging.

Low carbon microalloyed steels have positive strain rate sensitivity at room temperatures and below i.e. the yield strength increases with an increase in strain rate [145–148]. However, the magnitude of the strain rate sensitivity has been found to depend on composition and microstructure. For example, the increment in strength from quasi-static to dynamic was found to decrease with addition of solid solution strengthening elements [149,150]. Winkler et al. [145] reported that the increase in strength with strain rate is most notable between 0.003 and 500 s⁻¹ for both dual phase and HSLA steel for tests performed between 0.003 and 1500 s⁻¹ strain rate. This behaviour suggests that the decrease in the strain rate sensitivity with alloying additions is due to the facilitation of dislocation motion at high strain rates by the obstacles created due to solute atoms for dislocations to increase the quasi-static strength.

The solid solution strengthening contribution is achieved due to the interaction between the dislocation strain field and the strain field due to lattice misfit by the substitution and interstitial solutes. Alloying Fe with solute atoms with a large size difference relative to the Fe-atoms leads to a pronounced solid solution strengthening. Different models for solid solution strengthening predict different dependencies of the yield stress on solute concentration, size misfit and elastic modulus. Leslie did extensive work on alloying of Fe [144] and reported strong dependence of solid solution strengthening on temperature and strain rate. However, it remains a challenging task to determine the individual contribution from solute strengthening. The most common way to determine the base strength of the steel as a function of some of its alloying element i.e. manganese (Mn), silicon (Si) and phosphorus (P) in plain carbon steel was the empirical equation proposed by Choquet [151]:

$$\sigma_0 = 63 + 23Mn + 53Si + 700P \tag{2.5}$$

The grain boundary strengthening can be described by the classic Hall-Petch equation [7,152] which describes that the yield or flow stress (σ_y) of a polycrystalline material is inversely related to its grain size (*d*):

$$\sigma_y = \sigma_0 + k_y d^{-\frac{1}{2}} \tag{2.6}$$

where, σ_0 is the intrinsic strength, k_y is the Petch coefficient and *d* is the grain size. The Petch coefficient depends on how the grain size is quantified. For polygonal ferrite, the grain size is quantified by the average grain diameter or the linear intercept using optical metallography and image analysis [7,153]. For bainitic or martensitic microstructures, several researchers have proposed to use a measure of effective grain size. The appropriate length scale has been defined using the lath size [154,155] or the density of high angle grain boundaries [5] measured using EBSD.

The precipitate strengthening in linepipe steels derives from nanometer sized precipitates (such as the carbides, nitrides and carbo-nitrides of Nb, Mo, Ti and V). In the case where the precipitates cannot be sheared by the dislocations, the strengthening contribution can be described by the Ashby-Orowan equation i.e. [7]:

$$\sigma_{ppt.} = \frac{0.538Gbf_{ppt.}^{1/2}}{D} ln\left(\frac{D}{2b}\right)$$
(2.7)

where f is the volume fraction of precipitates, D is the diameter of the precipitate, G is the shear modulus and b is the magnitude of Burgers vector. In the case of shearable precipitates, Charleux et al. [142] have also proposed that the precipitation hardening contribution can be described as:

$$\sigma_{ppt.} = \frac{2MGbf_{ppt.}^{1/2}}{\pi^{1/2}D} \Gamma^{3/2}$$
(2.8)

 Γ is the normalized obstacle strength of the precipitate relative to the non-shearable limit and M is the Taylor factor. However, it was noted that quantifying Γ is difficult and in their work, it was back calculated from the precipitation strengthening contribution estimate which was made using Equation 2.4.

The Taylor equation [156,157] is used to model the dislocation strengthening contribution:

$$\sigma_{dis} = AMGb_{\sqrt{\rho_{dis}}} \tag{2.9}$$

where, *A* is a temperature dependent parameter, *M* is the Taylor factor, and ρ_{dis} is the dislocation density. Linepipe steels with irregular ferrite, bainite or martensitic microstructures tend to have high initial dislocation densities. The effect of martensite on the mechanical properties (strength and work hardening) will be discussed in Section 2.3.3.

2.3.2 Work hardening and tensile instability

There are two aspects of work hardening relevant to the current work: i) the dislocation-based workhardening of the bainitic microstructure and ii) the role of two-phase microstructure due to the presence of martensite. During tensile deformation, the evolution of dislocation density is frequently described by the Kocks-Mecking model [158,159]:

$$\frac{d\rho_{dis}}{d\varepsilon_p} = k_1 \rho_{dis}^{1/2} - k_2 \rho_{dis}$$
(2.10)

where ε_p is the plastic strain, k_1 is a constant related to dislocation storage, and k_2 is a constant related to annihilation due to the dynamic recovery of dislocations. While dislocation storage is not temperature dependent, the dynamic recovery happens by thermal activation aiding the cross-slip of screw dislocations allowing for dislocations to meet and annihilate. As a result, with decreasing temperatures less dynamic recovery is expected which should increase the strain-hardening response.

However, steels with some fraction of M/A or martensite, for example dual phase steels exhibit a high initial work hardening [3,56,160,161]. During deformation, the plastically deforming ferrite or bainite matrix transfers the applied stress to the load bearing martensite phase due to the plastic incompatibility between the phases. The initial work hardening rate of dual phase steels increases with an increase in the martensite content [160,162] and with the decrease in the size of the martensite islands [7]. Dual phase

microstructures show a high uniform strain and delayed necking compared to single phase ferritic microstructures and is attributed to the high work hardening rate of these microstructures [162–164].

The onset of necking in a tensile test occurs at the maximum load where the increase in local stress due to decrease in the cross-section of the sample becomes greater than the increase in its load carrying capacity due to work hardening [153]. According to the Considère criterion valid for strain rate insensitive materials, the work hardening rate $(d\sigma/d\varepsilon)$ of the material must fulfill:

$$\frac{d\sigma}{d\varepsilon} = \boldsymbol{\sigma} \tag{2.11}$$

at a true strain equal to the uniform strain (ε) and true stress is given by σ . This criterion defines the condition of plastic instability or necking during tensile deformation.

2.3.3 Strengthening effect of martensite

Martensite contributes to the mechanical properties of the steel in two different ways: i) strengthening due to the high yield strength of martensite and ii) improving the work hardening behaviour as a second phase such as in dual phase steel due to load transfer from a relatively softer matrix such as ferrite [163].

The hardness and yield strength of martensite is mainly controlled by its carbon content, as shown in early work by Leslie [165,166] in Figure 2.8. The strength of martensite is derived from its lath size [167,168], high dislocation density [168,169], the supersaturation of carbon and nitrogen in martensite and the presence of carbide particles [170]. Badinier et al. [170] interpreted the strength of martensite based on lath to lath variation in precipitation state, dislocation density and heterogenous precipitation of carbides on dislocations. Based on monotonic and non-monotonic (Bauschinger) loading experiments, Badinier et al. [170] has also attributed the high work hardening of martensite to its heterogenous structure of individual laths.



Figure 2.8: Upper bound and lower bound of yield strength of martensite as a function of its carbon concentrations (reprinted from Leslie [165])

In dual phase steels, the strengthening and work hardening effect of martensite is attributed to two factors: i) the higher load carrying capacity of martensite than ferrite that results in load transfer from ferrite to martensite in dual phase microstructures and ii) martensite introduces geometrically necessary dislocations in the ferrite matrix near the ferrite-martensite interface due to plastic strain from martensitic transformation [163]. The highest strength is obtained when martensite remains elastic [171]. However, elastic martensite may lead to particle decohesion or cracking during plastic deformation and the resulting negative effect on ductile fracture (i.e. enhanced void formation). Mazinani et al. [160,162] reported a negligible dependence of martensite morphology on the yield strength. They also reported that the strength of the steel decreases with increase in martensite content and attributed it towards a transition from elastic to plastic deformation behaviour depending on the carbon content of martensite [160].

The net yield strength of a multiphase steel such as ferrite/bainite-martensite steel can be expressed assuming that the stress partitioning is proportional to the fraction of each phase using:

$$\sigma_{\gamma}^{total} = (1 - f^m) \times \sigma_{\gamma}^{bainite} + f^m \times \sigma^m$$
(2.12)

where the fraction of martensite can be expressed as f^n , and the strength of bainite and martensite are $\sigma^{bainite}$ and σ^m respectively. The challenge here is to determine the stresses in the different phases.

2.3.4 Fracture

2.3.4.1 Ductile fracture

Linepipe steels and their HAZ exhibit ductile fracture in uniaxial tensile tests [3,56] and in the upper shelf regime of Charpy impact tests [52]. Generally, a large amount of plastic deformation is associated with ductile fracture and this provides high energy absorption during fracture. Ductile failure in metals has been extensively reviewed by Thomason [172]. The fracture process in ductile failure can be considered to occur in three steps: i) void initiation, ii) void growth and iii) void coalescence [173]. Void initiation occurs either by the separation of the particle-matrix interface (such as TiN, MnS inclusions or martensite/ferrite interface) or by cracking of particles. Void growth occurs by the plastic deformation of the matrix surrounding the interface [174]. It is the most energy consuming process among the three stages of ductile failure. Rice and Tracey [174] also suggested that the fracture strain increases when the size and spacing of the voids are non-uniform. After a critical amount of strain, localization of plasticity occurs and this results into void coalescence and final fracture. The criterion for coalescence is the least understood but it is generally accepted that coalescence occurs when the void height is approximately equal to the void spacing [175], as illustrated in Figure 2.9.



Figure 2.9: Ductile fracture showing (a) pre-existing voids near stress concentrations, (b) void elongation upon uniaxial elongation and (c) void coalescence when the length (2h) is about equal to their separation

 $(2l - 2r_v)$ (reprinted with permission from Elsevier [175])

2.3.4.2 Cleavage fracture

Catastrophic failures in service of gas pipelines, pressure vessels etc. in the early twentieth century have led to considerable research on the cleavage fracture mechanism. Fast fracture occurs due to unstable propagation of a crack due to dynamic loading. The mechanism of cleavage fracture in steels involves two steps [176–178]: i) nucleation of a micro-crack at regions of stress concentrations such as carbides, inclusions, hard phases etc. and ii) propagation of this microcrack.

Yielding by slip or twinning is necessary to nucleate a cleavage crack [176]. It is suggested that the stress level at the tip of a dislocation pile-up could be sufficient for cleavage crack nucleation [176]. Cleavage occurs on {100} planes [153,176,178]. Factors such as the relative orientation of ferrite slip planes with respect to the {100} cleavage plane also affects the nucleation of crack. For a particle induced cleavage, a particle is cracked by an impinging dislocation pile-up and the microcrack so formed subsequently propagates under the combined influence of the pile-up stress and the applied stress; experimental findings [176,177] of cracked carbides within plastic zones (very close to crack-tip or notch root) indicate that significant plastic deformation is needed to achieve microcrack nucleation. Particle

induced cleavage is precluded when the particle does not crack or if it cracks, it does not spread into the ferrite when the particle size is below a critical limit (< 1 μ m), as suggested by Knott [176].

Once a micro-crack is nucleated, the difficulty of crack propagation can be related to microstructure. An important mechanism of crack growth resistance is the deflection of the cleavage crack at high angle grain boundaries due to the crystallographic nature of the process [44,155,179–181]. For example, the Griffith-Orowan equation is a model that accounts for deflection of the cleavage crack at grain boundaries [176,182,183]:

$$\boldsymbol{\sigma}_f = \left[\frac{\pi E \gamma_{pm}}{2(1-\nu^2)d_p}\right]^{\frac{1}{2}}$$
(2.13)

where, σ_f is the cleavage stress, *E* is the Young's modulus, γ_{pm} is the effective surface energy, *v* is the Poisson's ratio and d_p is the particle diameter.

Orowan's theory of ductile to brittle transition is illustrated in Figure 2.10. Orowan proposed a competition between plastic yielding and cleavage fracture. He noted that the yield stress in steels increases with a decrease in temperature (see Figure 2.7), but to first approximation, cleavage fracture is independent of temperature [176]. The competition between ductile and brittle fracture is also affected by: i) the state of stress, ii) the temperature and iii) the strain rate or rate of loading. For example, a triaxial state of stress such as that exists at the root of a notch or crack and a low temperature leads to a higher local tensile stress and can lead to a brittle cleavage fracture [176]. Linepipe steel operate at a temperature between -60°C and +40°C and weld defects can act as notches and stress raisers. Therefore, tests are conducted in notched bars to determine the toughness and the material's tendency to behave in a brittle manner.

The effect of notch or the state of stress on the temperature dependence of the stress has been estimated by Orowan [176] using the Tresca yield criterion and a slipline field where the maximum tensile stress (σ_{11}) in the sample is given by:

$$\sigma_{11} = 2\tau_y \left(1 + \frac{\pi}{2}\right) = 2.57\sigma_y$$
 (2.14)
where, σ_y is the tensile yield stress of material and τ_y is the shear yield stress. The effect of smooth vs. notched bar on the stress on the brittle fracture stress is shown by Knott [176] schematically in Figure 2.10.

Knott modified Equation 2.14 by incorporating the effect of notch angle to distinguish between local and general yield and found the following equation:

$$\sigma_{11} = 2\tau_y \left(1 + \frac{\pi}{2} - \frac{\varphi}{2} \right) = 2.18\sigma_y \tag{2.15}$$

where, φ is the notch angle which is 45° for a Charpy notched bar.

As discussed in Section 2.3.1, steels have positive strain rate sensitivity on the flow stress, therefore the increase in strain rate from tensile tests (10⁻³) to Charpy tests (10³) can also promote cleavage failure [184].



Figure 2.10: Brittle fracture stress in a smooth and notched bar (reprinted from [176])

2.3.4.3 Microstructure effects on cleavage cracks

Knott [176] has shown that the brittle fracture stress or cleavage stress remains more or less constant as a function of temperature but the magnitude of the cleavage stress depends on composition and microstructure, as shown in Figure 2.11.



Figure 2.11: Experimental values of maximum local tensile stress at fracture for three mild steels, after Knott

[176]

Numerous researchers have correlated the cleavage fracture stress (σ_f) with the grain size *d* using a Hall-Petch type relation [178,185,186]:

$$\sigma_f = \sigma_0 + k_f d^{-\frac{1}{2}} \tag{2.16}$$

and results from Sandstrom and Bergstrom are shown in Figure 2.12 [178]. This shows that cracks can nucleate due to stress concentrations at the grain boundaries. Second phases such as iron carbides can also act as cleavage crack initiation sites as shown by Curry and Knott [176]. Further studies on microalloyed steels indicate that the presence of large TiN particles $(0.5 - 1 \ \mu m)$ [7,21,183], the M/A constituents [41,46,52] and MnS inclusions [181,187] can act as cleavage crack initiation sites.



Figure 2.12: Hall-Petch type assessment of ductile-brittle transition temperature for mild steel (reprinted with permission from [178])

2.3.5 Measurement of toughness

The Charpy V notch impact test is a common toughness assessment method widely used by the industry for linepipe steels [50,52,153,188], but other common tests include the compact tension (CT) [153,189], single edge bend (SEB) [153], and drop-weight tear test (DWTT) [173,190,191]. The DWTT is often used to assess linepipe steels, however the dimensions of the test pieces are not favourable for HAZ testing or simulated HAZ testing [173,190,191]. The most common test to directly determine the K_{IC} is the CT test. These tests involve static loading of the sample with a fatigue pre-crack. Similarly, SEB tests are three-point bending tests loaded statically with a notch and pre-crack oriented on the side of the specimen that will be in tension. In these tests, the K_{IC} values can be calculated using the load and the crack tip opening displacement (CTOD) or crack length measurements [153]. The critical J-integral (J_{IC}) can also be determined using CT tests [153]. Although the test results of both CT and SEB tests provide more robust toughness values, the requirements for sample thickness to obtain K_{IC} , the low strain rate and the difficulty of doing tests at low temperature limit the case of these tests for linepipe applications.

2.3.6 Charpy impact tests

The Charpy impact tests are conducted on a notched specimen where the sample is hit by a hammer at a strain rate ~1000 s⁻¹ [184] and the toughness is quantified by the energy loss (of the hammer) which is absorbed to fracture sample and a heat generation (relevant for fully ductile fracture). The tests are done over a range of temperatures. For low temperature tests, liquid nitrogen can be used (-196°C), for temperatures between -196 to -60°C, a mixture of liquid nitrogen and ethanol can be used, for tests between -60°C to 0°C, a mixture of dry ice and ethanol can be used and for temperatures up to 100°C, water can be used. As the temperature decreases, the fracture mechanism changes from ductile failure denoted by high energy, upper shelf energy (USE) to brittle cleavage failure, denoted by lower shelf energy (LSE). The ductile-to-brittle transition can occur over a range of temperatures and is often associated with significant scatter in absorbed energy values. Figure 2.13 is a schematic diagram of expected results for impact energy as a function of temperature.



Figure 2.13: Schematic showing the Charpy impact transition curves. Solid line represents impact energy transition curve and dotted line represents fracture appearance transition curve.

This ductile-brittle transition temperature (DBTT) is expressed in several ways: one of the way is to determine temperature corresponding to the 50% of the difference of upper and lower shelf energy [153,184]. It is also determined by the observation of shear area on the fracture surface or the temperature corresponding to 27 J impact energy [153,184]. Instrumented CVN tests provide load-displacement data, which is used to determine energy related to crack initiation and crack propagation where the peak load reached separates the portion of the load-time data relating. Less commonly, pre-cracked Charpy impact tests can be used to determine the dynamic critical stress intensity factor (K_{Id}) using a relation that require measurements of the critical stress intensity factor (K_{IC}) from statically loaded tests.

2.3.7 Mechanical behaviour of ICCGHAZ

Several researchers have suggested that the M/A constituents in coarse grain and inter-critically reheated coarse grain heat affected zones can play an important role in the control of the fracture process for microstructures found in the HAZ [50,53,57]. However, there are conflicting views on whether the effect of M/A on the toughness is positive or negative.

Earlier investigations have shown that the toughness of the ICCGHAZ is mainly controlled by the size and volume fraction of M/A constituents [58,65]. Yoneda and Nakanishi et al. [192] suggested that the M/A constituents act as an initiation sites for cracks and promote their propagation. According to Li et al. [188], the embrittlement of the ICCGHAZ is due to i) M/A along grain boundaries and sub-grain boundaries and ii) microstructure from coarse grain austenite forming granular bainite. They have also reported an increase in impact energy after post weld heat treatment owing to decomposition of non-equilibrium microstructures [188]. Andia et al. [54,137] compared the Charpy absorbed energy values obtained for different HAZ microstructures depending on the second peak temperature for commercial X80 steel. They simulated a thermal cycle on notched Charpy specimen with a first peak temperature of 1350°C and cooled at a rate of 25°C/s before heating it to different 2nd peak temperatures (1200°C, 1000°C, 800°C, 600°C). Upon controlled cooling to simulate welding cooling rates. They have suggested that the presence of blocky M/A constituents arranged in necklace fashion in ICCGHAZ as the reason for low toughness and brittle

fracture behaviour at -60°C. Mohseni et al. [46,57] investigated a commercial grade Nb-microalloyed API X80 pipeline steel and studied the fracture behaviour upon CTOD testing on simulated ICCGHAZ having large prior austenite grains and upper bainitic microstructures with blocky M/A constituents arranged in a necklace type fashion along the prior austenitic grain boundaries. The fracture surfaces from their results showed that fracture initiates by debonding of M/A constituents from the surrounding matrix, as shown in Figure 2.14 [46].



Figure 2.14: Fracture surfaces of opposite faces of crack for samples tested at (a) and (b) -30°C, (c) and (d) -60°C. Arrows indicate the position of M/A particles (*reprinted with permission from* [46])

Davis et al. [50,193] and Akselsen [194] et al. have proposed a theory to explain crack initiation by M/A constituents. The generally accepted mechanism for crack initiation caused by M/A constituents is based on the concentration and triaxiality of internal stresses in regions close to the M/A constituents and in the matrix/M/A interfaces. Very recently Li et al. [43] studied the toughness of HAZ in XI00 longitudinal submerged arc welding (LSAW) real weld joint by conducting Charpy tests at -20°C. They had prepared notches in the regions of the CGHAZ and the ICCGHAZ separately. The results showed that the existence of ICCGHAZ, with large prior austenite grains, low density of HAB and coarse necklacing M/A constituents along grain boundary, near the notch resulted in the sharp drop of Charpy absorbed energy from 180 J to 50 J [43]. The fracture surfaces were 100% brittle for the ICCGHAZ and 60% brittle for the CGHAZ. Their EBSD results suggested that the fracture mechanism changes from nucleation-controlled in the CGHAZ to propagation-controlled in the ICCGHAZ because of the presence of necklace-type M/A constituent in the ICCGHAZ region, as shown in Figure 2.15 [43,195].



Figure 2.15: Secondary microcracks underneath the ICCGHAZ fracture surface (reprinted with permission

from [43])

However, it has also been reported that the increase in DBTT is not only due to the presence of M/A but also related to the morphology and distribution of the M/A constituents, as well as the matrix microstructure [53]. According to Matsuda et al. [192] the elongated M/A constituents have only a small influence on the crack initiation energy as compared to the crack propagation energy. Their results show that the occurrence of a crack satisfying Griffith's condition is higher around the blocky M/A constituents than around the elongated ones. Nevertheless, the role of M/A constituents in crack propagation is not clear. On one hand, M/A constituents can promote brittle fracture by initiating cleavage cracks, either in the cracked M/A constituents or by generation of small cracks at the M/A constituent/matrix interface, but on the other hand, M/A constituents can act as crack deflection sites and thus hinder fracture propagation [196,197].

2.4 Summary

The ICCGHAZ has been shown to be a region of concern for low toughness at a high ductile-brittle transition. Further it has been shown that the microstructure in this region depends in a complex manner on the local heating and cooling conditions for multi-pass thermal profiles. It is generally understood that for X70-X80 steels, the matrix is bainitic, but its characteristics depend on the steel composition and the heat input from the weld (which determine the local cooling conditions). The formation of austenite and its subsequent decomposition during intercritical heating is not well understood. The role of M/A constituents has been shown to have conflicting effects on the DBTT (some evidence showing a negative effect, others showing positive). There is very little work where tensile tests and Charpy tests have been systematically studied together for microstructures relevant to the CGHAZ and ICCGHAZ. The objective of this work will be to study these issues as described in more detail in the next chapter.

Chapter 3: Scope and Objective

The formation of low toughness regions in the heat affected zone upon welding of linepipe steels is of concern to producers of linepipe as well as pipeline constructors and operators. There are two microstructures that have been identified in the literature and industry as of particular concern for the mechanical response in the HAZ: i) the coarse grain heat affected zone (CGHAZ) [41,48,64,68] and ii) the intercritically reheated coarse grain heat affected zone (ICCGHAZ), [46,52,55,61,64,65,122,198,199].

The main objective of this research is to identify the specific microstructural features or subunits responsible for low toughness in the CGHAZ and ICCGHAZ regions. It is challenging to study the effect of the different microstructural features on mechanical properties observed in the heat affected zones of an actual weld due to the complexity of the graded microstructure found in the heat affected zone. Therefore, the approach taken in this study is to produce bulk samples of relevant microstructures formed in the HAZ during industrial welding scenarios for girth welds. The samples were produced using specially designed laboratory thermal treatments and subsequently mechanical properties were evaluated on those microstructures. Materials from commercially produced high strength X70/X80 steel pipes were used as the starting materials and the heat treatment parameters such as peak temperature and cooling rates were designed considering temperature measurements during welding using gas metal arc weld (GMAW) and submerged arc weld (SAW) processes measured previously. The mechanical properties of the relevant microstructures include the yield strength, work hardening behaviour, and Charpy impact properties. These properties are investigated within the range of potential operating temperatures (-60°C to +40°C) and extreme conditions (-196°C and +100°C).

In order to accomplish the overall objective, the work is sub-divided into the following objectives: I. To quantify the microstructure after austenite decomposition from a coarse-grain austenite structure where the niobium based microalloying precipitates were dissolved for a low cooling rate (5°C/s, relevant to SAW) and a high cooling rate (50°C/s, relevant to GMAW). These microstructures are relevant to the CGHAZ.

- II. To measure the mechanical properties (tensile and Charpy) on the microstructures (produced in Objective I) and quantitively link the mechanical properties (yield strength, transition temperature etc.) to the microstructural parameters.
- III. To experimentally investigate austenite formation during intercritical annealing of the different initial microstructures and to then quantify the size distribution and morphological aspects for 5, 10 and 20% austenite.
- IV. To measure mechanical properties (tensile and Charpy) on the intercritically annealed microstructures and to develop relationships between the mechanical properties (yield strength, transition temperature etc.) and the microstructural features.

The overall experimental strategy has the goal of quantifying the mechanical behaviour of the CGHAZ and ICCGHAZ and relating this to measurements on the microstructure. The experimental dataset on the microstructures and mechanical properties relevant to CGHAZ and ICCGHAZ will be unique and will form the basis for developing a chemistry dependent process model to predict mechanical properties (yield stress, work hardening behaviour, tensile strength and Charpy impact toughness) based on the microstructural characteristics. This knowledge will aid linepipe producers to design chemistries and pipeline constructors to assess a variety of welding process conditions and then link these to the performance of the material in service.

Chapter 4: Experimental Methodology

4.1 Introduction

This chapter describes the experimental methods used in this study and the basic overall design of the experiments. The processing, microstructure, mechanical properties and fracture behaviour of samples relevant to the heat affected zone of industrially welded X80 steel have been considered. The experimental work involved several important tasks including i) the generation of different relevant microstructures using carefully designed thermal cycles, ii) intercritical annealing of these microstructures to obtain different fractions of intercritical austenite, iii) mechanical testing (tensile and Charpy) of these microstructures over a range of temperatures and iv) evaluation of the fracture behaviour by studying the microstructures on or near the fracture surface.

4.2 Materials

Two linepipe steels were industrially processed and supplied by Evraz Inc., NA for this investigation. The chemical composition of the two steels are shown in Table 4.1. The steels will be identified by their carbon and niobium contents. Both the steels have a similar level of Mn, Mo and the Ti/N ratio. The primary difference between the steels lies in the carbon content: 0.06 wt.% vs. 0.03 wt.% carbon and their Nb content, i.e. the higher carbon steel has 0.035 wt.% Nb, and the lower carbon steel has 0.091 wt.% Nb. Both steels were hot-rolled and spirally welded to form pipes of 16 mm and 10.5 mm wall thickness, respectively. Samples for this study were taken from sections of pipe, as shown in Figure 4.1 (a) and (b).

The initial microstructures for both as received alloys consisted primarily of irregular ferrite as shown in Figure 4.2 (a) and (b). Previous work [76] has shown that complex microalloy precipitates of TiN, Nb(C,N) and Mo₂C are also present in these two alloys in addition to fine distribution of martensite-austenite (M/A) constituents.

	С	Mn	Si	Nb	Мо	Ti	Ni	Cu	Al	Ν	Ti/N	Fe
06C03Nb	0.06	1.65	0.11	0.035	0.24	0.012	0.42	0.13	0.027	0.005	2.40	Bal
03C09Nb	0.03	1.70	0.31	0.091	0.29	0.017	0.13	0.25	0.041	0.008	2.13	Bal

Table 4.1: Chemical composition of investigated alloys in wt.%



Figure 4.1: (a) Spirally welded pipe (b) sections machined through thickness of the two base alloys



Figure 4.2: Microstructures of the as-received alloys (a) 06C03Nb and (b) 03C09Nb obtained using secondary

electron microscope

4.3 Thermodynamic equilibrium conditions

The equilibrium transformation and precipitation temperatures were studied using ThermoCalc TCFE7 database and Ae₁ and Ae₃ temperatures are listed in Table 4.2. The solubilities of Mo₂C, Nb(C,N) and TiN as a function of temperature are shown in Figure 4.3 and the Nb(C,N) dissolution temperature is reported in Table 4.2. It can be observed that TiN precipitates are stable up to high temperatures, i.e. more than 75% of TiN are stable at 1300°C; whereas the Nb(C,N) volume fraction decreases to zero at a temperature of ~1080°C for 06C03Nb steel and at ~1155°C for the 03C09Nb steel. The Mo₂C completely dissolves above ~ 680°C i.e. just above the Ae₁ temperature for both the alloys.

Table 4.2: Inter-critical and niobium precipitate dissolution temperature

Chemistry	Ae ₁ (°C)	Ae ₃ (°C)	Nb(C,N) dissolution temperature (°C)
06C03Nb	643	823	1080
03C09Nb	660	845	1155



Figure 4.3: Thermodynamic stability of phases in (a) 06C03Nb (b) 03C09Nb steel, from ThermoCalc 4.0

TCFE7 database

4.4 Sample geometries

Samples were designed such that a controlled thermal cycle could be applied in the GleebleTM3500 thermomechanical simulator and then machined for tensile and Charpy impact tests. Samples for the Gleeble thermal treatments were machined with two different geometries; the first was a rectangular strip $(93 \times 12 \times 1.7 \text{ mm} \text{ for } 06\text{C09Nb} \text{ and } 93 \times 10 \times 1.7 \text{ mm} \text{ for } 03\text{C09Nb})$ which could be subsequently machined for the tensile tests, and the second sample had dimensions of $100 \times 11 \times 11 \text{ mm}$ for 06C03Nb and $100 \times 10 \times 10 \text{ mm}$ for 03C09Nb, which could later be machined to produce full-size Charpy impact test samples. The difference in width for the two different alloys is due to the different wall thickness of the two alloys from which the samples were machined. The design and dimensions of the 06C03Nb samples are shown in Figure 4.4.



Figure 4.4: Design and dimensions of (a) rectangular strip sample for Gleeble (b) machined for tensile tests; (c) samples for Gleeble and (d) machined for Charpy tests for 06C03Nb steel (All dimensions in mm).

4.5 Heat treatment

4.5.1 Gleeble set-up

All heat treatments were conducted using the GleebleTM3500 thermomechanical simulator. Tests were conducted under high vacuum ($\sim 1.3 \times 10^{-5}$ Torr or $\sim 2 \times 10^{-3}$ Pa) until the onset of helium gas quench, if used. Owing to the differences in specimen geometry, samples for tensile and Charpy tests required two different types of experimental set-up. Sheet samples (for subsequent tensile samples) were heated and

cooled using the low force jaws so that thermal expansion could be accommodated with minimal load on the sample. A photograph of the experimental set up is shown in Figure 4.5. The temperature was controlled using a K-type thermocouple, spot welded to the centre of the specimens. Two additional K-type thermocouples were spot welded at ± 6 mm away from the centre on either side of the sample to monitor the temperature along the length of the sample. A contact mechanical dilatometer was attached at the location of the control thermocouple to measure the change in width during the heating and cooling cycle. Controlled cooling rates were obtained by blowing helium gas through a nozzle onto one surface of the sample where the theromocouples were attached and simultaneously applying resistance heating on the sample.



Figure 4.5: Gleeble set up for long strip geometry; the inset shows the quenching nozzle

Note the temperature on the tensile strip samples was recorded from the same side of the sample on which He-gas was purged for cooling. According to recent measurements and finite element modeling calculations [200–202] on the same steel using a heat transfer coefficient of 1500 $Wm^{-2}K^{-1}$ at the front and 20 $Wm^{-2}K^{-1}$ at the back side of the strip, there exists a temperature difference of ~23°C between the front surface on which He-gas was blown and the mid-thickness of the 1.7 mm strip for a cooling rate of 50°C/s, (see Figure 4.6). The subsequent results for the strip samples will report an estimate of the centre temperature, i.e. the temperature at the surface +23°C, over the range of temperatures where austenite decomposition occurred. Figure 4.7 shows the experimental measurements of temperature on the front and back of the strip sample. Here, it can be seen that the temperature difference remained approximately constant and the cooling rate was maintained ~50°C/s at both front and back of the sample (i.e. the thermal path was almost the same, but the back surface lagged the front surface). This suggests that there will be a uniform microstructure across the thickness. For future work, it is recommended that the He gas be applied to both sides of the sample.



Figure 4.6: Finite element model results for variation of temperature through the 1.7 mm strip sample cooled

using He gas on one surface at a surface temperature of 602°C [200]



Figure 4.7: Thermal path and cooling rate at the front and back of 1.7 mm thin strip due to purging He-gas at

the front during cooling

For the heat treatment of the precursor Charpy specimens, the high force jaw set-up was used, as shown in Figure 4.8. Copper grips with a square cut-out to accommodate the Charpy sample were used to ensure good heat transfer during heating and cooling. A 20 ± 1 mm free span between the copper grips was used. A K-type thermocouple was spot welded to the centre of the specimen to control the temperature during the thermal cycle. Two additional K-type thermocouples were spot welded on two sides, each 1 mm away from the centre. A contact dilatometer was attached at the location of the control thermocouple to measure the change in width during the heating and cooling cycles. External cooling medium such as water or helium has not been used to avoid any difference in cooling rates at surface and mid-thickness. Instead, heat was extracted through the high conducting copper grips and water-cooled high force jaws, all under high vacuum. The effect of the free span on the cooling rate, and the thermal gradient along the length of the specimen is presented in Appendix A. This set-up ensures homogenous thermal paths at ± 1 mm from the centre (at which the Charpy V notch is to be machined) and across the thickness (results shown in Chapter 5).



Figure 4.8: Gleeble set up for full size Charpy geometry

4.5.2 Thermal cycles

The thermal cycles were designed to produce microstructures representative of the CGHAZ and the ICCGHAZ for welding scenarios relevant to gas metal arc welds (GMAW) and submerged arc welds (SAW). As discussed in Section 2.1.3.2 of the literature review, Gaudet [3] and Kulakov [37] have shown that the average cooling rate at the start of austenite decomposition was 50°C/s and 5°C/s for typical GMAW and SAW parameters, respectively. A two-step heat treatment path, as shown schematically in Figure 4.9, was designed to produce specimens for subsequent tensile and Charpy tests.

The first step involved heating to a peak temperature of 1300°C at a heating rate of 100°C/s, holding for 5 s and then: i) cooling at ~50°C/s to below the temperature for complete austenite decomposition (Figure 4.9a) and ii) cooling at 50°C/s to 750°C and then at ~5°C/s (Figure 4.9b). Based on a previous study by Banerjee et al. [76], it was observed that for heating rates larger than 100°C/s, the austenite grain size is primarily a function of the peak temperature and is independent of heating rate. As a result, a heating rate of 100°C/s was chosen for the current experiments as it was easier to control compared to the heating rate of >1000°C/s in actual welds. Note the heating rate from 1250°C to 1300°C was reduced to 50°C/s to minimize overshooting of temperature at the peak temperature (the maximum overshoot was recorded to be 8°C).



Figure 4.9: Schematics showing thermal cycles to simulate (a) gas metal arc welding (GMAW) and (b) submerged arc welding (SAW).

The cooling rates were chosen based on experimental measurements (using embedded thermocouples) of the average cooling rate for laboratory based GMAW weld trials by Gaudet et al. [3] and SAW by Kulakov [89] using typical welding parameters. As described in the previous section, the cooling rate of 50°C/s was obtained using a helium gas quench in the tensile test sample and by heat conduction through the copper jaws for the Charpy samples. For the Charpy samples, obtaining a constant cooling rate of 50°C/s was difficult for temperatures below 450°C due to the exothermic nature of austenite to ferrite transformation and the decreasing heat extraction rate by conduction as the temperature decreases. Therefore, a cooling rate of 50°C/s was maintained until the transformation start temperature (~550°C) and then below this temperature, a gradually decreasing cooling path was programmed based on the cooling time obtained for 20mm free span during free cooling. Note that, the same thermal cycle was used for the tensile geometries, i.e. based on the cooling path upon free cooling of Charpy samples. The Gleeble program thermal cycle corresponding to this non-linear cooling profile is presented in Figure 4.10.



Figure 4.10: Thermal cycle programmed to Gleeble to obtain a non-linear cooling profile

For the cooling rate of 5°C/s, a step cooling path was designed to avoid further austenite grain growth at high temperature during cooling. Therefore, to maintain a constant prior austenite grain size for both the conditions after the first thermal cycle, the specimen was cooled to 750°C at a cooling rate of 50°C/s. Below 750°C, a cooling rate of 5°C/s was programmed, as shown in Figure 4.9b.

For cases where the formation of intercritical austenite was of interest, a second thermal cycle was imposed. The aim was to generate a microstructure typical of the intercritically reheated coarse grain heat affected zone (ICCGHAZ). Subsequent thermal cycles were designed where the as-austenitised and cooled samples (after 1st thermal cycle) were heated to different intercritical temperatures (700°C to 820°C) at a heating rate of 50°C/s and held for 3-5 minutes before heating it to 1050 °C to allow complete austenitization. This thermal cycle is schematically illustrated in Figure 4.11. The fraction of intercritical austenite formation during the heating and isothermal holding was calculated from the dilation measurements using Kop method [95], presented in next Section 4.6.



Figure 4.11: Schematic of the thermal cycles used to determine the kinetics of austenite formation upon intercritical isothermal annealing

Based on the analysis on the rate of intercritical austenite formation (discussed in detail in Chapter 6), samples were heated at a rate of 50°C/s to intercritical temperatures of 710, 725 and 760°C, held for 60 s followed by cooling at a rate of ~50°C/s, as shown in Figure 4.9. The temperatures and times for the intercritical annealing treatment were selected based on the dilation measurements to form approximately 5%, 10% and 20% austenite. A holding time of 60 s was employed instead of the thermal spike observed during welding to have a better control of the experiments and to ensure repeatability. Upon cooling, the intercritically formed austenite is expected to correspond to a similar fraction of M/A constituents assuming that the austenite only transforms to M/A. No evidence of a reverse transformation was observed from the dilation measurements.

4.6 Characterization of the fraction transformed using dilatometry

The measurement of transformation kinetics from dilation data was conducted using a wellestablished and validated methodology for strip specimen [5,68,76,89,128,200]. However, for the Charpy samples, it is much less common to use dilatometry to measure the transformation kinetics [203]. Further, a small amount of plastic deformation was observed at the centre of the Charpy samples which could affect the analysis. Hence, given the uncertainty in the transformation temperatures from the Charpy tests, the results from the strip samples will be used to characterize these steels.

The kinetics of austenite formation and decomposition were calculated from the measured change in width by a contact dilatometer attached adjacent to the control thermocouple on the sample during heating and cooling. The coefficient of thermal expansion for ferrite and austenite, obtained from dilation data analysis, before and after the transformation, was checked in all cases to ensure the reliability of the method. An example is shown in Figure 4.12. The measured thermal expansion coefficients had to be within ± 5 % of those reported in the literature [204,205]: $15.5 - 16.6 \times 10^{-6} \circ C^{-1}$ (in the subcritical temperature range of 500 to 700°C) and 22.5 - 24.8 x $10^{-6} \circ C^{-1}$ for ferrite and austenite, respectively; otherwise the test was not accepted as valid.



Figure 4.12: Coefficient of linear expansion for ferrite and austenite during heating and cooling

It is common to use the lever rule to analyze dilation data in order to characterize the transformation behaviour. However, the lever rule analysis assumes that the concentration of carbon in austenite remains constant (at the bulk composition) at all stages of the transformation, while, in reality, the local carbon concentration in austenite gradually decreases and this affects the thermal expansion coefficient of austenite. As a result of this, the lever rule analysis systematically underestimates austenite fraction in the beginning of austenite formation, but yields more accurate results in the later stages [94,95]. In order to address this shortcoming, the Kop method was employed to measure the fraction of austenite. The average atomic volume of a sample is determined by the fractions of the phases present multiplied by their respective atomic volume, according to the following equation:

$$V(T) = \sum_{i} f^{i} V^{i}(T) \tag{4.1}$$

where V(T) is the atomic volume of the sample at temperature *T* in Kelvin, f_i is the volume fraction of phase *i*, $V^i(T)$ is the atomic volume of phase *i* at temperature *T*. In this case, there are two phases: ferrite (α) and austenite (γ). The atomic volumes of these phases are related to the lattice parameters a_{γ} and a_{α} for austenite and ferrite, respectively.

$$\boldsymbol{V}_{\gamma} = \frac{1}{4}\boldsymbol{a}_{\gamma}^{3} \tag{4.2}$$

$$V_{\alpha} = \frac{1}{2}a_{\alpha}^{3} \tag{4.3}$$

The lattice parameter of austenite is calculated as a function of the atomic fraction of carbon, ξ_c [204], as shown below:

$$\xi_c = 1.34689 - 5.53646 * 10^{-3} * T + 10.3747 * 10^{-6} * T^2 - 9.16354 * 10^{-9} * T^3 + 2.995 * 10^{-12} * T^4$$
(4.4)

$$a_{\gamma} = (3.63 + 0.0078\xi_c) * [1 + (23.9 - 0.5\xi_c) * 10^{-6} * (T - 1000)]$$
(4.5)

$$a_{\alpha} = 2.8863 * [1 + 15.9 * 10^{-6} * (T - 800)]$$
(4.6)

The fraction transformed austenite, f_{γ} is then calculated as follows:

$$f_{\gamma} = \frac{V - V_{\alpha}}{V_{\gamma} - V_{\alpha}} \tag{4.7}$$

considering that $f_{\gamma} + f_{\alpha} = 1$.

The volume change of the sample is calculated from the measured change in width ΔW of the sample using dilatometer following the relation:

$$V = k_s V_0 \left(1 + \frac{3\Delta W}{W_0} \right) \tag{4.8}$$

where, k_s is the scaling factor, ideally equal to 1, W_0 is the initial width of the sample and is related to the initial volume V_0 by:

$$\frac{\Delta W}{W_0} = \frac{1}{3} \frac{\Delta V}{V_0} \tag{4.9}$$

Figure 4.13 shows an example of (a) the thermal cycle (b) the calculated atomic volume of the sample using the Kop method, (c) the fraction of austenite as function of temperature and (d) the austenite fraction as a function of isothermal hold time at 750°C. Note that in Figure 4.13c and Figure 4.13d, the lever rule analysis is also shown for comparison to see the effect of the more rigorous analysis.

For this example, the coefficients of thermal expansion (CTE) for ferrite and austenite is consistent with literature values [95]. The transformation kinetics shown in Figure 4.13c,d shows that a significant

amount of austenite forms during heating before the isothermal holding starts. Upon isothermal holding, the fraction transformed increases at a decreasing rate until the temperature resumes increasing after 3 minutes to 1050° C. Note that the time, t = 0 s in Figure 4.13d corresponds to the beginning of isothermal holding at a given temperature. The comparison of the lever rule with the Kop method shows that the lever rule underestimates the volume fraction of intercritical austenite as it does not take into account the carbon enrichment of austenite at the beginning of transformation. During the later stages of transformation, the carbon content of the austenite approaches the bulk composition, therefore the lever rule and Kop method calculates identical austenite fraction at later stages of transformation.



Figure 4.13: (a) Thermal cycle used to investigate the kinetics of intercritical austenite formation, (b) dilation data analysis using Kop method, (c) representative transformation kinetics comparing lever rule and Kop method for a intercritical annealing at 750°C and (d) transformation kinetics in the intercritical region

4.7 Microstructural characterization

Microstructure characterization was conducted on the region of the Gleeble sample discarded when machining the tensile samples i.e. when the gauge section was produced. Within these pieces, the microstructure was observed near the centre where the temperature had been measured during the thermal cycle.

4.7.1 Sample preparation for metallography

Samples were mounted using conductive thermosetting phenolic compression mounting resin, KonductoMet, supplied by Buehler. Standard metallographic procedures were followed for grinding, polishing and etching. Wet grinding was performed progressively on 320, 600, 800 and 1200 grit silicon carbide papers. Mechanical polishing was then carried out using 6 µm followed by 1 µm diamond polish and then rinsed with distilled water and denatured ethyl alcohol. This ensured a scratch free clean surface before etching for optical microscopy and scanning electron microscopy (SEM).

In order to reveal the microstructures by optical microscopy, the samples were etched using a 2% nital (a solution of 2 ml concentrated nitric acid in 98 ml of absolute ethyl alcohol where the nitric acid had a concentration of 70% HNO₃ by weight in water) for ~20 seconds and then rinsed immediately with distilled water and denatured ethyl alcohol before drying. Ferrite-pearlite-bainite microstructures with clear grain boundaries are usually revealed when these steels are etched using nital. However, it is not possible to differentiate martensite and bainite or martensite-retained austenite (MA) constituents. In order to reveal the martensite-austenite constituents, LePera etching was conducted. Two separate solutions; (a) 4% picral (4 gm dry picric acid in 100 ml denatured ethyl alcohol) and (b) 1% aqueous solution of sodium meta-bisulfite (Na₂S₂O₅) (1gm of sodium meta-bisulfite in 100 ml distilled water) were prepared in two separate beakers. After the last step of sample polishing, the samples were rinsed in distilled water and ethanol to prevent any pre-oxidation of the surface and were dried under warm air flow. Simultaneously, the two solutions were freshly mixed in equal volume (1:1 ratio) in a small beaker just before immersing the sample

for 20 s. Finally, after rinsing with distilled water and ethanol and drying, the samples were examined using optical microscopy.

Unmounted samples were also prepared following similar mechanical polishing procedures. 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 50 mA/cm², corresponding to a voltage of \approx 16V, for 20-30 seconds. The samples were then rinsed under running water and cleaned in an ethanol ultrasound bath. This electropolishing procedure was employed to ensure high quality electron back-scattered diffraction (EBSD) patterns.

4.7.2 Optical microscope imaging

Initial identification and quantification of all transformation products were performed using a Nikon EPIPHOT 300 series inverted optical microscope equipped with a digital camera. In the LePera etched samples, the martensite and retained austenite are usually revealed as bright white islands in brown ferritic or baintic matrix [125].

4.7.3 Scanning electron microscopy and Electron back-scattered diffraction

High resolution images of the etched microstructures were obtained using the secondary electron (SE) as well as the in-lens detector in the secondary electron mode of SEM. Due to the magnetic field at the pole piece, the secondary electrons are collected with high efficiency in the in-lens detector. Thus, images with high contrast and high lateral resolution can be obtained that provides information about morphology and surface topography.

EBSD measurements were conducted by a Zeiss- Σ igma field emission gun scanning electron microscope (FEGSEM) using a Nikon high speed camera and EDAX/TSL OIM Data collection (6th edition) software. For EBSD measurements, the samples were tilted at 70° angle. An acceleration voltage of 15 kV, an aperture size of 60 µm, and a working distance of \approx 12 mm were used. Diffraction patterns were captured by OIM Data collection software using a binning size of 8 x 8 with a capture speed of \approx 50 frames per second. A step size of 50 nm was used for obtaining high resolution maps of ~ (60 x 60 µm) during a 15 h scan. For selected low-resolution larger area maps (200 x 200 µm), a step size of 200 nm was used. Automated indexing of bcc and fcc phases were allowed from the patterns collected using the software. No automated cleaning methods were applied for the quantification of martensite and retained austenite. Data processing and analysis were carried out following Reichert's method [107] to determine the M/A fraction after the first thermal cycle. The image quality maps wee normalized between the minimum and maximum values following Reichert's method [107].

Kernel average misorientation (KAM) method within OIM software was used to obtain a semiquantitative measure of geometrically necessary dislocations (GNDs). The KAM represents the average misorientation $\Delta \overline{g}$ of a point in the middle of a kernel with all its neighbours. The size of the kernel can be varied by choosing the nth nearest neighbour environment. The KAM is then calculated according to:

$$KAM = \{ \Delta \overline{g} \left(g_{point}, g_{neighbor} \right) | \Delta g < \Delta g_{max} \}$$

$$(4.10)$$

where, Δg_{max} is the threshold for the maximum misorientation that that is considered in the average. A maximum misorientation must be selected to avoid unreasonably high KAM values at grain boundaries. 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 neighbors can be selected. In this study the third nearest neighbors are considered, calculating the orientation gradient over 150 nm in a square grid.

4.8 Image Analysis

Quantitative analysis of the microstructures was carried out on the high-resolution images obtained from optical microscopy and SEM using the image analysis software ImageJ.

4.8.1 Measurement of prior austenite grain size after 1st thermal cycle

Prior austenite grain boundaries cannot easily be distinguished from Nital or LePera etched microstructures. To quantify the prior austenite grain sizes, selected specimens were tempered in a tube furnace back-filled with argon at 500°C for 24 hours to segregate impurities at the grain boundaries to provide better contrast during etching. Those tempered specimens were etched in 4% aqueous picric acid solution at 60°C for 3-5 minutes and then examined under optical microscope. The average equivalent circle area diameter of the prior austenite grains was determined on at least 1000 grains according to ASTM E1382-97 by tracing the grain boundaries using ImageJ software and verified with in-situ measurements by Romualdi [128].

4.8.2 Characterisation of M/A constituents after intercritical annealing

The image analysis software ImageJ was used to determine the area fraction, size and shape of M/A constituents from the LePera etched microstructures of the intercritically annealed samples. The digital grey scale images were transformed into a binary black and white image and a threshold was applied to highlight the M/A constituents from the background. A sensitivity analysis on the threshold value shows that the area fraction measured based on optical evaluation was strongly dependent on the threshold level. Examples of the results for different threshold values applied to the same image are shown in Figure 4.14a-c. Figure 4.14d shows the area fraction of M/A as a function of the threshold level.

Given this intrinsic uncertainty in differentiating M/A from the matrix using optical methods, the austenite fraction obtained from the dilation data using the Kop method was chosen as a reliable method to estimate the fraction of intercritical austenite. The accuracy or experimental error of the austenite fraction measured from dilation was estimated from 15 repeat tests for each condition. Then it is assumed that all the austenite formed during the intercritical annealing transformed to M/A constituents due to fast cooling (~50°C/s) and there being no evidence in the dilation measurements of a reverse transformation. Finally, a suitable threshold was chosen so that the fraction obtained from image analysis matched the dilatometry analysis. The consistency of this method was examined by overlapping the particle outlines resulting from

threshold on top of the original LePera micrograph. Figure 4.15 shows the overlay (in red) of particles identified as M/A, based on the threshold, on top of the original micrograph. Particles touching the edge of the picture were excluded from consideration. To minimize the measurement errors, at least 5 micrographs, yielding ~1000 particles on average, were analyzed for each condition.

To characterize the fraction of M/A constituents located on the prior austenite grain (PAG) boundaries, an additional criterion was applied which includes cluster of four pixels where 1 μ m is ~ 9 pixels. This criterion excludes particles less than 0.25 μ m². The M/A inside the PAGs were then manually removed and the remaining fraction was considered to be the fraction of M/A at the PAGBs. The major axis and the minor axis were calculated from the best fit ellipses on the particles of the thresholded image. Finally, the minor axis was reported as size of the M/A to quantify the morphology and the aspect ratio are reported based on them. The percentage of the grain boundaries covered by M/A constituents were calculated manually by tracing the grain boundary with and without M/A constituents. Approximately 5 images in each case were calculated to measure an average grain boundary length of 5000 µm for each condition. An average number of 3000 M/A constituents were considered for calculating the size and aspect ratio.



Figure 4.14: Sensitivity of area fraction measurement using different image thresholding parameter grey

scale from 0 (black) to 255 (white) on same image



Figure 4.15: LePera-etched micrograph and overlay of particles identified based on dilation and image analysis to determine the size and morphology of M/A constituents

4.9 Mechanical characterization

4.9.1 Hardness measurement

Hardness was measured using Vickers micro-hardness tester applying 1 kg load and 10 s dwell time. The average of the two diagonal lengths of the projected square indentation made by the pyramidal indenter was measured optically and the hardness HV was measured in MPa under constant load using the following equation:

$$HV = \frac{0.1891F}{{d_i}^2} \tag{4.11}$$

where, F is the applied load in N and d_i is the measured diagonal length of the indentation in mm. A gap equal to at least 2.5d between two nearest indentations were maintained to avoid the increase in hardness due to the work-hardening of the deformed structure due to indentation. At least seven indentations were taken for each structure, readings of which were averaged.

4.9.2 Tensile tests

Uniaxial tensile tests were conducted on sub-size tensile specimens, (see Figure 4.4a) using an Instron 10M table-top screw driven machine, with an imposed displacement rate. The crosshead speed of 1.5 mm/min, which corresponds to a nominal strain rate of 2 x 10^{-3} s⁻¹ and a load cell with maximum load of 5 kN were used for all tests. An ethanol-glycol mixture cooled to the desired temperature using dry ice was used for conducting the low temperature tests at -20°C and -60°C and the temperature was monitored with a K-type thermocouple and kept within ± 2 °C throughout the tests. The axial strain was calculated from measurements on the change of length of the sample from a clip-on extensometer with a gauge length of 10 mm. During the low temperature tests, the extensometer was attached using steel springs instead of rubber and were immersed with the sample in the cooled fluid. At least three tensile tests were conducted to verify their reproducibility for each sample type. The engineering stress-strain curves were calculated from the load-elongation curves obtained directly from the testing machine using standard formula:

Engineering Stress:
$$S = \frac{F}{A_0} = \frac{F}{wt}$$
 (4.12)

Engineering Strain:
$$e = \frac{\Delta L}{L_0} = \frac{L - L_0}{L_0}$$
 (4.13)

where, applied load, initial cross-sectional area, width, thickness and initial gauge length of the tensile specimen are denoted by *F*, A_0 , *w*, *t* and L_0 respectively. In our work, a tensile test, where the measured elastic modulus deviated by more than ± 5 % of the nominal value of 200 GPa for a low carbon steel, were discarded. The yield stress was determined by the 0.2 % offset method. The true stress and true strain were calculated up to the necking point from the engineering stress (S) and engineering strain (e) using the following:

True Stress:
$$\sigma = S(1+e)$$
 (4.14)

True Strain:
$$\varepsilon = ln(1+e)$$
 (4.15)

Due to the onset of inhomogeneous plastic deformation beyond the maximum after necking, the true stress and true strain values calculated from the force and displacement recorded by the load cell and extensometer can no longer be used. However, the cross-sectional area of the fractured sample was measured in the SEM, see Figure 4.16. The true stress and true strain at fracture were calculated using Equations 4.16 and 4.17.



Figure 4.16: Schematic showing (a) broken tensile sample (b) area chosen to look under the SEM (c) fracture surface under SEM (d) area measured for evaluation of true fracture area under SEM

True stress at fracture:
$$\sigma_f = \frac{F_f}{A_f}$$
 (4.5)

True strain at fracture:
$$\varepsilon_f = \ln\left(\frac{A_0}{A_f}\right)$$
 (4.6)

where, applied load F, initial cross-sectional area A_0 , width w, thickness t and initial gauge length of the tensile specimen L_0 , were considered. The subscript f was used to denote the parameters at fracture. Finally, a linear interpolation between the necking point and the fracture was constructed.

4.9.3 Charpy impact tests

Standard Charpy V-notch specimens (10 x 10 x 55 mm) were machined from the Gleeble heat treated samples following ASTM E23 [206], as shown in Figure 4.4b. The notch was machined at the position where the control thermocouple was attached in the Gleeble. The Charpy impact tests were conducted over a range of temperature (-196°C to +100°C) to determine the ductile-to-brittle transition temperature using an Instron Charpy machine at Evraz Regina facility for 06C03Nb steel and Zwick 450 J instrumented impact machine at UBC for 03C09Nb steel. The test temperature was achieved by mixing different proportions of methanol and liquid nitrogen or dry ice to form a bath. Specimens were soaked at desired temperature for at least 15 min before testing and the bath temperature was maintained within \pm 2°C, using a thermo-couple monitoring the temperature. The time span between removing the specimens from bath and the impact test was kept within 5 s according to the ASTM E23 standard for Charpy impact tests [206]. Three repeat tests were conducted for each condition at each temperature.

A mathematical fit to the Charpy impact data was constructed using the experimentally obtained data points, following the procedure given by Sakai et al. [207]. The impact energy, Y, has been fitted as a function of temperature, T, to the following Equation 4.18:

$$Y = A + B \tanh\left(\frac{T - T_0}{c}\right) \tag{4.7}$$

where *A*, *B*, *C* are defined as: Lower shelf energy = A - B, Upper shelf energy = A + B, transition temperature = T_0 and Slope at $T_0 = B/C$. The transition temperature in this work is referred to as the temperature corresponding to 50 % of the difference between upper and lower shelf energies.

4.10 Fractography

The fracture surfaces of the tensile and Charpy specimens were examined by secondary electron imaging in the Zeiss FEGSEM to evaluate the nature of fracture. For samples that failed by cleavage fracture, some samples were chosen to examine the primary crack front and the secondary cleavage cracks (which did not propagate to cause complete failure) beneath the fracture surface. The propagation paths of the secondary cleavage cracks were studied by EBSD on the cross-section of the impact tested specimens, perpendicular to the fracture surface, shown in Figure 4.17. For edge preservation, the fracture surfaces were protected from further damage during sectioning and sample preparation for EBSD using electroless Ni-plating following the procedure stated in literature [80]. The specimens were immersed in a solution of 45 g nickel chloride, 11 g sodium hypophosphite, 100 g sodium citrate, 50 g ammonium chloride and 1000 mL distilled water at a temperature of $70 - 80^{\circ}$ C at a pH of 8.5 - 9 for 5 hours to obtain a plate thickness of ~ 5 µm. After sectioning perpendicular to the fracture surface, the specimens were mounted, and polished following standard metallographic procedure stated in Section 4.7.1. In this case, final surfaces for EBSD were obtained using 0.05 µm colloidal silica manual polishing at 75 rpm for 30 – 45 mins.



Figure 4.17: A schematic of the area underneath the primary fracture surface of Charpy specimen where observations were made

4.10.1 Quantitative examination of void formation

The void formation process in the neck region of the fractured tensile specimens was also quantitatively examined using ImageJ software. The goal was (a) to measure the density of voids in the non-uniform deformation region i.e. in the neck region and (b) to determine the strain at which void density is ~zero. Fractured tensile specimens were first cut in the longitudinal direction followed by polishing and etching with 2% Nital. High resolution images were captured under FEGSEM. The density of voids was calculated in the neck region near the fracture surface according to the following formula:

$$Density of \ voids = \frac{Number \ of \ voids}{Area \ measured}$$
(4.8)

Since the fracture strain was different for all samples, voids were measured within 100 μ m from fracture surface for all samples i.e. up to a true strain of ~ 0.4 to 0.55.

Chapter 5: Experimental Results and Discussion: Simulation of a Single Thermal Cycle

5.1 Introduction

This chapter describes the results for experimental simulations of a single thermal cycle which involves heating to 1300°C followed by controlled cooling at rates relevant to submerged arc welds (SAW) and gas metal arc welds (GMAW). The thermal cycle was designed to generate materials/microstructures similar to that observed near the fusion line of a real weld, i.e. a region with a large prior austenite grain size (in this case \sim 50 µm) and decomposition products seen in the heat affected zone (HAZ) of SAW and GMAW welds. The results for the thermal treatment, microstructure and mechanical properties (tensile and Charpy impact) will be discussed in this Chapter. In addition to being relevant for single weld passes, the microstructure produced in these thermal cycles will form the starting point for two pass welds where the thermal fields overlap, considered in the Chapter 6.

5.2 **Results for the thermal cycles**

The thermal cycle was designed to produce an austenite microstructure where the microalloying Nb(C,N) precipitates had dissolved and an austenite grain size of ~50 μ m was produced. In the first thermal cycle, all the specimens were heated to 1300°C at 100°C/s from an initial microstructure of irregular ferrite (shown in Figure 4.2) [76,79]. The dissolution of Nb(C,N) precipitates was predicted to occur at 1300°C after 5 s in 06C03Nb steel and 10 s in 03C09Nb steel using the model by Garcin et al. [68]. The austenite grain size was chosen to be ~50 μ m, i.e. a relatively large grain size relevant to the HAZ which could be produced in a controlled manner. Further, the cycle incorporated cooling rates of 5°C/s and 50°C/s representative of SAW and GMAW processes, respectively, based on experimental measurements previously made by UBC group [3,37] as described in Section 2.1.3.3. For the cooling condition of 5°C/s, a step cooling path was chosen i.e. cooling at a rate of 50°C/s down to 750°C and then 5°C/s from 750°C to
200°C, to minimize austenite grain growth during cooling. Below 750°C the kinetics of grain growth are expected to be negligible, thus the phase transformation will start from similar austenite grain sizes (~50 μ m) for both cooling conditions. In order to compare the mechanical properties obtained from Charpy samples with that of tensile samples, it is important that the thermal cycles for Charpy square cross-section (11 x 11 mm) and tensile strip (12 x 1.7 mm) geometries are as close as possible to produce similar microstructures.

5.2.1 Cooling rate of 5°C/s

Figure 5.1a shows the temperature histories for a 06C03Nb steel Charpy square cross-section specimen (11 x 11 x 100 mm) and tensile strip (93 x 12 x 1.7 mm) with a peak temperature at 1300°C, an isothermal hold of 5 s followed by controlled cooling at 50°C/s until 750°C and 5°C/s from 750°C to 200°C. It can be observed that there was a small overshoot at the peak temperature. The maximum temperature at the peak from approximately 100 tests done in this study was recorded to be 1308°C for tensile strip and 1303°C for Charpy square cross-section (see examples in Figure 5.1b). Figure 5.1c shows an expanded view of the cooling curve between 700°C and 300°C, i.e. the cooling region relevant for austenite decomposition. Free cooling in vacuum was chosen for these Charpy geometries with a 20 mm free span (see Appendix A for more details), whereas He-gas was blown on one side of the samples to adjust the cooling rate in tensile strip samples Here, it can be observed that the cooling of the sample closely follows the program cooling rate of 5°C/s. The measured cooling rates (from numerical differentiation of the temperature-time data) for the square cross-section and strip geometries are compared in Figure 5.1d. It is observed that similar cooling profiles were obtained in both the geometries.



Figure 5.1: Gleeble thermal cycle showing (a) the overall profile (b) the peak temperature region (c) expanded view of the cooling region relevant to austenite decomposition at 5°C/s and (d) instantaneous cooling rate for the Charpy square cross-section and tensile strip samples of 06C03Nb steel

5.2.2 Cooling rate of 50°C/s

Figure 5.2a shows the temperature history for a 06C03Nb steel Charpy square cross-section specimen with a peak temperature at 1300°C, an isothermal hold of 5 s followed by controlled cooling at 50°C/s. A 3°C overshoot at 1300°C is observed in Figure 5.2b. During cooling at 50°C/s (see Figure 5.2c), the tests show good agreement with the programmed temperature until ~550°C and then a deviation is

observed i.e. the cooling rate slows down. This deviation is related to the heat released during the phase transformation. At a cooling rate of 50°C/s, the heat loss due to convection and conduction was not sufficient to compensate for the heat released and thus the cooling rate decreased. A similar thermal profile was used to produce Charpy specimen of 03C09Nb steel where the samples were heated to 1300°C for 10 s at 100°C/s and cooled at ~50°C/s up to 550°C followed by a non-linear cooling profile. The isothermal holding time was adjusted to 10 s to maintain an austenite grain size of ~50 μ m (see Section 5.3).



Figure 5.2: Example of a Gleeble thermal cycle and variation across the Charpy specimen showing (a) the overall profile (b) the overshooting at the peak temperature and (c) recoalescence during cooling at 50°C/s showing deviation from constant 50°C/s cooling rate

Figure 5.3 shows the temperature distribution along the length of Charpy square cross-section specimen for the 03C09Nb steel. The centre of the sample is the control thermocouple and thermocouples located at ± 1 mm from the centre measured a temperature 7°C lower than the programmed peak temperature of 1300°C, a difference of 0.5%. This shows that there is a negligible temperature gradient along 2 mm length of the sample after isothermal holding for 10 s at 1300°C and cooling. More details on the thermal gradient during the Gleeble treatment can be found in Appendix A. The presence of a region approximately 2 mm in length at centre where the temperature and cooling rates are uniform (i.e. within 0.4%) is important since the Charpy V- notch will be machined at the centre where the control thermocouple was located.



Figure 5.3: Example thermal profile showing homogeneity along the Charpy sample showing (a) overall thermal profile (b) peak temperature and (c) expanded cooling curve for 50°C/s cooling rate in 03C09Nb steel

The non-linear cooling profile obtained in the Charpy specimen for 50°C/s was used to program the cooling path for the strip samples. To obtain the programmed cooling rate, helium gas was blown onto one side of the sample. The temperature versus time data for the Charpy square cross-section and tensile strip samples are compared in Figure 5.4a for four different tests of each sample. It can be observed in Figure 5.4b that there is some overshoot at the peak temperature (similar as shown in Figure 5.1b) where the maximum temperature at the peak were consistently recorded between 1306 - 1308°C for tensile strip and 1303°C for Charpy square cross-section. The expanded view of the cooling profile between 600°C to 300°C in Figure 5.4c shows that the recoalescence starts at ~500°C in the Charpy samples and ~480°C for the tensile samples. This difference is also reflected in the measured cooling rates (from numerical differentiation of the temperature-time data) for the square cross-section and strip geometries as shown in Figure 5.4d.

It is observed that a cooling rate of ~50°C/s was maintained until ~700°C. Between 700°C to 530°C, the cooling rate gradually decreases to 40°C/s. At ~530°C, the cooling rate decreases reaching a minimum of ~18°C/s at 500°C for the Charpy and ~20°C/s at 480°C for the strip geometry. The cooling rate increased to 40°C/s at ~400°C. Below 400°C, the cooling rate again decreases gradually to 25°C. As discussed previously, this decrease in cooling rate corresponds to the heat released in the sample due to phase transformation. The 20°C difference in the transformation start temperature between the two different test sample geometries could be due to low surface to volume ratio in the Charpy samples.

Figure 5.5 shows the temperature distribution along the length of tensile strip specimen for the 50° C/s cooling condition of 06C03Nb steel. The control thermocouple is at the centre of the sample and the thermocouples located at ± 6 mm from the centre measured a temperature 5°C lower, a difference of 0.45% at the peak temperature. The presence of a region approximately 12 mm in length, where the temperature and cooling rates are uniform (i.e. within 0.45%), is important since this region will later form the gauge length of the tensile specimen.

The thermal profile corresponding to obtain 50°C/s was also applied on the 03C09Nb steel where the samples were heated at 100°C/s to 1300°C, held for 10 s and cooled at 50°C/s (as explained before) to produce Charpy and tensile samples.



Figure 5.4: Gleeble thermal cycle showing (a) the overall profile (b) the peak temperature region (c) expanded view of the cooling region relevant to austenite decomposition at 50°C/s and (d) instantaneous cooling rate for the Charpy square cross-section and tensile strip samples of 06C03Nb steel



Figure 5.5: Example thermal profile along the length of the tensile strip samples showing (a) overall thermal profile (b) peak temperature and (c) expanded cooling curve for 50°C/s cooling rate in 06C03Nb steel

5.2.3 Hardness of as-cooled specimen

Vickers microhardness tests were conducted using 1 kgf load with a dwell time 15 s on the ascooled specimen after heat treatment. Seven repeat tests were conducted for each condition. The mean Vickers hardness number and standard deviations on the tensile strip and Charpy samples after heat treatment are compared in Table 5.1. It is observed that the hardness results are similar (i.e. within the error margin) in tensile and Charpy specimen, i.e. a maximum difference of 3% between the tensile strip and Charpy measured at the cross-section of for different conditions.

Table 5.1: Vickers hardness results measured at 1 kgf lo	able 5.1:	ole 5.1: Vickers har	dness results	measured at	t 1 kgf loa
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C I	Vickers's hardness (HV)			
Sample	Tensile strip	Charpy square cross section		
06C03Nb 5°C/s	217 ± 4	220 ± 3		
06C03Nb 50°C/s	284 ± 5	293 ± 5		
03C09Nb 50°C/s	263 ± 4	256 ± 6		

*Results are presented as mean ± standard deviation, calculated from 7 repeat tests for each condition.

5.2.4 Summary of thermal history

At the end of the 1st thermal cycle, samples with three different conditions (i.e. 06C03Nb steel cooled at 5°C/s and 50°C/s; and 03C09Nb steel cooled at 50°C/s) were produced. For each of the heat-treatments, tensile strips and Charpy square cross-section samples were produced where the thermal profiles were very similar for the two geometries. For the cooling rate of 5°C/s, the temperature profiles for the strip and the Charpy samples were almost identical. The hardness values taken from the different geometries were within the error of measurements. However, in the case of a cooling rate of 50°C/s, the heat released from the phase transformation could not be removed quickly enough by heat transfer to the environment and as a result, the cooling rate decreased as the transformation proceeded. The onset of the recoalescence was observed to occur in the Charpy sample at 500°C vs. 480°C in the strip, possibly due to the lower surface to volume ratio in this sample. This difference is considered to be minor, given the similar hardness values measured on the different samples after the transformation was complete. In addition, the samples were produced in such a way that there is a homogenous zone of 12 mm in the tensile strip and 2 mm in the Charpy square cross-section specimen at the middle.

5.3 Austenite grain growth

The objective of the heat treatment was to have an austenite grain size of $\sim 50 \,\mu\text{m}$ with the Nb(C,N) dissolved in austenite. The precipitate dissolution temperature as predicted using ThermoCalc 4.0 with the TCFE7 database predicts that the coarse TiN precipitates are stable up to very high temperature (~ 1500°C),

and the Nb(C,N) precipitates dissolve at a temperature of ~ 1080°C for 06C03Nb steel and ~ 1155°C for 03C09Nb steel. The Mo-rich precipitates are predicted to dissolve at relatively low temperatures of ~ 680°C, i.e. close to Ae₁ (shown in Figure 4.3 in Chapter 4). The model developed by Garcin et al. [68] considers the kinetics of micro-alloy precipitate dissolution in 06C03Nb steel and predicts that 200 ppm niobium is in solution at after isothermal holding at 1300°C for 5 s, resulting in an austenite grain size of ~ 60 μ m. Based on this, it is assumed that after 5 s holding at 1300°C for 06C03Nb steel, Mo and Nb will be completely dissolved in austenite, whereas Ti will be partially precipitated. For the 03C09Nb with triple the Nb than 06C03Nb steel, a 10 s holding time at 1300°C was used to allow dissolution of Nb.

Figure 5.6 shows the results for the evolution of austenite grain size (i.e. measured in-situ during heating and holding at 1300°C using laser ultrasonics [79,128,208]. In this plot, austenite grain size is plotted as a function of time from the beginning of the thermal cycle in the Gleeble. The specimen reaches 1300°C at 37 s. These results show that if the 06C03Nb steel and the 03C09Nb steel were held at 1300°C for 5 s and 10 s respectively, it will result in an average austenite grain size of $55 \pm 5 \,\mu$ m, considering the scatter of data points within one test as well as the variation between repeat tests.

The in-situ grain size measurements were verified with metallography measurements on 06C03Nb and 03C09Nb steel cooled at 50°C/s from 1300°C after 5 s and 10 s isothermal holding, respectively. The grain size distributions are shown in Figure 5.7 for the 06C03Nb and 03C09Nb steels. The average grain size was found by calculating the arithmetic average of grain size area from ~1000 grains. The average equivalent area diameter (EQAD) is found to be ~ 49 μ m for 06C03Nb steel and ~55 μ m for 03C09Nb steel and is, therefore, in good agreement with the grain size measured with laser ultrasonics and metallography by Romualdi [128] on both steels and on 06C03Nb steel by Maalekian [79] and Garcin [68] using laser ultrasonics.



Figure 5.6: In-situ austenite grain growth kinetics during heating and holding at 1300°C, using LUMet [128]



Figure 5.7: Austenite grain size distribution of (a) 06C09Nb steel and (b) 03C09Nb steel upon heating and

holding at 1300°C

5.4 Austenite decomposition

Two cooling rates (i.e. 5 and 50 °C/s) were chosen to study the decomposition of austenite in the 06C03Nb steel from a similar austenite grain size (i.e. ~50 μ m). The kinetics of austenite decomposition were analyzed using the Kop method analysis of dilation measurements, as described in Section 4.6. The fraction transformed during cooling at 5°C/s and 50°C/s for six different tests on the tensile strips are plotted in Figure 5.8a and Figure 5.8b, respectively. The average transformation temperatures corresponding to 5%, 50% and 95% transformation, i.e. T_{5%}, T_{50%} and T_{95%} respectively, were calculated from twenty repeat tests and are shown in Table 5.2.

The transformation start temperatures ($T_{5\%}$) corresponding to 5% transformation for all the repeat tests are found to be within ± 12°C on average, (i.e. an error of 2%) for 95% of sample population. As the transformation progresses to 50%, the average variation decreases to 9°C among all samples. Towards the end of transformation, the average variation in the transformation temperature ($T_{95\%}$) again increases to ± 12°C.



Figure 5.8: Repeatability of transformation kinetics as calculated from dilation measurements from tensile strip geometries in 06C03Nb steel upon cooling at (a) 5°C/s and (b) 50°C/s



Figure 5.9: Average transformation kinetics of 06C03Nb steel cooled at 5°C/s and 50°C/s; and 03C09Nb steel cooled at 50°C/s

Table 5.2: Average transformation temperatures during cooling for the 06C03Nb and 03C09Nb steels

Cooling condition	T _{5%} (°C)	Т _{50%} (°С)	T _{95%} (°C)
06C03Nb - 5°C/s	585 ± 10	543 ± 8	501 ± 12
06C03Nb - 50°C/s	538 ± 16	476 ± 11	409 ± 11
03C09Nb - 50°C/s	556 ± 11	509 ± 8	450 ± 13

* Mean and standard deviation (s) were calculated from 20 repeat experiments.

**The data are reported as the mean $\pm 2s$.

The average transformation curves for the three conditions were chosen from the centre of the distribution and are compared in Figure 5.9. Comparing the effect of two different cooling rates, i.e. 5°C/s and 50°C/s on the austenite decomposition kinetics of 06C03Nb steel, it is observed that the average transformation temperature corresponding to 50% transformation ($T_{50\%}$) decreases from 543°C to 476°C when the cooling rate is lowered from 50°C/s to 5°C/s, i.e. a difference of 67°C. Therefore, with an increase in cooling rate, the transformation shifts to a lower temperature, from similar sized austenite grains, i.e. an expected observation [5,39,68,209,210].

The 03C09Nb steel was also cooled at 50°C/s from a fully austenitic microstructure of ~ 55 μ m grain size. The results for the 5%, 50% and 95% fraction transformed are reported in Figure 5.9 and Table 5.2. It can be observed that the average transformation start temperature (T_{5%}) increases from 538°C to 556°C, i.e. by 18°C when the carbon decreases from 0.06 wt.% to 0.03 wt.%. These observations are consistent with the results obtained by Robinson et al. [6,208] on the same steel chemistry where they have reported T_{5%} to be 540°C for a cooling rate of 30°C/s from 35 µm prior austenite grain and Nb in solution.

The results of the decomposition kinetics can be rationalized as follows. Austenite decomposition to ferrite is well-documented as a diffusional nucleation and growth process, where ferrite grows from parent austenite involving movement of the interface as well diffusion of solutes due to the difference of solubility in the two phases. The kinetics of the austenite decomposition are described with the different assumptions: i) carbon diffusion to be the rate controlling step i.e. diffusion-controlled mode, ii) interface mobility as the rate controlling step i.e. interface controlled mode and iii) both diffusion and interface controlled i.e. mixed mode [25,211–216]. Thermodynamically, carbon is an austenite stabilizer and therefore an increase in carbon moves the austenite to ferrite phase boundary to lower temperatures. Therefore, for the same cooling rate, presence of high carbon in 06C03Nb steel than 03C09Nb steel can alone lower the austenite decomposition temperature, as extensively reported by several researchers [68,217–220].

On the other hand, presence of substitutional solutes like Nb in austenite can lead to a decrease in the ferrite growth rate due to solute drag at moving interfaces [211,221,222]. Fossaert [16] theorized that Nb segregates to the austenite grain boundary due to large lattice misfit of Nb atoms in Fe, thereby lowering its energy, which retards the nucleation of product phases by reducing its efficiency as a heterogeneous nucleation site. The reduction of boundary mobility, both by Nb solute drag, and by the interaction of segregated Nb atoms with the diffusion of C across the austenite/ferrite interface have also been proposed as the underlying mechanism for the kinetic effect of Nb on austenite decomposition [222,223]. Robinson [6,208] reported that the transformation start temperatures are lowered from 540°C to 475°C when the Nb content is raised from 0.034% to 0.091% for similar carbon level of 0.06 wt.% and austenite grain size \sim 30 µm for a cooling rate of 30°C/s. In our results, for 50°C/s cooling rates, the transformation start increases by 18°C when the carbon decreases from 0.06 wt.% to 0.03 wt.% and Nb increases from 0.03 wt.% to 0.09 wt.% which implies carbon diffusion at ferrite-austenite interface plays a more important role compared to Nb solute drag during austenite decomposition.

5.5 Characterization of microstructure after austenite decomposition

The microstructure of the samples with different cooling rates were examined using a field emission gun scanning electron microscope (FEGSEM) with a secondary electron detector. The SEM images of the microstructures for the 06C03Nb steel with nominal cooling rates of 5 and 50°C/s are illustrated in Figure 5.10. A fine lath structure is observed for the 50°C/s cooling rate while a coarser structure is observed for a cooling rate of 5°C/s. In contrast, the microstructure observed for the 03C09Nb steel cooled at 50°C/s shows elements of both fine laths and coarse features as shown in Figure 5.11. The prior austenite grain boundaries (PAGBs) can be observed in all cases as the laths do not extend across PAGBs. However, it is hard to quantitatively characterize these microstructures from the SEM images. For advanced quantitative analysis, the microstructures were characterized with EBSD as described in the next Section 5.6.



Figure 5.10: Microstructure of 06C03Nb steel at (a) 5°C/s and (b) 50°C/s after 1st thermal cycle under high resolution FEGSEM (Nital etch)



Figure 5.11: Microstructure of 0309Nb steel upon cooling at 50°C/s under FEGSEM (Nital etch)

5.6 EBSD characterization of transformation products

The different types of bainitic microstructures could not be easily quantified using optical microscopy or SEM imaging due to the complexity in the microstructure. Therefore, electron backscatter diffraction (EBSD) analysis was adopted to distinguish the microstructure parameters that characterize the transformation products obtained upon cooling after the first thermal cycle (described in Section 5.5). Figure 5.12 shows examples of the inverse pole figure (IPF) colored orientation maps for the three conditions. The different colors represent the normal macroscopic direction (ND) as shown in the IPF triangle. The black areas represent the presence of retained austenite and martensite and are analyzed separately in Section 5.6.2. A coarse blocky structure with nearly uniform color gradient within the blocks was observed in the 06C03Nb steel microstructure cooled at 5°C/s, as shown in Figure 5.12a, similar to the features observed in the SEM microstructure (see Figure 5.10a). On the other hand, a fine elongated lath structure with different orientations in neighboring laths was observed for the 50°C/s cooled microstructure of 06C03Nb steel, shown in Figure 5.12b. Therefore, with increase in cooling rates from 5 to 50°C/s, two distinctly different microstructures are observed. The microstructure observed for the 03C09Nb steel cooled at 50°C/s (see Figure 5.12c) shows elements of both elongated lath-like features with different orientations in neighboring laths as well as some blocky structures. These microstructural features of bainite at different cooling rates have also been reported by several researchers [45,105,107,114]. Reichert [107] and Wang [45] have shown similar features of bainite in Nb, Mo containing linepipe steels, whereas Takayama's [105,114] results were obtained from 0.15 wt.% C steels with and without Nb upon continuous cooling.



Figure 5.12: Inverse pole figure EBSD maps of the two steels after first thermal cycle for (a) 06C03Nb steel cooled at 5°C/s, (b) 06C03Nb steel cooled at 50°C/s and (c) 03C09Nb steel cooled at 50°C/s. Note the sample orientation selected for the IPF map is shown in the color bar.

5.6.1 Analysis of crystallographic texture

The crystallographic texture has also been characterized for each of the three conditions from measurements on large EBSD maps with ~2000 bainite grains. Figure 5.13 shows the results for (001), (011) and (111) pole figures. Some preferred orientation can be observed partially in the 50°C/s samples. This presumably relates to the texture of austenite which is inherited by the orientation relationship of the decomposition products which will be discussed in next section. However, the overall textures are relatively weak with a maximum intensity of 2.7 (a strong texture would have a maximum intensity > 5 [224]).



Figure 5.13: (001), (111) and (0111) pole figures showing the intensity of texture components on 06C03Nb steel cooled at (a,b,c) 5°C/s and (d,e,f) 50°C/s; and (g,h,i) 03C09Nb steel cooled at 50°C/s. (Note that the sample direction is the ND of the sample and RD-TD was not known.)

5.6.2 Martensite / Austenite constituents

The retained austenite together with the martensite were separated from the matrix following Reichert's method [107] and are shown in Figure 5.14. The area fraction of martensite and austenite in the M/A constituents as obtained from the EBSD measurements are presented in Table 5.4.



Figure 5.14: M/A constituents as characterized from the EBSD measurements on (a) 06C03Nb steel cooled at 5°C/s, (b) 06C03Nb steel cooled at 50°C/s and (c) 03C09Nb steel cooled at 50°C/s.

Sample T5% (°C) * R		Retained Austenite (%)**	Martensite (%)**	Total M/A (%)**	
06C03Nb - 5°C/s	585 ± 10	1.2 ± 0.6	5.2 ± 0.7	6.4 ± 0.8	
06C03Nb - 50°C/s	538 ± 16	0.1 ± 0.02	2.8 ± 0.5	2.9 ± 0.5	
03C09Nb - 50°C/s	556 ± 11	0.2 ± 0.03	3.5 ± 0.8	3.7 ± 0.7	

Table 5.3: Martensite / Austenite area fraction, calculated from EBSD measurements

* Mean and standard deviation (s) were calculated from 20 repeat experiments, reported as 2s.

** Mean and standard deviation (s) were calculated from 4 different areas, reported as 2s.

Previous work has shown that the fraction of M/A is related to the transformation start temperatures $(T_{5\%})$ [45,112,114]. In the current study, it is observed that the highest amount of M/A, i.e. 6.4%, is observed in the 06C03Nb steel cooled at 5°C/s with a transformation temperature of 585°C. As the transformation temperature decreases to 538°C upon increasing the cooling rate for the same steel, the M/A area fraction is found to decrease to 2.8%. For an intermediate transformation temperature of 556°C, the M/A fraction is found to be 3.5%. In all cases, the amount of martensite in the M/A is higher than the amount of retained austenite. However, the amount of retained austenite might be underestimated due to the potential transformation into martensite during sample preparation. The results for the fraction of M/A constituents are consistent with previous measurements [5,68,225] on the same steel under similar conditions for lower transformation temperatures <560°C, as shown in Figure 5.15 [5]. However, there is a discrepancy in the fraction of M/A constituents formed at higher temperature. This discrepancy could be possibly due to difference in heat treatments. Nevertheless, the measurement procedures are complicated and require further investigation in future. Thus, when the transformation takes place at higher temperatures, a reduction of the driving force for bainite transformation results in carbon enrichment in untransformed austenite, which results in incomplete transformation. A significantly higher carbon content in untransformed austenite retards subsequent decomposition, which leads to the formation of M/A constituents, as discussed by Takayama et al. [114] and Wang et al. [45].



Figure 5.15: Experimental results of M/A fractions as a function of transformation temperatures overlapped on the literature data, adapted from Reichert et al. [5].

5.6.3 Orientation relationship between parent and product phases

The orientation relationship between austenite and bainitic ferrite has been extensively discussed by Takayama et al. [105]. Bainitic ferrite decomposes from austenite with an orientation relationship close to the Kurdjumov-Sachs orientation relationship (KS OR) as was discussed in Section 2.2.4.1. 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 austenite reconstruction programs. To investigate the different orientations observed in bainite, regions representing a single prior austenite grain were identified based on a single retained austenite orientation. Figure 5.16a shows an inverse pole figure EBSD map for the 06C03Nb specimen cooled at 5°C/s, with a prior austenite grain selected (marked by dashed lines). The prior austenite grain was determined from the small amount of retained austenite present in the final microstructure as shown in Figure 5.16b and the orientation of the parent austenite grain was extracted. Based on the FCC symmetry of the austenite, the KS OR yields 24 possible variants that fulfill the $\{111\}\gamma \parallel \{011\}\alpha < 101 > \gamma \parallel < 111 > \alpha$ orientation relationship. The orientation of a single austenite grain is shown by the red dots in the (001) pole figure shown in Figure 5.16c and the corresponding 24 variants as calculated following KS OR are shown by small black circles in Figure 5.16c. Variants here are referred to the different orientations of ferrite laths in the bainite that derive from a single prior austenite grain. The calculated variants are then compared with EBSD data of the transformation products formed within that prior austenite grain. The experimental results for the orientation are superimposed on the ideal orientation relationships and have been colored red, blue and yellow to distinguish the three main Bain groups each containing 8 variants. It can be observed that the experimentally determined orientations correspond closely to the theoretical values. In Figure 5.16d, the prior austenite grain has been colored based on the 3 Bain groups, predominantly the brown OR. In order to confirm these results, the Bain group maps have been plotted for several other prior austenite grains in Figure 5.17. In all the cases, a relatively coarse structure is observed with the prior austenite grain decomposing into one major Bain group with lesser components of other Bain groups.

Figure 5.18 shows a similar analysis for the 06C03Nb steel cooled at 50°C/s. In this case, the amount of retained austenite is only 0.1% (shown in Table 5.3), barely visible (therefore the austenite orientation map is not shown here) but just enough to extract the austenite orientation information. A very different result in terms of the Bain map is obtained. While the KS orientation relationship between austenite and the decomposition products is observed, the austenite grain is subdivided into many variants of the main Bain groups (Figure 5.18b) which form a lath like structure. Figure 5.19 shows three additional examples consistent with this observation.



Figure 5.16: EBSD maps of (a) ferrite and (b) austenite, with a prior austenite grain selected by dotted line; (c) (001) pole figure of the selected grain (the orientation of the prior austenite grain is indicated by red dots and calculated 24 KS variants are shown as black circles); (d) Bain map showing three Bain groups according

to (a). (For the 06C03Nb steel cooled at 5°C/s).



Figure 5.17: Bain maps of four different austenite grains of 06C03Nb steel specimen cooled at 5°C/s



Figure 5.18: (a) Inverse pole figure (IPF) map, (b) Bain group map and (c) corresponding pole figures for 06C03Nb steel cooled at 50°C/s following KS orientation relationship (Note the retained austenite map is omitted due to presence of only 0.02% fraction, barely visible)



Figure 5.19: Bain maps of three different austenite grains of 06C03Nb steel specimen cooled at 50°C/s

The microstructure of the 06C03Nb steel at two different cooling rates i.e. 5 and 50°C/s was found to be very different in terms of a characteristic length scale for the transformation products. However, a near KS orientation relationship between the parent austenite and product bainite phases is satisfied in both cases. Takayama et al. [105] have shown that the variant selection of bainite is strongly dependent on the transformation temperature. Plastic deformation of austenite is required to accommodate the different variants and the flow stress of austenite is temperature dependent [105]. Therefore, at higher transformation start temperature ~585°C (i.e. when cooled at 5°C/s), variant pairing with small misorientations are favored as the austenite flow stress is relatively low and the transformation strain can be accommodated by plasticity in austenite. Thus, variants belonging to the same Bain group tend to form adjacently forming a large single Bain group. In contrast, as the transformation temperature drops by ~50°C to 538°C, (i.e. in the case of 50°C/s cooling rate), plastic accommodation becomes difficult. Variants sharing the same parallel relation of close packed planes become more favored as compensating strains from the different variants lowers the effective misfit, therefore almost an equal representation of all three Bain groups are observed in this case. Wang et al. [44,45] have also reported similar instances of variant selection in bainite for 6°C/s and 37.5°C/s in a X80 grade steel.

Next, the results for the 03C09Nb steel cooled at 50°C/s are presented in Figure 5.20. Once again, the decomposition products show the KS orientation relationship to the prior austenite grain. However, this appears to be an intermediate case relative to the two previous cases, i.e. each austenite grain decomposes into several variants of the major Bain groups and their morphology appears to be relatively "lath" like. This is also consistent with the intermediate transformation start temperature of ~565°C versus 585°C and 538°C in the previous two cases respectively. This observation was also confirmed by analyzing several other prior austenite grains (see Figure 5.21).

However, it is worth noting that, the size, morphology and distribution of the Bain groups are very different when transformed at different transformation temperatures. We have found that the bainite laths are elongated with high aspect ratio when the transformation temperature is the lowest among the three

cases, i.e. 538°C. As the transformation temperature increases to 565°C, the bainite laths are still elongated, but the aspect ratio decreases for the elongated laths, similar to observation by Singh et al. [110]. For a high transformation temperature close to ~600°C, a blocky structure is observed. These results are also consistent with the recent results of Speer et al. [226] where they analyzed the bainitic ferrite morphologies in details through quantitative characterization of inter-variant boundaries.



Figure 5.20: (a) Inverse pole figure (IPF), (b) Bain group map and (c) corresponding pole figures for 03C09Nb steel cooled at 50°C/s following KS orientation relationship. (Note the retained austenite map is omitted due to presence of only 0.01% fraction, barely visible).



Figure 5.21: Bain maps of (a-d) four different austenite grains of 03C09Nb steel specimen cooled at 50°C/s

5.6.4 Spatial distribution of misorientations within the microstructure

Figure 5.22 shows the misorientation angle maps for the three conditions. To quantify the differences, the boundary misorientation angle distribution of all the three conditions are compared in Figure 5.23. The first observation to note is that due to cubic symmetry, the maximum misorientation angle is 63° . Low angle grain boundaries (LAGBs) have been defined as between 2 - 15° and are shown in green. High angle grain boundaries (HAGBs) are divided into boundaries with a rotation angle of $15 - 50^{\circ}$, shown in black and boundaries with a rotation angle of $50 - 63^{\circ}$, shown in red. These definitions are adopted following the conventions used in the literature which indicate that the misorientation of the high angle boundaries able to arrest cleavage cracks is mainly above 50° [44,45,47,48,107,227].

It is observed that the Bain groups are separated by boundaries > 50°, while prior austenite grain boundaries fall into the range of 15 - 63°, as also reported by several researchers [44,45,47,48,107,227]. The bainitic microstructures formed for 06C03Nb cooled at 5°C/s cooling rate was observed to have a coarse network of high angle grain boundaries with low angle grain boundaries within a given Bain group (see Figure 5.22a). This microstructure contains a relatively large fraction of M/A (~6.5%), as reported in Table 5.3. For the same steel cooled at 50°C/s, the microstructure is comprised of fine laths which are separated by HAGBs, with small density of LAGBs within the laths (Figure 5.22b). Turning to 03C09Nb steel cooled at 50°C/s, this microstructure is comprised of coarse laths with a high fraction of HAGBs separating the major Bain groups and LAGBs within the laths (Figure 5.22c). It also reveals that the spacings between HAGBs are qualitatively much higher than that of the 06C03Nb steel cooled at 50°C/s shown in Figure 5.22b.



Figure 5.22: Distribution of the misorientation angles within the microstructures for (a) 06C03Nb steel cooled at 5°C/s, (b) 06C03Nb steel cooled at 50°C/s and (c) 03C09Nb steel cooled at 50°C/s. Note that (a) is the same area as Figure 5.16a, (b) is the same area as Figure 5.18a and (c) is the same area as Figure 5.20a



Figure 5.23: Frequency distribution of boundary rotation angles in different microstructures obtained after 1st thermal cycle at different cooling rates

From Figure 5.23, the coarse bainite of the 06C03Nb steel formed at a cooling rate of 5°C/s shows a strong peak below 15°, small peaks at 28° and 36°, followed by overlapping peaks at ~55° and ~59°. The same steel when cooled at 50°C/s with fine lath bainitic structure shows three apparent peaks, i.e. one below 15° and two centred at ~ 55° and ~ 59°. For the 03C09Nb steel cooled at 50°C/s, similar features are observed, i.e. a peak below 15°, a small peak at 28°, a similar peak at 55° and a smaller peak at 60°. Grain boundaries with a misorientation of 60° are known to have the lowest interface energy and are favored at low transformation temperatures [228]. Within a prior austenite grain these high misorientations can only be achieved by the adjacent formation of variants belonging to different Bain groups. Takayama et al. [105] proposed that variants in a single Bain group have misorientation angles less than 15° and always form side by side so that the boundary energy between variants can be decreased. Boundaries between prior austenite grains contribute to the misorientation angles peak between 15° - 50° [45,48,130]. No misorientations between 15 - 50° were found inside the prior austenite grains.

Later in this chapter (Section 5.8), the stress-strain response will be characterized. To first approximation, all high angle grain boundaries i.e. $>15^{\circ}$ and the M/A constituents will be considered to be strong obstacles for dislocation slip transmission. As such, the current data has been analyzed to characterize the line length of the HAGBs in the different microstructures. The normalized line length of strong obstacles (HAGB and M/A) was characterized as:

$HAGB \ density, H = \frac{Line \ length \ of \ HAGBs \ (in \ between \ laths \ and \ with \ M/A \ constituents)}{Area \ of \ the \ microstructure}$

(5.1)

The reciprocal of the HAGB density is a measure of the characteristic length scale, l of the microstructure, i.e.:

Characteristic length scale,
$$l = \frac{1}{HAGB \ density}$$
 (5.2)

The characteristic line lengths are reported in Table 5.4. Figure 5.24 shows the results for the misorientation maps $>15^{\circ}$ from EBSD for the three microstructures Considered in this work.

Steel	Cooling rate (°C/s)	T5% (°C)	HAGB (>15°) density, H (µm ⁻¹)	Characteristic length scale, <i>l</i> (µm)	M/A (%) (from EBSD)
06C03Nb	5	585 ± 10	0.42	2.4	6.4 ± 0.8
	50	538 ± 16	1.43	0.7	2.8 ± 0.5
03C09Nb	50	556 ± 11	0.67	1.5	3.7 ± 0.7

Table 5.4: HAGB density and M/A content for two steels cooled at 50°C/s and 5°C/s



Figure 5.24: EBSD maps showing high angle grain boundaries (>15°) and M/A constituents for (a) 06C03Nb steel cooled at 5°C/s, (b) 06C03Nb steel cooled at 50°C/s and (c) 03C09Nb steel cooled at 50°C/s.

The 06C03Nb steel cooled at 50°C/s cooling rate has an average transformation start temperature of 538°C, resulting in very high density of HAGBs along with very low fraction of M/A constituents. On decreasing the cooling rate to 5°C/s for the same steel, the transformation temperature $T_{5\%}$ increases to 585°C, which results into formation of a structure with a very low density of HAGBs, but a relatively high fraction of M/A constituents. For the 03C09Nb steel with a cooling rate of 50°C/s, the transformation start temperature increases to 556°C and the density of HAGBs is lowered to 0.67 μ m⁻¹ vs. 1.43 μ m⁻¹ for the 06C03Nb steel.

5.6.5 Strain induced local misorientations

In theory, geometrically necessary dislocations (GNDs) introduced during the formation of bainitic transformation products cause small lattice rotations which can be detected with EBSD [229]. Several methods can be applied to evaluate the local variations of the lattice orientation caused by GNDs [230]. Britton and Wilkinson [123,124] have done extensive work on measurements of residual elastic strain and lattice rotations using high resolution 3D-EBSD. This is a challenging task which requires the rotations in 3D calculated over an appropriate length scale. However a simple semi-quantitative estimate can be inferred using point based methods, where a kernel is defined by a point and its nearest neighbors [5,231,232]. In

this work, the kernel average misorientation (KAM) is used. The step size and the number of points in the kernel is crucial and therefore a 50 nm step size and points up to 3rd nearest neighbor were considered during data acquisition.

Figure 5.25 shows the KAM maps of the three investigated microstructures and the KAM distribution is plotted in Figure 5.26. A log normal fit was applied to the KAM distributions and the mean value is used to compare the KAM. The mean KAM values of 0.62°, 0.68°, 0.66° for 06C03Nb steel cooled at 5°C/s, 06C03Nb steel cooled at 50°C/s and 03C09Nb steel cooled at 50°C/s. respectively, i.e. no significant difference in KAM values could essentially be measured. These values are in close agreement with a study by Reichert et al. who reported KAM values of 0.62 and 0.7 for upper bainite and lower bainite microstructures and 0.42 for polygonal ferrite using the same method [5].



Figure 5.25: Kernel average misorientation maps for (a) 06C03Nb steel cooled at 5°C/s (b) 06C03Nb steel cooled at 50°C/s and (c) 03C09Nb steel cooled at 50°C/s. Measurements were obtained using 3rd nearest neighbors, calculating the orientation gradient over 150 nm in a square grid.



Figure 5.26: Experimentally measured KAM distribution and fitted log normal distribution (shown in lines)

5.7 Summary of microstructures

It is worth to briefly summarize the differences in morphology of the austenite decomposition products as a function of the composition cooling rates. In our results, it is clearly observed that the morphology of the austenite decomposition product changes continuously over a range of transformation temperature and the variant pairing is strongly dependent on the temperature of transformation, as discussed by Takayama [105]. At higher temperatures, for example, in the case of 06C03Nb cooled at 5°C/s, variants with low misorientations 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. for the case of 06C03Nb steel cooled at 50°C/s, the microstructure is characterized by variants belonging to the different Bain groups form adjacently. Generally, variants of different Bain groups are divided by HAGBs leading to an increase of HAGB area. The steel with lower carbon content i.e.

03C09Nb steel cooled at 50°C/s shows an intermediate microstructure: multiple Bain groups variants but coarser lath dimensions compared to 06C03Nb steel with the same cooling rate.

5.8 Tensile test results after first thermal cycle

Tensile tests were conducted on samples with the three distinct microstructures described in the previous section. Tests were conducted at ambient temperature and -20°C, -60°C and -196°C. The engineering stress-strain curves for each condition at ambient temperature are shown in Figure 5.27. Table **5.5** summarizes the results for the yield stress, ultimate tensile stress and uniform elongation. Note that the values for total % elongation are not reported due to the non-standard gauge length used for these tests.



Figure 5.27: Engineering stress-strain behaviour of the three characteristic microstructures described in Section 5.7 at ambient temperature after first thermal cycle

Steel	Charac- teristic length scale, <i>l</i> (µm)	M/A fraction (%)	0.2 % Yield strength (MPa)	Ultimate tensile strength (MPa)	Uniform Elongation (%)	True stress to failure (MPa)	True strain to failure
06C03Nb, 5°C/s	2.4	6.4 ± 0.8	559 ± 5	710 ± 8	6.8 ± 0.5	1086 ± 12	0.6 ± 0.1
06C03Nb, 50°C/s	0.7	2.8 ± 0.5	682 ± 12	808 ± 18	3.0 ± 0.3	1970 ± 40	1.40 ± 0.2
03C09Nb, 50°C/s	1.5	3.7 ± 0.7	644 ± 9	810 ± 6	6.1 ± 0.2	1475 ± 65	1.10 ± 0.1

Table 5.5: Tensile properties of the austenite decomposition products

*Mean and average of the deviations from mean value in tensile results were calculated from three repeat tests for each condition.

All conditions show a ductile stress-strain response. For the 06C03Nb steel, the yield stress increases from 559 MPa to 682 MPa when the cooling rate is increased from 5 to 50°C/s. The yield stress for 03C09Nb steel cooled at 50°C/s is 644 MPa, i.e. in between the results for 06C03Nb steel. On the other hand, the ultimate tensile stress (UTS) is almost the same as 06C03Nb 50°C/s sample. The uniform elongation is ~ 7% for 06C03Nb steel cooled at 5°C/s and ~ 3% for the same steel obtained from 50°C/s cooling rate. The 03C09Nb steel cooled at 50°C/s cooling rate has a uniform elongation of 6%.

The strain was measured with a clip-on extensioneter. Therefore, the true stress – true strain data obtained from extensioneter measurements are only valid until the point of necking where localization of strain occurs. Figure 5.28 shows the results for the true stress-true strain curves up to the necking point. The work hardening rate $d\sigma/d\varepsilon$ is also plotted as a function of the true strain. It can be observed that the Considère criterion of localization, as described in Section 2.3.2, is satisfied according to Equation 2.11.



Figure 5.28: Considère plot showing strain hardening response of the three conditions, together with true stress - true strain for samples tested at ambient temperature

During the post uniform strain, the fracture is preceded by the formation of a diffuse neck which develops a sharp localized neck where the sample breaks. Most of the test specimen (except the specimen tested at -196°C) failed with a fracture angle of $\sim 30^{\circ}$ with respect to the tensile axis. The true fracture stress and strain were calculated from the area at the final fracture point. The true strain to failure were measured from the broken tensile specimen and are reported in Table 5.5.

5.9 Charpy impact tests

Charpy impact tests were conducted on the three characteristic microstructures as described in Section 5.7 over a range of temperatures from -196° C to $+100^{\circ}$ C. Three repeat tests were performed per temperature per condition. Figure 5.29 illustrates the results for the Charpy impact energy as function of test temperature for these three conditions. The mean impact energy for each condition is indicated with the solid symbols (the vertical lines represent the range of the impact energies measured, i.e. maximum and
minimum). The transition temperature (DBTT) in this work has been defined as the temperature corresponding to 50% of the difference between upper and lower shelf energy. The temperature corresponding to 95% brittle failure has also been calculated for the three conditions for the purpose of estimating cleavage stress in later Section 5.11.3. The results are summarized in Table 5.6.



Figure 5.29: Charpy impact behaviour bainite microstructures obtained at 5 and 50°C/s for the 06C03Nb and 03C09Nb steels tested at different temperatures

It can be observed that for the case of the 06C03Nb steel with a cooling rate of 50°C/s, the upper shelf energy is ~ 270 J and the transition temperature is ~ -55°C. As the cooling rate is decreased to 5°C/s for the same steel, the upper shelf energy increases to ~ 400 J, but the transition temperature increases to $+10^{\circ}$ C. For the case of 03C09Nb steel with a cooling rate of 50°C/s, the transition temperature is highest among three case, $+35^{\circ}$ C with an upper shelf energy of 305 J. To compare the lower shelf energies, Charpy V-notch impact tests were performed at -196°C on interstitial free steel (Fe - 0.15 wt.% Ti) having coarse polygonal ferrite and an average impact energy of 2 J was recorded. In the present study, ~ 3 J impact energy were recorded at -196°C on the 06C03Nb steel cooled at 5°C/s and 03C09Nb steel cooled at 50°C/s.

A higher impact energy to 5 J was obtained for the microstructure obtained at 50°C/s cooling rate on the 06C03Nb steel. As the fractures at -196°C are all cleavage, this shows the fine laths in the 06C03Nb steel cooled at 50°C/s do play a role (albeit small) in increasing the cleavage stress, presumably due to deflection of cleavage cracks at the high angle grain boundaries.

Steel	Characterist ic length scale, l (µm)	M/A fraction (%)	0.2 % Yield strength (MPa)	Lower Shelf Energy (J)	T95% Brittle (°C)	DBTT T50% Brittle (°C)	Upper Shelf Energy (J)
06C03Nb, 5°C/s	2.4	6.4	559 ± 5	3.0 ± 0.5	-30	10	$400 \pm 3^{*}$
06C03Nb, 50°C/s	0.7	2.8	682 ± 12	5.0 ± 0.8	-105	-55	270 ± 10
03C09Nb, 50°C/s	1.5	3.7	644 ± 9	3.5 ± 0.5	0	35	$305 \pm 20*$

Table 5.6: Tensile and Charpy impact properties after 1st thermal cycle

*Mean and average of the deviations from mean value in Charpy results were calculated from three repeat tests at one temperature for each condition.

5.10 Characterisation of fracture surface and crack propagation

The fracture surfaces were observed under FEGSEM for three different failure conditions: the regions corresponding to the lower shelf energy (A), transition from lower to upper shelf energy (B) and the upper shelf energy (C) as marked in the schematic shown in Figure 5.30. Samples from region A were then further sectioned perpendicular to the fracture surface to observe cleavage crack propagation using SEM and EBSD.



Figure 5.30: Schematic showing three regions from which samples were chosen for fractography

5.10.1 Microstructure I: 06C03Nb steel cooled at 5°C/s

Figure 5.31a shows a FEGSEM image of the fracture surface for the 06C03Nb steel cooled at 5°C/s and tested at -196°C. The notch is located at the lower end of the Figure 5.31a. It shows a typical flat fracture behaviour with 100% brittle fracture area, consistent with the impact energy of 3 J obtained at -196°C. When examined at higher magnification near the notch in Figure 5.31b, large cleavage facets and river-line features are observed. The fracture surface for the same microstructure tested at ambient temperature, having an impact energy of ~200 J is shown in Figure 5.31c. A ductile fracture behaviour is observed near the notch and a brittle fracture surface away from the notch at the centre of the sample. The fracture areas were measured to be approximately 50% brittle and 50% shear, which is consistent with the 10°C DBTT calculated for this microstructure. The sample tested at 40°C, i.e. in the upper shelf energy region which had an impact energy of ~400 J impact energy did not completely fracture as shown in Figure 5.31f.

Examination of the region where fracture occurred at higher magnification revealed a 100% ductile fracture mode, as shown in Figure 5.31g.

However, details about the crack initiation and propagation cannot easily be obtained from these images. Therefore, the fracture surface was sectioned perpendicular to the fracture plane to observe the non-propagating secondary microcracks nucleated close to the notch during the Charpy tests. Figure 5.32 shows cross-section FEGSEM image perpendicular to the fracture surface and below the fracture surface (within 200 µm from the fracture surface beyond which no cracks were observed). The cleavage crack density in this region was measured according to:

$$Crack \ density, C = \frac{Number \ of \ cleavage \ cracks \ near \ fracture \ surface}{Area \ measured}$$
(5.3)

The crack density is found to be \sim 78 mm⁻². Looking into the non-propagating secondary cracks in Figure 5.32, it appears that the fracture path is transgranular and arrested at the prior austenite grain boundaries (see crack number 2, 3, 4, 6). Crack 1 is observed to change its direction at the PAGB. Crack 5, 7 and 8 are observed to be arrested at the randomly distributed inter-lath particles which appear to be M/A constituents.



Figure 5.31: Fracture surface of 06C03Nb steel cooled at 5°C/s and impact tested at (a,b) -196°C, 3 J,

(c-e) ambient temperature, 200 J and (f,g) 40°C, 400 J



Figure 5.32: Surface beneath the fracture surface (as shown in inset) showing the non-propagating secondary cracks (shown by orange arrows) in 06C03Nb steel cooled at 5°C/s (a) Example 1 and (b) Example 2

During the EBSD characterization of this microstructure before mechanical testing, it was found to contain a very low density of high angle grain boundaries and the decomposition product belongs primarily to a single Bain group. Therefore, it appears that the low angle boundaries within the bainite are unable to significantly restrict crack propagation. These observations are supported by the EBSD characterization on these secondary fracture surface shown in Figure 5.33. The IPF colored maps with the crack path is shown in Figure 5.33 and the black lines in Figure 5.33 (b, c) mark the HAGBs > 15°. The cracks are observed to propagate through the grains with relatively little deflection. However, the crack path changes direction when it crosses a HAGB. The cracks are generally observed to follow the path devoid of any high angle boundaries.



Figure 5.33: EBSD of the surface beneath fracture surface of 06C03Nb steel cooled at 5°C/s tested at -196°C showing (a) secondary crack path in IPF colored maps and (b, c) interaction of crack path with high angle grain boundaries (HAGB >15°)

Literature data based on 2D characterization indicate that although {100) is the most common crack propagation plane in bcc-iron, cleavage cracks can propagate along the {110}, the {112}, the {310} and the {123}-planes [233–235]. However, this is not a definitive proof as 2D-EBSD measurements alone cannot provide the exact orientation of the crack propagation plane. They can only show the orientation of the matrix surrounding the secondary cracks and a range of possible orientations of the secondary cracks. Recent experimental studies using 3D-EBSD show that most of the macroscopic cleavage facets have a crack propagation direction parallel to one of the {100} planes, but some also shows orientation direction parallel to {110} plane [179].

5.10.2 Microstructure II: 06C03Nb steel cooled at 50°C/s

Figure 5.34 shows the fracture surface of 06C03Nb steel cooled at 50°C/s, tested at -196°C, i.e. the region of lower shelf energy. The fracture energy was measured to be 4.5 ± 0.5 J. A flat 100% brittle fracture surface is observed in Figure 5.34a, where the notch is located at the bottom of the image. Figure 5.34 b-d shows the magnified fracture surface close to the notch. In all cases, the fracture mode appears to be cleavage. The cleavage facets are observed to be very fine, < 1 µm which are noticeable different from the results of 5°C/s cooled samples as shown in Figure 5.31d.



Figure 5.34: Fracture surface of Charpy specimen tested at -196°C for 06C03Nb steel cooled at 50°C/s showing (a) full surface (b-d) magnified images close to the notch. (Notch is located at the bottom)

Figure 5.35a shows the fracture surface of 06C03Nb steel cooled at 50°C/s, tested at -60°C, i.e. near the DBTT. A 143 J impact energy was recorded for this sample. A fracture area measurement revealed ~40% ductile and ~60% brittle fracture surface. The notch is located at the lower end of Figure 5.35a and Figure 5.35d. The brittle area at the centre and the ductile-brittle transition region close to the notch are shown in Figure 5.35b and Figure 5.35c respectively, where a brittle surface and a mixed ductile-brittle fracture surface are observed.



Figure 5.35: Fracture surface of 06C03Nb steel cooled at 50°C/s and impact tested at (a-c) -60°C, 143 J,

(d,e) ambient temperature, 263 J

The sample from the upper shelf energy region is shown in Figure 5.35d. A 100% ductile fracture area is observed. A mixture of large and small dimples was also observed in the higher magnification image shown in Figure 5.35e.

However, it is was not possible to determine details about the crack initiation and propagation from these fracture surfaces. Therefore, the fracture surfaces were sectioned perpendicular to the fracture surface to observe the non-propagating secondary microcracks nucleated close to the notch during the Charpy tests. Figure 5.36 shows cross-section FEGSEM image perpendicular to the fracture surface and below the fracture surface (within 200 μ m from the fracture surface). The yellow arrows mark the locations where a crack front changes its direction. The crack density is found to be ~ 40 mm⁻² which is half the value for the same steel cooled at 5°C/s. The examples of secondary fracture surfaces in Figure 5.36 a, b and d reveal cracks propagating through the fine bainite laths, continuously changing directions in their path. Figure 5.36c reveals a trans-granular crack propagating through bainite laths and arrested at a PAGB.



Figure 5.36: Surface beneath the fracture surface (as shown in inset) showing the non-propagating secondary cracks in 06C03Nb steel cooled at 50°C/s (a) Example 1, (b) Example 2, (c) Example 3 and (d) Example 4

Figure 5.37 shows the EBSD IPF colored maps and the misorientation angle maps for examples. The HAGBs are defined as > 15° (black lines) in Figure 5.37 b, c, e, g. The stark change in color between adjacent laths signifies the presence of variants with high misorientation angles. Most of the cleavage cracks are arrested or deflected at these HAGBs. Due to higher density of HAGBs (see Figure 5.18 vs. Figure 5.16), the tortuosity of the crack path is more in this microstructure compared to the one cooled at 5°C/s.



Figure 5.37: EBSD showing surface beneath fracture surface of 06C03Nb steel cooled at 50°C/s tested at - 196°C showing (a, d, f) crack propagation in lath bainite and (b, c, e, g) crack deviation at high angle grain

boundaries (>15°) 118

5.10.3 Microstructure III: 03C09Nb steel cooled at 50°C/s

Figure 5.38a shows a FEGSEM image of the fracture surface for the 03C09Nb steel cooled at 50°C/s and tested at -196°C. It shows a typical flat fracture behaviour with 100% brittle fracture area, consistent with the impact energy of 3.5 J obtained at -196°C. When magnified near the notch in Figure 5.38b, large cleavage facets and river-line features are observed. The fracture surface for the same microstructure tested at +40°C, i.e. near the DBTT (impact energy of 143 J) is shown in Figure 5.38c. A brittle fracture surface away from the notch at centre (see Figure 5.38d) and a ductile fracture behaviour is observed near the notch (Figure 5.38e) The fracture area were measured to be 60% brittle and 40% shear, which is consistent with the 40°C DBTT calculated for this microstructure. The sample tested at 100°C, i.e. in the USE region with 321 J impact energy, did not completely fracture. Observations at higher magnification show a 100% ductile fracture surface, as seen in Figure 5.38g.



Figure 5.38: Fracture surface of 03C09Nb steel cooled at 50°C/s and impact tested at (a,b) -196°C, 3.5 J

(LSE), (c-e) +40°C, 131 J (DBTT) and (f,g) +100°C, 321 J (USE)

Figure 5.39 shows some representative secondary fracture surfaces of the 03C09Nb steel cooled at 50°C/s. The secondary fracture surfaces were obtained from a Charpy fractured specimen tested at -196°C resulting in an impact energy of 3.5 J. The fracture surface was flat and brittle, similar to the 06C03Nb steel cooled at 50°C/s. A large number of secondary cleavage cracks were observed and the crack density was measured to be 105 mm⁻², the highest among three microstructures investigated. The orange arrows mark all the regions where the crack front appear to be arrested or changes its direction. Transgranular cracks were observed, which are arrested at prior austenite grain boundaries, similar to the previous cases (see Figure 5.39b,d).



Figure 5.39:Surface beneath the fracture surface (as shown in inset) in 03C09Nb steel cooled at 50°C/s tested at -196°C showing the non-propagating secondary cracks in (a) Example 1, (b) Example 2, (c) Example 3 and

(d) Example 4

The EBSD characterization on the secondary fracture surface of the 03C09Nb steel cooled at 50°C/s is shown in Figure 5.40. The HAGBs are marked in black lines and shown in Figure 5.40b,d. A relatively coarse microstructure is observed with a characteristic length of 1.5 μ m (see Section 5.6.4) and 3.7% M/A constituents (see Section 5.6.2), which provides little resistance to crack propagation.



Figure 5.40: EBSD showing surface beneath fracture surface of 03C09Nb steel cooled at 5°C/s tested at -196°C showing (a, c) secondary crack path in IPF colored maps and (b, d) interaction of crack path with high angle grain boundaries (HAGB >15°)

5.11 Discussion of microstructure-property relationships

5.11.1 Effect of microstructural parameters on the yield stress

The bainitic microstructures observed in the current study can be characterized by variants of laths (corresponding to the KS orientation relationship) separated by low angle boundaries ($< 15^{\circ}$) and high angle grain boundaries, consistent with reports from other researchers [5,90,102,105] as described in the Section 2.2.4.1 of the literature review.

The factors contributing to the strength of bainite include units separated by high angle grain boundaries, distribution of M/A constituents and the dislocation density [5,166,236–238]. In our current work, a decrease in transformation temperature from 585 to 538°C results in a decrease of the characteristic length scale which describes the bainite from 2.4 to 0.7 μ m in 06C03Nb steel, as shown in Section 5.6.4. In addition, the amount of M/A decreases from 7% to 2.5% with a decrease in transformation start temperature consistent with previous reports [107,110,223]. The dislocation density is also expected to increase with decreasing transformation temperature, as qualitatively suggested by the KAM maps in Section 5.6.5. In the following, a simple, first order analysis of the yield stress will be conducted where boundary strengthening (both grain boundaries and M/A islands) is the most significant factor for the yield stress. The results from the current work of yield stress (σ_y) are modeled using the following equation:

$$\sigma_y = \sigma_0 + \sigma_{dis} + \sigma_{boundary} \tag{5.4}$$

where, σ_0 is the intrinsic strength of ferrite due to lattice friction stress, $\sigma_{boundary}$ is a boundary strengthening term and σ_{dis} is related to the dislocation strengthening. A contribution to the yield strength due to precipitation strengthening is neglected as Mo and Nb are expected to be in solution at 50°C/s cooling rate and the TiN precipitates would be too coarse to contribute to precipitation strengthening.

For the current work, the empirical equation given by Choquet [151] for plain carbon steel, also shown in Equation 2.5, is used to calculate the chemistry dependent term. This equation estimates a strengthening contribution of 114 MPa for 05C03Nb steel and 125 MPa for the 03C09Nb steel.

The Taylor equation [156,157] as shown in Equation 2.9, is used to model the dislocation strengthening. The constants A = 0.3 and M = 3.06 are adopted from a previous study on the investigated X80 [3,5]. The approach of Reichert [5] on similar steels has been adopted to estimate the dislocation density ρ from the kernel average misorientation (KAM) values. In this present study, there was only a small difference in KAM values measured in the three microstructures, as shown in Section 5.6.5. To estimate the dislocation density from the KAM measurements, Reichert [5] has previously given an empirical equation by benchmarking the dislocation density from KAM measurements in polygonal ferrite on the 06C03Nb steel and is given by:

$$\rho_{dis} = 3.4 x \, 10^{13} * KAM - 1.6 \, x 10^{13} \tag{5.5}$$

where KAM is measured in rad and ρ is expressed in m⁻². This method yields a dislocation density of 6.4 x 10^{12} m⁻² and contributes to ~50 MPa strength using Equation 2.9.

The grain size strengthening component could not be analyzed for the complex bainitic microstructures using the traditional Hall-Petch equation [7]. Instead, the characteristic length (*l*) as defined in Section 5.6.4, is used which includes the blockage of slip by high angle boundaries and M/A islands and is given by:

$$\sigma_{boundary} = k_y l^{-\frac{1}{2}}$$
(5.6)

where k_y is the strengthening Petch coefficient. Here, the intrinsic strength, σ_0 and the dislocation strengthening contribution, σ_{dis} are subtracted from the experimental yield strength to estimate $\sigma_{boundary}$ such that,

$$\sigma_{boundary} = \sigma_{YS} - \sigma_0 - \sigma_{dis} \tag{5.7}$$

Then a plot of $\sigma_{boundary}$ vs. $l^{-1/2}$ was plotted as shown in Figure 5.41. The $k_y = 6.6$ MPa $\sqrt{\text{mm}}$ is obtained from the slope.



Figure 5.41: Yield strength related to the characteristic length (1) of microstructure

The results from the current study, although limited, are found to be consistent with a Hall-Petch type relation. Pickering and Gladman [7] reported $k_y = 21.4$ MPa $\sqrt{\text{mm}}$ using the linear intercept method to determine grain size of equiaxed ferritic microstructure whereas the results of Gaudet and Reichert [3,5] reported a value of 5.35 MPa $\sqrt{\text{mm}}$ for the constant k_y on the same steel of 06C03Nb for irregular ferrite and bainitic microstructures. A reduction in the characteristic length scale in the microstructure creates a higher density of barriers for the dislocation slip. Therefore, a higher stress is needed for further motion of dislocations resulting in an increase of the yield strength.

5.11.2 The temperature dependence of yield stress

The temperature dependence of the yield stress is relevant as there is a competition between plastic yielding and cleavage fracture, as proposed by Orowan (see Section 2.3.1 of the literature review). In our current work, the yield stresses obtained at different temperatures have been plotted as a function of test temperature in Figure 5.42. For the comparison, the experimental measurements for a Fe-0.15% Ti alloy from Leslie [144] has also been included in the plot. For the 06C03Nb steel, the yield stresses at all

temperatures were measured from tensile tests where as for the Fe-0.15%Ti alloy, the yield stress data below ambient temperature were obtained using compressive tests [144]. It is observed that the yield stress for the 06C03Nb steel cooled at 50°C/s and 5°C/s show little change from ambient temperature to -20°C; and then increase by ~ 35 MPa at -60°C and an additional ~ 300 MPa from -60°C to -196°C. On the other hand, for the Fe-0.15%Ti alloy, an approximately linear portion is observed between -23°C to -196°C where the yield stress is markedly dependent on the temperature i.e. an increase from 80 MPa to 640 MPa is noted. Leslie [144,165] also reported that the temperature dependence of the yielding of as-quenched carbon martensites is less than that of titanium-gettered iron. According to Leslie [144], the very large temperature dependence of the yield stress in iron has been attributed to a combination of three factors: i) carbon and nitrogen interstitials, ii) the temperature dependence the Peierls-Nabarro stress and iii) thermally-activated sessile-glissile transformations of screw dislocations. However, in the current work on bainitic steels, the mechanism for the temperature dependence of the yield stress is not clear although one might speculate that in the temperature range of -60°C to 20°C, the strength is dominated by boundary strengthening which would expect to be nearly athermal, i.e. due to long range internal stresses associated with this mechanism.



Figure 5.42: Temperature dependence of yield stress obtained from our experiments on 06C03Nb steel and as

adapted from Leslie's experiments on Fe-0.15%Ti [144]

5.11.3 Effect of microstructural parameters on Charpy impact behaviour

Charpy impact tests were conducted on notched specimen at high strain rate and the impact energy was used as a measure of the total energy to fracture the sample. This involves the energy required for fracture initiation as well as its propagation through the sample in addition to the energy spent in plastic work if the hammer indents the sample at the strike for ductile samples. As observed in Section 5.9, the Charpy impact behaviour is dependent on the temperature. At low temperature, the fracture process is controlled by brittle failure mechanisms. The fracture process in the transition region is dependent on the local stress state (in particular, the level of triaxiality), i.e. the spatial variation of cleavage vs. ductile fracture observed in the Charpy fracture surfaces described in Section 5.10. At high temperatures, ductile failure is prevalent.

The Charpy impact behaviour is dependent on microstructural features which control nucleation, and propagation of cleavage cracks at low temperature and plasticity around the notch at high temperature, as widely shown by several researchers [127,165,176,185,186,239]. The beneficial effect of grain refinement on the impact toughness of steel is well established [176,178,240,241]. Grain refinement provides higher grain boundary area per unit volume and high angle grain boundaries (HAGB) such as, prior-austenite grain boundaries and variant boundaries with misorientations > 15° retard or deviate the propagation of cleavage crack, thereby increasing the cleavage stress. Low-angle boundaries (LAGB) such as, lath boundaries in coarse bainite, variant boundaries < 15° and dislocation substructures are not thought to be very effective in resisting the cleavage crack propagation [155,242–245]. The presence of M/A constituents and its effect on a propagating crack is not clear. In the current work, the Charpy impact properties are quantified in terms of the lower shelf energy (LSE), ductile-brittle transition temperature (DBTT) and upper shelf energy (USE). Their relations to the microstructure are discussed in the following sections.

5.11.3.1 Cleavage fracture at low temperatures

The lower shelf energy (LSE) is determined by the energy required for cleavage fracture i.e. in the low temperature regime, cleavage fracture is favored over yielding and general plasticity. In Section 5.11.2, it was shown that the yield stress increases with decreasing temperature. However, a Charpy test has two important differences compared to a tensile test. First, the notch leads to higher local tensile stresses and a higher degree of triaxiality. Second, the strain rate is approximately 10⁶ times greater (10⁻³ s⁻¹ for tensile test and 10³ s⁻¹ for Charpy test). Using Tresca's yield criterion and a slip-line field, Knott [176] estimated that the maximum tensile stress (σ_{11}) in the sample due to the notch as shown in Equation 2.15.

The effect of strain rate on the flow stress has been studied by Winkler et al. [145] for an HSLA steel and they found that the flow stress increases from 500 MPa to 650 MPa when the strain rate increases from 10^{-3} to 10^{3} s⁻¹. Using Equation 2.14 and considering the effects of the notch and the strain rate, the following equation gives a simple estimate of the tensile stress under dynamic loading as:

$$\sigma_{modified} = 2.18 x 1.3 \sigma_{y} = 2.84 \sigma_{y}$$
(5.8)

The modified flow stresses for the two conditions after the corrections for the notch and the strain rate are plotted in Figure 5.43 as a function of temperature. The temperature corresponding to 95% brittle failure from our experimental Charpy impact transition plots (see Table 5.6) is also shown in Figure 5.43. If following Cottrell, it is assumed that at this temperature, the cleavage stress is equal to the yield stress, then an estimate of cleavage stress can be made. In our current work, the estimated cleavage stresses are ~1600 MPa and ~2245 MPa for the 06C03Nb steel cooled at 5°C/s and 50°C/s, respectively. These values are relatively insensitive to the fraction brittle chosen, i.e. choosing values between 90% to 99% brittle behaviour only changes the cleavage stress by ± 60 MPa.



Figure 5.43: Modified stresses in notched bar for Charpy tests as estimated from yield stresses from smooth tensile strips

At low temperature, where the cleavage fracture stress is lower than the yield stress, the plastic deformation preceding fracture is very low and the stress ahead of the machined notch root is high enough that multiple microstructural features at the notch-root (a large grain, a M/A particle or an inclusion) can act as initiation sites for cleavage cracks [165,176,246]. For the 03C09Nb steel cooled at 50°C/s, the low temperature yield stresses are not available, however the temperature corresponding to 95% brittle failure for that sample is ~0°C. If it is assumed that the yield stress for this steel is insensitive to temperatures between 0°C and 21°C as in the two other bainitic steels, then the cleavage fracture stress can be estimated to be ~1836 MPa.

The literature suggests that the cleavage fracture stress σ_f can be correlated to the grain size *d* using a Hall-Petch type relation [178,185,186] shown in Equation 2.16. In our present work, the estimated cleavage fracture stresses of the three investigated conditions are plotted as a function of the characteristic length scale (*l*) for the bainitic microstructure in Figure 5.44. The results are consistent with a Hall-Petch type relation and the slope of $\sigma_{fracture}$ vs. length scale is calculated to be 38 MPa.mm^{1/2}.



Figure 5.44: Estimated cleavage fracture stress as function of characteristic length of bainite

Moreover, it is of interest to rationalize the lower shelf energies with the microstructural length scale. The lower shelf energy includes the energies for fracture initiation and propagation. In our present work, an attempt has been made to compare the lower shelf energies of the three investigated microstructures and that of an interstitial free (IF) steel as a function of the characteristic length for the bainitic microstructure and grain size for the IF steel (see Figure 5.45 below). The results are consistent with the linear Hall-Petch type relation.



Figure 5.45: Lower shelf energy as a function of the characteristic length (*l*) for the bainitic microstructure and equiaxed ferrite grain size for the IF steel

Returning to observations on the brittle fracture surfaces of the four microstructures, the fracture surfaces from Charpy impact tests at -196°C are compared in Figure 5.46. The appearance of the fracture surface in terms of the cleavage facets changes drastically from IF steel to the micro-alloyed steels. In the IF steel, only the ferrite grain boundaries act as barrier to the cleavage crack propagation. However, in the microalloyed steels with bainitic microstructure, the brittle cleavage facets correspond to the size of the laths or groups of laths separated by HAGBs [65,155,180,247,248]. Therefore, the effective grain size i.e. the crystal units to restrict crack propagation are much smaller than the ferrite grains in IF steel (grain size of 65 μ m), due to the high density of HAGBs which act as barriers to the propagating cleavage cracks. Moreover, the lower shelf energy is higher in the microalloyed bainitic steel. However, the M/A constituents present in the bainitic microstructure may also act as an obstacle for the propagating cleavage cracks, it is however challenging to separate their individual role from the fracture surfaces and the cleavage facets.

Among the three bainitic microstructure, the 06C03Nb steel cooled at 50°C/s shows a very rough fracture surface with finer cleavage facets than the other two. This brittle fracture behaviour corresponds to a lower shelf energy of 6 J and the characteristic length scale is 0.7 μ m (measured from inverse of HAGBs >15° from EBSD). Further, in Section 5.10.2, the secondary crack path was shown to be more tortuous i.e. every time the crack encounters a HAGB, it must change its direction to remain on the {001} plane. In the other two cases with coarse bainite microstructure, the distance between crack deflection features (i.e. either HAGBs or M/A islands) is much larger. Thus, the cleavage facets are larger, and the LSE is lower.



Figure 5.46: Brittle fracture surface upon Charpy impact testing at -196°C of (a) IF steel (ferrite grain size, d = 65 μm, LSE = 1.6 J), (b) 06C03Nb cooled at 5°C/s (characteristic length, l = 2.4 μm, LSE = 3 J)
(c) 06C03Nb cooled at 50°C/s (characteristic length, l = 0.7 μm), LSE = 6 J) and (d) 03C09Nb cooled at 50°C/s (characteristic length, l = 1.5 μm), LSE = 3.5 J)

5.11.3.2 Ductile to brittle transition temperature

The fracture process in the ductile-brittle transition (DBTT) region can be viewed as a competition between ductile fracture and brittle failure. An attempt has been made to correlate the microstructural unit to the DBTT evaluated in the present work. The effect of ferrite grain size on the DBTT of low-carbon ferrite-pearlite steels has been proposed as [185,249–251]:

$$DBTT = A - Kd^{-\frac{1}{2}}$$
(5.9)

where, *A* and *K* are constants for any particular grade of steel and *d* is the grain size measured from equiaxed ferrite grains. For the complex non-equiaxed microstructures, researchers [65,154,155,240,243,252] have defined the concept of crystallographic unit or effective grain size, as determined from EBSD. In the present study, instead of *d*, the characteristic length (*l*) as defined in Section 5.6.4, is used which includes the blockage of slip by high angle boundaries and M/A islands and is plotted in Figure 5.47a. DBTT has also been plotted as a function of the fraction of M/A constituents in Figure 5.47b.



Figure 5.47: Ductile-brittle transition temperature (DBTT) correlated to (a) characteristic length of bainite microstructure and (b) M/A fraction

It can be observed that neither of theses approaches gives a particularly satisfying result. The DBTT is the lowest among the three cases for a low characteristic length scale (0.7 μ m) and low M/A fraction (2.8%). The DBTT is observed to be better for a high characteristic length scale (2.4 μ m) and high M/A (6.4%) than the microstructure with medium characteristic length scale (1.5 μ m) and relatively low M/A (3.7%). Thus, it appears that the fine distribution of high fraction of M/A constituents can also play key role in controlling the cleavage vs. ductile failure along with the HAGBs. Predicting DBTT from the microstructural features in these bainitic steels remains a challenging task and is suggested for future work.

5.11.3.3 Upper shelf energy region

As described in the literature review, ductile fracture involves void nucleation, void growth and void coalescence. It is generally assumed in highly ductile materials like the current case that the void growth stage consumes the maximum energy. In the upper shelf energy (USE) region of the three investigated microstructures, fracture occurs completely in a ductile mode. Vodopivec [253] calculated the plastic zone size ahead of the Charpy notch-tip (root radius, r = 0.2 mm) at room temperature (+20 °C, where, 100 % ductile fracture has been found) for a 0.17 wt.% C steel (other elements, 0.32 Si, 1.28 Mn, 0.02 P, 0.01 S, 0.045 Al, all in wt.%), with irregular ferrite microstructure having a grain size of 3.5 µm, to be in the order of 0.62 – 0.76 mm. The plastic zone in our microalloyed steels (expected to be close to that calculated by Vodopivec [253] due to similar order of length scale), therefore, will sample a large number of fine bainite or coarse bainite grains, but the tensile stress within that zone, however, will remain insufficient to initiate cleavage fracture. As a result, the failure will occur in a ductile mode (similar to the room temperature tensile test). The fractographs shown in Section 5.10 corresponding to the USE region shows extensive plastic deformation from the surface appearance and presence of micro-voids.

The plane strain plastic zone radius can be correlated to the yield strength of these three characteristic microstructures according to the following equation:

$$r_p = \frac{1}{2\pi} \left(\frac{K}{\sigma_y}\right)^2 \tag{5.10}$$

where, the plastic zone radius is given by r_p , yield stress is denoted by σ_y and the stress intensity factor K [184]. The upper shelf energy i.e. the energy to propagate ductile failure is proportional to the volume of the material. In the current work, it is assumed that there is a plastic cylinder in front of the propagating crack (i.e. no correction has been made for surface effects). The radius of the cylinder is assumed to be proportional to the square of the plastic zone. Considering Equation 5.12, this suggests that the USE would be proportional to the inverse of the yield stress to the 4th power. Figure 5.48 shows that this simple analysis gives a reasonable description of the experimental results. The yield stress of the 06C03Nb steel cooled at 50°C/s is the highest and the upper shelf energy is found to be the lowest among the three. Similarly, the highest upper shelf energy is observed in the microstructure with lowest yield stress, i.e. in the case of 06C03Nb steel cooled at 5°C/s. The 03C09Nb steel cooled at 50°C/s has an intermediate yield stress as well as upper shelf energy among the three cases.



Figure 5.48: Experimental upper shelf energy as a function of the experimental yield strength for the three

investigated microstructures

5.12 Summary: Relevance to weld heat affected zones

The microstructure evolution after 1st thermal cycle in this study is a representation of the region next to the fusion line of a weld, commonly known as coarse grain heat affected zone (CGHAZ). This region reaches a very high temperature during weld pass resulting into dissolution of Nb(C,N) microalloying precipitates and austenite grain growth. The heat input of the weld thermal cycle controls the cooling rate which in turn controls the transformation temperature of austenite decomposition and therefore the final microstructure. A very high heat input (i.e. in submerged arc welding) results in a lower cooling rate (\sim 5°C/s) whereas a low heat input (i.e. in gas metal arc welding) results in a higher cooling rate (~50°C/s). This is confirmed from weld trial measurements by Gaudet [3] on GMAW and Kulakov [4,89] on SAW. The results of our microstructure evolution study conclude that in SAW, a higher heat input i.e. a slow cooling rate leads to an evolution of coarse bainite microstructure with a low fraction of high angle grain boundaries with considerable amount of M/A constituents. This microstructure has poor tensile and impact properties compared to one produced using GMAW where the heat input is lower (i.e. higher cooling rates) and a fine bainite microstructure is produced. The fine bainite laths in the samples with high cooling rates are separated by a high density of high angle grain boundaries which act as a barrier for dislocation motion and crack propagation, thereby improving both the tensile and impact properties in 06C03Nb steel. The presence of 6.5% M/A in the coarse bainite microstructure may also have resulted in crack deflection thereby improving its impact properties. The tensile and impact properties of a steel with half the carbon content of the previous steel was also cooled at 50°C/s to simulate a CGHAZ microstructure of a GMAW weld. However, lowering the carbon content of the steel by 50% (with thrice the amount of Nb) leads to a higher transformation temperature by 20°C leading to a bainite microstructure with laths coarser than the fine bainite microstructure of the 06C03Nb steel and low M/A fraction (~3.5%). The impact properties are the worst for this microstructure among the three and can be attributed towards the low density of high angle boundaries as well as low fraction of M/A, both of which act as barrier to the propagation of cleavage cracks.

Chapter 6: Intercritical Annealing of the Decomposition Products from Coarse Grain Austenite: Experimental Results and Discussion

6.1 Introduction

In Chapter 5, it was shown that austenite decomposition products with different morphologies can form from the same austenite grain size by employing different cooling rates or a different steel chemistry. This chapter considers a systematic study of microstructure evolution and mechanical properties for intercritical annealing of three different initial microstructures which were described in Chapter 5. Intercritical austenite fractions of 5 - 20% were studied in terms of their: i) microstructures, ii) tensile stress-strain responses and iii) ductile-brittle transition temperatures. The final microstructures after intercritical annealing is relevant to the intercritically reheated coarse grain heat affected zone (ICCGHAZ) in linepipe steels. The results from 06C03Nb steel will be discussed in the first part of Chapter 6 and they will then be compared to that of the 03C09Nb steel later in this Chapter.

6.2 Kinetics of austenite formation upon intercritical annealing

The kinetics of austenite formation in the 06C03Nb steel during intercritical annealing were investigated by experiments where the samples were heated into the intercritical region at a rate of 50°C/s, held isothermally for 3-5 minutes at various intercritical temperatures, followed by rapid heating to 1050°C at 100°C/s to complete austenite formation, as shown schematically in **Figure 4.11**. The 1st cycle (as described in Chapter 5) was conducted to produce the initial microstructure for intercritical annealing. The progression of the phase transformation was characterized by change in width using a dilatometer, attached onto the sample during the heat treatment cycle. The volume fraction of the austenite phase is obtained by analyzing dilatometric data using the Kop method [95], as explained in Section **4.6**.

The temperatures for the isothermal holding steps were designed such that they would result in the formation of 5 - 20% intercritical austenite with a good control of the final fraction of austenite. The results for the austenite fraction during heating and holding of the 06C03Nb steel cooled at 50°C/s forming a fine

bainitic microstructure are shown in Figure 6.1. The time '0' seconds implies the beginning of isothermal holding at a given temperature. In Figure 6.1, it is observed that for every test temperature, there is some austenite formed during heating, i.e. there is a non-zero fraction of austenite at t = 0 s. The fraction of austenite formed prior to reaching the isothermal hold temperature depends on the temperature. For example, when the isothermal hold temperature increases from 710°C to 760°C, the amount of austenite transformed during heating increases from 2.5% to 8%. The transformation rate is fast at the beginning of the hold and decreases with time. As expected, the fraction of intercritical austenite is larger at higher temperatures and longer holding times. Note that the equilibrium austenite start (Ae₁) and finish (Ae₃) temperature for this 06C03Nb steel were calculated to be 643°C and 823°C using ThermoCalc TCFE7 database. The equilibrium austenite content at 710, 725 and 760°C are 14.2%, 17.5% and 28%, respectively.



Figure 6.1: Kinetics of intercritical austenite formation at different temperature upon isothermal holding from an initial fine bainite microstructure of 06C03Nb steel (Note that at 710°C, the specimen was held for 3 mins before heating to 1050°C, the data during heating to 1050°C is not shown.)

Based on these experiments, two temperatures were chosen: 725°C and 760°C to analyze austenite formation kinetics for the fine and coarse bainite microstructures produced in the first cycle. The results are compared in Figure 6.2. The kinetics of austenite formation are similar in both cases. This is consistent with results reported in the literature on the effect of different bainitic microstructures on austenite formation where little impact was observed [71,81,88,254,255]. Upon heating, it has been proposed that austenite grows from the carbon enriched retained austenite island [71].

Based on these experiments, a hold time of 60 s was chosen (i.e. an easy, repeatable thermal treatment) at 710°C, 725°C and 760°C to produce austenite fractions of approximately 5%, 10% and 20%, respectively. Note that the fraction of retained austenite present in the initial microstructure was added to the fraction obtained from dilation measurements and the final fractions are presented in Table 6.1.



Figure 6.2: Effect of initial microstructures on kinetics of austenite formation upon intercritical annealing of 06C03Nb steel which was cooled at 50°C/s, fine bainite (LB) and 5°C/s, coarse bainite (UB)

Initial microstructure	Isothermal temperature for 60 s holding (°C)	Retained austenite (RA) in initial microstructure (%)	Intercritical austenite (IA) fraction from Kop method (%)	Total Austenite (RA +IA) expected (%)
Coarse bainite by	725	1.2 ± 0.6	11.0 ± 2.1	12.2 ± 2.2
cooling at 5°C/s	760	1.2 ± 0.6	20.1 ± 2.3	21.3 ± 2.4
	710	0.1 ± 0.02	5.5 ± 1.9	5.6 ± 1.9
Fine bainite by cooling at 50°C/s	725	0.1 ± 0.02	11.6 ± 1.7	11.7 ± 1.7
	760	0.1 ± 0.02	20.7 ± 2.1	20.8 ± 2.1

Table 6.1: Summary of austenite fraction in the microstructure upon intercritical annealing of 06C03Nb steel

Mean and errors in dilation data are reported from 15 tests for each condition.

6.3 Thermal cycles to produce intercritical austenite

Figure 6.3 shows a schematic of the thermal cycle employed to form microstructures with 6%, 12% and 21% intercritical austenite for characterization and use as samples for subsequent tensile and Charpy impact tests. A heating rate of 50°C/s was employed to an intercritical temperature of 725°C and 760°C, the sample was held for 60 s followed by cooling at a rate of ~50°C/s. For the fine bainite initial structure, an additional condition of isothermal intercritical annealing at 710°C was employed to obtain 6% austenite during intercritical annealing.



Figure 6.3: Schematic of the complete thermal cycle used to produce 6%, 12% and 21% M/A in the final microstructure from initial (a) 06C03CNb steel cooled at 50°C/s and (b) 06C03CNb steel cooled at 5°C/s

6.3.1 Intercritical austenite formation

Examples of the dilation measurements during intercritical annealing of the 06C03Nb steel with a fine bainite initial microstructures are shown in Figure 6.4 at 725°C and 760°C. Complete austenite transformation did not occur in these tests, therefore the $\Delta W_{100\%}$ was not available providing a challenge to calculate the fraction transformed from these tests. Therefore, the average net change in width (ΔW) during isothermal holding at 725°C and 760°C after 60 s at the intercritical temperatures were compared to the dilation measurements after 60 s in the previous thermal cycles and were found to be consistent. The standard deviations from mean in the fraction transformed after intercritical annealing for 60 s were calculated from these 15 tests and reported in Table 6.1.



Figure 6.4: Dilatometry results measuring relative change in width (ΔW/W₀) during intercritical annealing of 06C03Nb steel with a fine initial bainite structure at (a) 725°C and (b) 760°C.

6.3.2 Intercritical austenite decomposition

In order to check for the possible reversion of austenite during the cooling, the dilation data during cooling was examined. Figure 6.5 shows the relative change in width recorded using dilatometer during cooling at 50°C/s after intercritical annealing i.e. from the fine bainite - austenite microstructure. It is important to keep in mind that 80 - 90 % of the microstructure is bainite, and only 10 - 20 % austenite is

available for phase transformation upon cooling. Therefore, the slope during cooling represents thermal contraction coefficient of a dual phase ferrite-austenite microstructure at high temperature. The slope of the mixture (CTE) can be theoretically estimated using a simple rule of mixture i.e.:

$$CTE = f_{\alpha}CTE_{\alpha} + f_{\gamma}CTE_{\gamma} \tag{6.1}$$

where, f_{α} and f_{γ} are the fraction of bainite and austenite and $CTE_{\alpha} = 16 \times 10^{-6} \,^{\circ}C^{-1}$ is the thermal expansion/contraction coefficient of ferrite and $CTE_{\gamma} = 23 \times 10^{-6} \,^{\circ}C^{-1}$ is the thermal expansion/contraction coefficient of austenite [93,95]. This approach estimates the CTE of the mixture of bainite – 12% austenite formed at 725°C to be 16.8 x 10⁻⁶ °C⁻¹ and 17.5 x 10⁻⁶ °C⁻¹ for the mixture of bainite – 21% austenite. The experimental measurement of the slope for fine bainite – 12% austenite yields the CTE to be 16.4 x 10⁻⁶ °C⁻¹ which is very close to the estimate. No significant deviation from the coefficient of thermal contraction was observed in the temperature range between 650°C to 250°C in the case of fine bainite – 12% austenite formed at 725°C. This suggests that there is no austenite to ferrite (or bainite) reverse transformation upon cooling. For the case of ~21% austenite, the coefficient of thermal contraction is measured to be 17.9 x 10⁻⁶ °C⁻¹ from the rule of mixture calculation. Below 500°C, a deviation is observed starting at ~450°C. This could possibly be attributed to the austenite to martensite phase transformation. The results are similar for coarse bainite initial microstructure, i.e. no change in slope was observed during cooling to 500°C when cooled after intercritical annealing. Therefore, for the final microstructure, it is assumed that all the austenite will transform to M/A constituents upon cooling at 50°C/s to room temperature.


Figure 6.5: Transformation kinetics during cooling at 50°C/s after intercritical annealing of 06C03Nb steel at (a) 725°C forming ~12% austenite and (b) 760°C forming ~21% austenite from fine bainite initial microstructure

6.3.3 Summary of thermal cycles

The thermal cycles and corresponding dilation result show that a combination of two thermal cycles (i.e. the austenitizing treatment at 1300°C followed by cooling at 5°C/s and 50°C/s and intercritical annealing treatment at 725°C and 760°C) produced two bainitic matrices, (i.e. fine bainite and coarse bainite) with ~12% and ~21% M/A constituents in the final microstructure in both the matrix and an additional case of ~6% M/A in the fine bainite matrix. The characterization of the microstructure is described in the next section.

6.4 Microstructure characterization

6.4.1 Fine bainite + intercritical annealing: 06C03Nb steel

LePera's reagent was used to characterize the microstructures where the martensite appears bright white upon observation with an optical microscope [125]. The LePera etched microstructures as observed under optical microscope are shown in Figure 6.6. The microstructure of the fine bainite before intercritical annealing shows bright white M/A islands arranged in a necklace fashion along the prior austenite grain boundaries and some M/A inside the prior austenite grains. Note that the fine bainite microstructure obtained by cooling at 50°C/s in the first thermal cycle was measured to have ~ 2.8 % M/A constituents of which ~ 0.1 % is retained austenite (see Section **5.6.2**). Turning to the intercritically annealed samples, the fraction of martensite increases with increasing temperature as expected. Qualitatively, it appears that the fraction of the prior austenite grain boundary covered by M/A particles increases from Figure 6.6b (i.e. 6% M/A) to Figure 6.6c (i.e. 12% M/A). In Figure 6.6d (i.e. 21% M/A) the M/A particles appear to cover the majority of the prior austenite grain boundaries but have also increased in size.



Figure 6.6: LePera etched optical micrographs of (a) fine bainite and intercritically annealed 06C03Nb steel at (b) 710°C (c) 725°C and (d) 760°C for 60s to obtain 6%, 12%, 21% M/A in the final microstructure

The samples were also characterized by EBSD as shown in Figure 6.7. The inverse pole figure (IPF) maps of the ferrite are shown in Figure 6.7a,d,g and that of austenite in Figure 6.7b,e,h. The image quality maps of the same area for the ferrite are shown in Figure 6.7c,f,i.



Figure 6.7: EBSD maps showing IPF of ferrite (a,d,g), austenite (b,e,h) and image quality maps (c,f,i) upon intercritical annealing of fine bainite of 06C03Nb forming (a,b,c) 6% M/A , (d,e,f) 12% M/A and (g,h,i) 21% M/A (Note that 50 nm step size is used in all cases)

In these cases, it was possible to measure the amount of retained austenite and this data is reported in Table 6.2. The retained austenite was measured to be 0.3% and 0.5% for 12% M/A and 21% M/A microstructures, i.e. comprising only ~2.5% of the total M/A. The martensite regions are usually known to have low image quality and provide poor index quality as reported in literature [5,107] as well as observed in our results in Section **5.6.2**. However, in the intercritically annealed microstructures with 6, 12 and 21% M/A, the image quality of the martensite islands was observed to improve with increasing amount of M/A as shown in Figure 6.7c, f, i. The martensite islands were indexed as ferrite with good quality of indexing as evident from Figure 6.7a, d, g. The quality of indexing of martensite improves with increase in martensite from 6 % to 21 % as observed from the decrease in randomly indexed points in Figure 6.7g and relatively high image quality in Figure 6.7i for the 21% M/A condition. Therefore, it is challenging in these cases to find a suitable criterion to distinguish the martensite from the bainite matrix for further analysis of M/A using EBSD.

Further, it was not possible to find a unique threshold value to differentiate martensite from bainite in the LePera tinted samples due to sensitivity of the area fraction on the thresholding value, as was discussed in Section **4.8.2**. Therefore, the dilation measurements were deemed to be the most reliable method and have been used to characterize the fraction of M/A assuming that all the intercritical austenite is transformed to martensite upon cooling (see Appendix B for the overlapped images). On the other hand, the size and fraction of the M/A could be analyzed from the LePera etched microstructures by choosing a threshold which matches the M/A fraction to the results from dilatometry (described in methodology Section **4.8.2**), as shown in Figure 6.8. It was challenging to find a suitable parameter to threshold and further separate the martensite on PAGBs from the ones inside. Thus, the M/A inside the PAGs were manually removed for all different cases and the final thresholded images showing the M/A constituents at prior austenite grain are shown in Figure 6.9. These images were analyzed to quantify the fraction of M/A at the prior austenite boundaries and the minor axis or width of the particles are reported as the size. The results are summarized in Table 6.2.



40 µm

Figure 6.8: Thresholded image using fraction from dilatometry for fine bainite after intercritical annealing 06C03Nb at (a,b) 710°C, (c,d) 725°C and (e,f) 760°C for 60 s forming 6%, 12% and 21% total M/A in the

microstructure 147



Figure 6.9: Thresholded image to highlight grain boundary M/A constituents for fine bainite after intercritical annealing 06C03Nb steelat (a) 710°C, (b) 725°C and (c) 760°C for 60 s forming 6%, 12% and

21% total M/A in the microstructure

 Table 6.2: Microstructure characterization of fine bainite 06C03Nb steel before and after intercritical

Condition	Total M/A fraction (from dilation) (%)	Retained austenite from EBSD (%)	Fraction of M/A on PAGBs (%)	Fraction of M/A inside PAGs (%)	PAGB covered by M/A (%)	Size of GB M/A (µm)	Aspect ratio of M/A
Fine bainite before intercritical annealing (IA)	$2.8 \pm 0.5*$	0.1 ± 0.02	NA	NA	NA	$0.5 \pm 0.2*$	1.4 ± 0.8
IA 710°C-60s	5.6 ± 1.9	2.1 ± 0.4	3.8	1.8	62	1.1 ± 0.5	2.1 ± 1.9
IA 725°C-60s	11.7 ± 1.7	0.3 ± 0.1	7.8	3.9	81	1.9 ± 0.8	2.8 ± 1.7
IA 760°C-60s	20.8 ± 2.1	0.5 ± 0.1	16.8	4.3	91	3.8 ± 1.4	2.3 ± 1.0

M/A fraction before IA measured from EBSD and the size represents the EQAD (see Section* **5.6.2*) Mean and standard deviations are reported from five images in each case with ~3000 M/A constituents.*

The characterization of the thresholded image shows that the average fraction of M/A on the prior austenite grain boundaries (PAGB) increases from 3.8 % to 7.8 % to 16.8 % when the total M/A constituents in the microstructure increases from 6 % to 12 % to 21 %. However, the M/A inside the prior austenite grains only increases to 4.3% maximum in the 21% M/A sample from 2.9 % in the initial fine bainite

microstructure. The M/A constituents cover 62% of the PAGBs when the total M/A is 6 %. However, as the M/A fraction increases to 12 and 21% M/A, the fraction of the PAGBs covered by intercritical M/A is 81% and 91% respectively. The size/width of these intercritical M/A constituents formed at the PAGBs were measured to increase from 1.1 μ m to 1.9 μ m to 3.8 μ m with an increase in the fraction of total M/A constituents from 6 to 12 to 21 % and the corresponding aspect ratio changes from 2.1 to 2.8 to 2.3. This change in morphology of M/A signifies that the M/A particles become blocky and more rounded in 21% case compared to the more elongated shape in the 12% case.

EBSD-KAM analysis was performed on the intercritically annealed fine bainite matrix to quantify any change in the local misorientations of the matrix microstructure due to annealing, following the same methodology and step size of 50 nm reported in Section 5.6.5 of the previous chapter. The KAM maps of the three cases: i.e. intercritically annealed fine bainite with 6, 12 and 21% M/A are presented in Figure 6.10.

The black regions in Figure 6.10 are the austenite regions and are not considered for the KAM analysis. Compared to Figure 6.7(c,f,i), it is observed that the regions with poor image quality (blue and green) have the highest KAM values, i.e. close to 5° indicating a high degree of misorientations and dislocation density, presumably these are the martensite regions. The KAM distributions of the overall dataset are plotted in Figure 6.10d. A lognormal fit was applied to the KAM distributions. A small peak is observed close to 5° in the 12% and 21% M/A samples. However, the primary misorientation peaks are at < 2°. The mean KAM values of 0.68°, 0.69°, 0.62° and 0.55° were recorded for the fine bainite before annealing and after annealing at 710°C, 725°C and 760°C forming 6, 12 and 21% M/A in the region from 0-3° such that the martensite regions can be eliminated. A significant decrease in KAM value from 0.68° in as-austenitised sample to 0.55° was observed in the 21% M/A sample intercritically annealed at 760°C. A possible explanation for the decrease in the mean KAM could be that there is a decrease in the dislocation density due to tempering of fine bainite during the 60 s hold at 725°C and 760°C.



Figure 6.10: EBSD-KAM maps showing intercritically annealed fine bainite forming (a) 6% M/A , (b) 12%
M/A, (c) 21% M/A in 06C03Nb steel and (d) KAM distribution and fitted log normal distribution (shown in lines). Black regions are the points indexed as austenite.

(Note that 50 nm step size is used in all cases covering 150 nm in a square grid using 3rd nearest neighbor)

6.4.2 Coarse bainite + intercritical annealing: 06C03Nb steel

The coarse bainite microstructure obtained in the first thermal cycle by cooling 06C03Nb steel at 5° C/s has ~ 6.5 % M/A constituents of which ~ 1.2 % is retained austenite (see Section **5.6.2**). The optical microscope images of the initial state and after intercritical annealing for LePera etched samples are shown in Figure 6.11. Figure 6.11a shows that before intercritical annealing, the M/A particles are randomly distributed in the coarse bainitic microstructure. However, upon intercritical annealing at 725°C for 60 s,

new austenite preferentially nucleates and grows at the prior austenite grain boundaries transforming to martensite (with some retained austenite) upon cooling as shown in Figure 6.11b. Increasing the intercritical temperature to 760°C increases the total fraction and size of these grain boundary M/A constituents, as shown in Figure 6.11c, similar to what has been observed in fine bainite upon intercritical annealing as shown in Section 6.4.1.



Figure 6.11: LePera etched optical images of 06C03Nb (a) coarse bainite after 1st thermal cycle; intercritically annealed at (b) 725°C and (c) 760°C for 60s to obtain 12%, 21% M/A in the final

microstructure

In order to further analyze the evolution of austenite formation from coarse bainite, two additional experiments were conducted where the samples were quenched after 1 s and 20 s at 725°C. Optical images of the LePera etched microstructures are shown in Figure 6.12. Measuring the M/A constituents in the intermediate stages, therefore, can provide information about the intercritical austenite formation and growth. Observations reveal that holding in 725°C for 1 s leads to nucleation of new austenite in the prior austenite grain boundaries which grow larger upon increasing the holding time to 20 s along with further nucleation. Eventually upon 60 s holding, the size and fraction of austenite further increases. However, the amount of M/A constituents inside the prior austenite grains appear to remain constant.



Figure 6.12: LePera etched optical images of 06C03Nb steel showing (a) coarse bainite before intercritical annealing at 725°C for (b) 1 s (c) 20 s and (d) 60 s

Image analysis was performed by thresholding these images to match the dilation measurements and are shown in Figure 6.13. Then, the M/A constituents inside the prior austenite grain boundaries were manually removed in order to quantify the volume fraction, size, aspect ratio of the M/A constituents at the grain boundaries for all different cases. The thresholded images showing the M/A constituents at prior austenite grain boundaries are shown in Figure 6.14 and the quantitative results of fraction and aspect ratio of M/A constituents are reported in Table 6.3. The size of these intercritical M/A formed at the grain boundaries were calculated following the methodology described in Section **4.8.2** and reported in Table 6.3. Note that the retained austenite fraction reported in the table was calculated from EBSD.

It is observed that the fraction of retained austenite in these microstructures are ~0.7% as measured from EBSD which indicates that 95% of the intercritical M/A are martensite. The average fraction of M/A at the PAGB increases from 8.2% to 16.4% when the total fraction increases from 12% to 21%, however the fraction of M/A inside the prior austenite grains also increasing the grain boundary coverage by M/A from 85% to 90%. The size of the grain boundary M/A increases from 2.1 μ m to 4.6 μ m with an increase in the austenite formed i.e. when total M/A increases from 12 to 21%, the corresponding increase is aspect ratio is from 2.8 to 3.1. Note that detailed KAM analysis was not conducted on these samples as the initial coarse bainite structure had a lower KAM value than that of the initial fine bainite (0.62 vs. 0.68) indicating low degree of internal misorientations in the initial coarse bainite sample (see Section **5.6.5**). Therefore, intercritical annealing at the same temperature is expected to produce some changes in the internal misorientations of the coarse bainite, may be not as high as that of fine bainite.



Figure 6.13: Thresholded image (by ImageJ) using fraction dilatometry coarse bainite after intercritical annealing at (a,b) 725°C for 1 s, (c,d) 725°C for 60 s and (e,f) 760°C for 60 s forming 9%, 12% and 21% M/A in final microstructure



Figure 6.14: Thresholded image to highlight grain boundary M/A constituents for coarse bainite after intercritical annealing at (a) 725°C for 1 s, (c,d) 725°C for 60 s and (e,f) 760°C for 60 s forming 9%, 12% and

21% total M/A in the microstructure

 Table 6.3: Microstructure characterization of coarse bainite of 06C03Nb steel before and after intercritical annealing (IA)

Condition	Total M/A fraction (from dilation) (%)	Retained Austenite from EBSD (%)	Fraction of M/A on PAGBs (%)	Fraction of M/A inside PAGs (%)	PAGB covered by M/A (%)	Size of GB M/A (µm)	Aspect ratio of GB M/A
Coarse Bainite before intercritical annealing	$6.4\pm0.8*$	1.2 ± 0.6	NA	NA	NA	$0.9 \pm 0.5*$	1.3 ± 0.5
IA 725°C-1 s	9.1 ± 1.5	NA	5.9	3.2	74	1.6 ± 0.8	3.1 ± 1.2
IA 725°C-20 s	10.9 ± 1.8	NA	6.4	4.5	81	1.8 ± 0.6	3.2 ± 1.1
IA 725°C-60 s	12.2 ± 2.1	0.6 ± 0.2	8.2	4.0	85	2.1 ± 0.9	2.8 ± 1.1
IA 760°C-60 s	21.3 ± 2.3	0.7 ± 0.1	16.4	4.9	90	4.6 ± 2.7	3.1 ± 2.3

*M/A fraction measured using EBSD and the size represents the EQAD

Mean and standard deviations are reported from five images in each case with ~3000 M/A constituents.

6.4.3 Summary of microstructural analysis: 06C03Nb steel

The initial conditions studied here (fine and coarse bainite) were designed to produce microstructures representative of GMAW (fine bainite, cooling rate of ~ 50°C/s [3]) and SAW (coarse bainite, cooling rate of ~5°C/s [37]) as discussed in Section 2.1.3.3 of the literature review. After

intercritical annealing (i.e. from the 2nd pass of multi-pass weld) and rapid cooling, a necklace structure of M/A constituents are produced, primarily along the prior austenite grain boundaries.

The distribution of M/A constituents in the microstructure, i.e. the fraction of M/A located inside the prior austenite grains (PAGs) or at the prior austenite grain boundaries (PAGBs) are plotted in Figure 6.15. It shows that the M/A constituents at the PAGBs increases with increase in total fraction of intercritical M/A, however there is little change in the fraction of M/A inside the PAGs. The coverage of the prior austenite grain boundaries by M/A constituents for different fractions of inter-critical M/A are summarized in the histogram shown in Figure 6.16. It shows that with increasing degree of intercritical annealing, the fraction of M/A constituents increases forming a nearly continuous necklace at the prior austenite grain boundary for the 12% and 21% M/A in the microstructure. The size of the M/A constituents at the prior austenite grain boundaries also increase with increase in the fraction of M/A, as shown in Figure 6.17. Finally, in both the cases of coarse and fine bainite intercritically annealed structures, the M/A constituents consists of \geq 95% martensite and \leq 5% retained austenite. In the next section, the mechanical properties, i.e. the tensile and Charpy impact behaviour of the intercritically annealed samples will be presented as a function of the fraction of M/A.



Figure 6.15: Distribution of M/A constituents before and after inter-critical annealing of (a) fine bainite and

(b) coarse bainite initial state of 06C03Nb steel 156



Figure 6.16: Connectivity of intercritical M/A constituents at prior austenite grain boundaries in 06C03Nb



Figure 6.17: Change in the size of M/A constituents with increasing fraction of intercritical M/A (for bainite before intercritical annealing, size represent EQAD from EBSD and after intercritical annealing, the size represents the width of IA M/A)) in 06C03Nb steel

6.5 Tensile behaviour upon intercritical annealing

In the previous section it was shown that the intercritical annealing treatments in the Gleeble produced microstructures with 12 and 21% M/A constituents in the final microstructure with fine bainite and coarse bainite initial structure and an additional case of 6% M/A in the fine bainite microstructure in 06C03Nb steel. Tensile testing was conducted on these samples at ambient temperature using sub-size flat tensile specimens machined from the Gleeble samples. Selected cases were also tested at sub-zero temperatures (-20°C, -60°C, -196°C). The following sections will show the results of tensile tests on the intercritically annealed samples with fine bainite and coarse bainite initial structure.

6.5.1 Fine bainite + intercritical annealing: 06C03Nb steel

Samples with 6, 12 and 21% M/A constituents were chosen for tensile tests. Figure 6.18 shows the results from the tensile tests conducted at ambient temperature. The results for the yield stress (YS), ultimate tensile stress (UTS) and uniform elongation are summarized in Table 6.4.





06C03Nb steel for 60 s at 710°C, 725°C and 760°C producing 6%, 12% and 21% M/A

	0.2% YS (MPa)	UTS (MPa)	Uniform elongation (%)	YS/UTS	$d\theta/d\sigma_{true}$	True stress at failure (MPa)	True strain at failure
Fine Bainite (50°C/s)	682 ± 8	808 ± 7	3 ± 0.5	0.84	-106	1970 ± 40	1.40 ± 0.20
IA-6% M/A	738 ± 5	834 ± 8	8 ± 0.5	0.88	-26	2215 ± 80	1.55 ± 0.18
IA-12% M/A	694 ± 6	868 ± 5	7.5 ± 0.5	0.80	-34	1540 ± 20	0.95 ± 0.15
IA-21% M/A	698 ± 9	893 ± 4	5 ± 0.5	0.78	-48	1515 ± 25	0.75 ± 0.15

Table 6.4: Tensile properties of fine bainite followed by intercritical annealing 06C03Nb steel

Mean and average of the deviations from mean value in tensile results were calculated from three repeat tests for each condition, Slope of work hardening with stress = $d\theta/d\sigma_{true}$ where $\theta = d\sigma_{true}/d\varepsilon$

It can be observed that the yield stress is similar for the initial fine bainite sample and the samples with 12 and 21% M/A with values between 680 - 700 MPa. The sample with 6% M/A has a higher yield stress of 738 MPa. On the other hand, the ultimate tensile stress increases from 808 MPa to 893 MPa as the fraction of M/A increases to 21%. Finally, the largest effect of the fraction of M/A is on the uniform elongation increases from 3% to 8% as the intercritical M/A is increased to 6% and then decreases to 7.5% and 5% for 12 and 21% M/A, respectively. The yield strength to UTS ratio (which is a measure of the margin of safety against failure by plastic collapse and is frequently quoted by American Petroleum Institute (API)), is observed to be the highest (~0.88) for the intercritically annealed 12 and 21% M/A have YS/TS ratio of 0.8 and 0.78, respectively.

The true stress – true strain data was calculated up until necking. Figure 6.19 shows the work hardening response, $d\sigma/d\epsilon$, from beginning of the tensile test until necking as a function of true strain. It is observed that the $d\sigma/d\epsilon$ is equal to the elastic modulus of this steel, i.e. ~200 GPa in the elastic region. The elastic-plastic transition region is marked by a steep decline in the slope, $d\sigma/d\epsilon$ and is followed by a gradual decrease in slope in the plastic region for all three conditions. For the three intercritically annealed samples with 6, 12 and 21% M/A, the transition from elasto-plastic to plastic region is marked by a rapid change in slope for 6% M/A and a much gradual change in slope for 21% M/A, a typical behaviour for dual phase steel with high fraction of M/A (> 20%), as reported in the literature [160,163,256].



Figure 6.19: Analysis of tensile test data of 06C03Nb steel showing the room temperature work hardening in elastic, elasto-plastic and plastic region until necking

The work hardening response (θ) has also been plotted as a function of true strain together with the true stress – true strain curves in Figure 6.20 to test if the Considère criterion for localization is satisfied. As can be seen from Figure 6.20, this condition was satisfied for all conditions. The true uniform strain increases as the M/A fraction increases, reaches a maximum at 6 % M/A and then decreases for 12% and 21% M/A. To further analyze the work hardening behaviour, the work hardening rate (θ) was also plotted as a function of true stress in Figure 6.21. The slope $d\theta/d\sigma$ was calculated by fitting a straight line between stress values of 800 and 2000 MPa. This value represents the rate of decrease of the work hardening rate in the plastic regime and is reported in Table 6.4. The rate of decrease of work-hardening rate is -106 MPa for fine bainite prior inter-critical annealing, increases to -26 MPa upon intercritical annealing at 710°C for 60 s. It is found to decrease from -26 MPa to -34 MPa to -48 MPa as the fraction of M/A constituents increases from 6 to 12 to 21 %. As also observed in Table 6.4, the 6 % M/A steel shows the highest YS/UTS ratio, therefore the lowest work hardening between yielding and necking. The intercritically annealed 12 and 21 % M/A has 0.8 and 0.78 YS/UTS ratio respectively, signifying that the work hardening in the plastic region increases with increase in M/A.



Figure 6.20: Considère analysis of tensile tests data at room temperature showing true stress – true strain data and strain hardening response of 06C03Nb steel



Figure 6.21: Work hardening response at the plastic region of the fine bainite microstructure before and after intercritical annealing (IA) of 06C03Nb steel

The relationship between the change in the decrease of work hardening with stress and the microstructure is complex, but some general comments can be made. The fine bainite has a high dislocation density and ~2.5 % M/A i.e. limited ability to work hardening and a high rate of decrease of θ with σ . With the increase in the fraction of M/A, there are two competing effects: i) load transfer to the harder M/A phase and ii) static recovery in the bainite microstructure (see Section 6.4.1). The combination of these two effects results in an increase in work hardening capacity and the commensurate increase in uniform elongation in the intercritically annealed microstructure with respect to the initial fine bainite structure. However, with the increase in intercritical M/A from 6 to 12 to 21%, the work hardening ability and the uniform elongation decreases. This will be discussed in detail in Section 6.5.4 with respect to the stress in martensite.

The true fracture stress and strain were calculated from the projected area of the fracture surface from the broken tensile specimen. It was then assumed that the linear hardening rate occurred between the necking point and the fracture point. Figure 6.22 shows the plots of the complete true stress – true strain curves from yielding to fracture. It is observed that, the as-austenitised fine bainite sample has a higher true fracture stress and strain as compared to the intercritically annealed 12 and 21 % sample. This signifies that the bainite microstructure undergoes a higher post uniform strain deformation i.e. necking before fracture than the intercritically annealed 12 and 21 % M/A samples. Comparing the 12 and 21 % M/A cases, the true strain to failure decreases to 0.8 from 0.95 as the amount of M/A increases from 12 to 21 %.



Figure 6.22: True stress – true strain to failure for fine bainite of 06C03Nb steel before and after intercritical annealing (IA)

Finally, the true stress – true strain results for the intercritically annealed samples with 12% and 21% M/A at different test temperatures i.e. at +21, -20, -60, -196°C (up to the necking points) are compared in Figure 6.23a and Figure 6.23b, respectively noting that the linepipe steels operate in the temperature range from +40°C to -60°C during use in the field. The Considère criterion was satisfied in each case. Tests were also conducted at -196°C to see if the samples would be brittle at this very low temperature.



Figure 6.23: Considère analysis of tensile tests data over a range of temperature for intercritically annealed fine bainite of 06C03Nb steel forming (a) 12% M/A and (b) 21% M/A

The change in the slope of work hardening rate $(d\theta/d\sigma_{true})$ is plotted as a function of temperature in Figure 6.24. The yield stress, UTS, uniform elongation, YS/UTS ratio, slope of work hardening $(d\theta/d\sigma_{true})$ and the true strain to failure results from the different test temperatures are summarized in Table 6.5. It is

observed that both the yield strength and UTS increase with decrease in test temperature for both 12 % and 21 % M/A samples. The yield stress increases only by 20 MPa from 21°C to -60°C in the 12% M/A sample and by 12 MPa from 21°C to -60°C in the 21% M/A sample. However, upon further decreasing the test temperature from -60°C to -196°C, the yield strength increases by ~330 MPa in both 12% M/A and 21% M/A samples respectively, an observation similar to Section 5.11.2. On the other hand, the UTS increases by ~60 MPa from 21°C to -60°C and by ~300 MPa from -60°C to -196°C in 12% M/A and 21% M/A samples, respectively. The work hardening rate increases with decrease in temperature presumably due to a reduction in the rate of dynamic recovery at low temperature (see Figure 6.24) [3,145]. Thus, in both the cases of 12 and 21% M/A, the increased work hardening rate stabilizes the deformation, so the uniform elongation also increases with decrease in the temperature. The tensile results are discussed in further detail with respect to the microstructure in Section 6.5.4 after presenting the tensile results of the intercritically annealed coarse bainite microstructure.



Figure 6.24: Slope of the decrease of work hardening with stress ($d\theta/d\sigma$) as a function of test temperature obtained from tensile tests for intercritically annealed fine bainite structure of 06C03Nb steel

Sample	Test temper ature (°C)	0.2% YS (MPa)	UTS (MPa)	Uniform elongation (%)	YS/ UTS ratio	$d\theta/d\sigma_{true}$	True stress to failure (MPa)	True strain to failure
Fine bainite + IA-12% M/A	+21	694 ± 6	868 ± 5	7.5 ± 0.5	0.80	-34	1540 ± 20	0.95 ± 0.15
	-20	711 ± 3	897 ± 3	7.8 ± 0.5	0.79	-22	1653 ± 25	0.96 ± 0.13
	-60	714 ± 2	931 ± 8	8.5 ± 1.4	0.77	-27	1066 ± 12	0.36 ± 0.05
	-196	1042 ± 12	1237 ± 2	11.4 ± 1.8	0.84	-8	1457 ± 3	0.17 ± 0.02
Fine bainite + IA-21% M/A	+21	698 ± 9	893 ± 4	5 ± 0.5	0.78	-48	1515 ± 25	0.75 ± 0.15
	-20	697 ± 5	922 ± 4	6.1 ± 1.1	0.76	-30	1265 ± 18	0.61 ± 0.17
	-60	710 ± 6	954 ± 5	8.2 ± 1.5	0.74	-31	1092 ± 7	0.43 ± 20
	-196	1040 ± 4	1244 ± 1	9.9 ± 0.5	0.84	-10	2010 ± 40	0.6 ± 0.03

Table 6.5: Tensile test results for intercritically annealed fine bainite samples of 06C03Nb tested at different

*Mean and average of the deviations from mean value are reported from three repeat tests for each condition. Slope of work hardening with stress = $d\theta/d\sigma_{true}$ where $\theta = d\sigma_{true}/d\varepsilon$

6.5.2 Coarse bainite + intercritical annealing: 06C03Nb steel

The coarse bainite initial microstructures were intercritically annealed at 725°C and 760°C for 60 s to form 12 % and 21 % M/A constituents in the final microstructures. The engineering stress - engineering strain tensile curves are plotted in Figure 6.25 with the main results summarized in Table 6.6. The yield stress is almost independent of the fraction of M/A constituents, i.e. 555 - 559 MPa. However, the ultimate tensile stress increases from 710 to 786 MPa as the fraction of M/A increases to 21 %. The uniform elongation increases from 6 % to 10 % upon the formation of 12 % intercritical M/A and then decreases to 8 % for the presence of 21 % M/A.



Figure 6.25: Engineering stress – strain behaviour of the coarse bainite followed by intercritical annealing (IA) of 06C03Nb steel for 60s at 725°C and 760°C

Sample	0.2% YS (MPa)	UTS (MPa)	Uniform elongation (%)	YS/UTS ratio	$d\theta/d\sigma_{true}$	True stress to failure (MPa)	True strain to failure
Coarse Bainite	559 ± 5	710 ± 8	6 ± 1	0.80	-27	1086 ± 12	0.60 ± 0.1
IA-12 % M/A	555 ± 3	752 ± 8	9 ± 0.5	0.74	-24	1350 ± 12	0.75 ± 0.15

Table 6.6: Tensile properties at room temperature of coarse bainite + intercritical annealing of 06C03Nb steel

Mean and average of the deviations from mean value in tensile results were calculated from three repeat tests for each condition. Slope of work hardening with stress = $d\theta/d\sigma_{true}$ where $\theta = d\sigma_{true}/d\varepsilon$

0.71

-26

 1245 ± 12

 0.8 ± 0.1

 8 ± 0.8

IA-21 %

M/A

 558 ± 4

 786 ± 7

Figure 6.26 shows the plots of the true stress – true strain areas up to fracture (again assuming a linear hardening rate between necking and fracture). It is observed that the 12 % and 21 % M/A samples show higher strains to failure than the coarse bainite initial structure before intercritical annealing.



Figure 6.26: True stress - true strain to failure for coarse bainite of 06C03Nb before and after intercritical annealing to produce 12 % and 21 % M/A in the final microstructure

The yield strength to UTS ratio is also summarized in Table 6.6, and it decreases from 0.8 for coarse bainite before intercritical annealing to 0.74 for upon intercritical annealing to form 12 % M/A to 0.71 in 21 % M/A sample. Thus, it is found that the yield to UTS ratio decreases with increase in the amount of M/A in the microstructure which is a significant characteristic of dual phase steels found in literature [161,163]. In dual phase ferrite-martensite samples, the yielding starts at ferrite and it starts to deform plastically whereas the martensite remains elastic thereby the increasing UTS [162]. Further analysis on the work hardening on these microstructures are presented in Figure 6.27. The initial region of the strain hardening plot is the elastic region with an elastic modulus of ~200 GPa followed by a very steep slope in the elastic-plastic region and then a relatively flat slope in the plastic region denoting a decreasing strain hardening rate as it approaches necking.



Figure 6.27: Work hardening response at room temperature of 06C03Nb coarse bainite before and after intercritical annealing showing θ vs ε_{true} at elastic, elastoplastic and plastic regime

The true stress – true strain data measured using extensometer until necking is shown in Figure 6.28. The work hardening response $d\sigma/d\epsilon$ is also plotted as a function of true strain and Considère criterion of localization is observed to be satisfied i.e. necking is initiated when the work hardening rate equals the flow stress. The true uniform strain decreases with increase in volume fraction of M/A constituents in the final microstructure upon inter-critical annealing, as also observed in our previous cases i.e. fine bainite initial microstructures.

To further quantify the work-hardening rate, the work hardening response ($\theta = d\sigma/d\epsilon$) is also plotted as a function of true stress in Figure 6.29. The slope $d\theta/d\sigma$ is calculated between 700 to 3000 MPa. This value represents the work hardening rate in the plastic regime and is reported in Table 6.6. There is a negligible change in the work-hardening rate which increases from -28 MPa for coarse bainite before intercritical annealing to -24 MPa upon intercritical annealing at 725°C for 60 s forming 12% M/A. It is found to hardly decrease from -24 MPa to -26 MPa although the fraction of M/A constituents increases from 12 to 21 %. However, the overall change in the work hardening rate is small in comparison with the fine bainite samples under same condition (see Section 6.5.1). This is proposed to be the case since the coarse bainite initial structure has 6.5% M/A compared to the fine bainite initial structure with only 2.5% M/A. This will be discussed in detail in Section 6.5.4.



Figure 6.28: Considère analysis of tensile tests data at room temperature for 06C03Nb coarse bainite before and after intercritical annealing (IA) to form 12 % M/A and intercritically annealed 21 % M/A



Figure 6.29: Work hardening responses from tensile test data at room temperature showing work hardening

rate (θ) as a function of σ_{true} before and after intercritical annealing of 06C03Nb coarse bainite sample

Finally, the tensile test results for the intercritically annealed coarse bainite samples with 12 % and 21 % M/A at different test temperatures i.e. at +21, -60, -196°C (up to the necking points) are plotted in Figure 6.30 and the results are summarized in Table 6.7. The tests were also conducted at -196°C to see if the samples would be brittle at this low temperature. The yield stresses increase by 15 MPa and 72 MPa in 12 % and 21 % M/A samples respectively when the test temperature was decreased from 21°C to -60°C. However, upon further reducing the test temperature to -196° C, the yield stresses increase by ~ 370 MPa in both the cases. Similarly, the UTS also increases by ~73 MPa and 100 MPa up to -60°C and ~250 MPa up to -196°C. The samples tested at -196°C showed ~3% uniform elongation and very high yield to UTS ratio, i.e. 0.9, signifying that at -196°C, the work hardening was low, and the sample fails right after yielding i.e. at the elastic to plastic transition region. The value of $d\sigma/d\epsilon$ was ~3500 MPa at failure i.e. before the maximum tensile stress was reached, thus the Considère criterion was not satisfied for the coarse bainite 12% M/A and 21% M/A tested at -196°C. The slope of the decrease of work hardening was calculated between 2500 MPa and the necking point for all samples. No work hardening data was available for the samples tested at -196°C below 2500 MPa. It is observed that there is a small increase in the slope of work hardening from -24 at room temperature to -18 at -60°C for the 12% M/A sample and from -26 at room temperature to -22 at -60°C for the 21% M/A sample indicating that both the samples are ductile upto -60°C. The increased work hardening at -60°C implies that the dynamic recovery decreases with temperature.



Figure 6.30: Considère analysis of tensile tests data over a range of temperature for 06C03Nb coarse bainite + intercritically annealed (a) 12% M/A and (b) 21% M/A tested at +21°C, -60°C and -196°C. Note that Considère analysis was not satisfied for -196°C due to fracture at yielding.

Sample	Test temperatu re (°C)	0.2% YS (MPa)	UTS (MPa)	Uniform elongation (%)	YS/UTS ratio	$d\theta/d\sigma_{true}$	True stress at failure (MPa)	True strain to failure
Coarse	+21	555 ± 3	752 ± 8	10 ± 0.5	0.74	-24	1350 ± 12	0.75 ± 0.15
+	-60	569 ± 4	825 ± 5	12.2 ± 1.4	0.69	-18	1053 ± 18	0.47 ± 0.18
IA-12% M/A	-196	938 ± 2	1046 ± 7	2.6 ± 0.7	0.90	NA	1083 ± 14	0.03 ± 0.01
Coarse	+21	558 ± 4	786 ± 7	8 ± 0.8	0.71	-26	1245 ± 12	0.8 ± 0.10
+	-60	632 ± 6	885 ± 9	8.7 ± 1.4	0.71	-22	1317 ± 15	0.51 ± 0.20
IA-21% M/A	-196	992 ± 1	1151 ± 5	3.2 ± 1.1	0.86	NA	1173 ± 26	0.03 ± 0.01

Table 6.7: Tensile results of intercritically annealed coarse bainite of 06C03Nb at different test temperatures

Mean and average of the deviations from mean value in tensile results were calculated from three repeat tests for each condition, Slope of work hardening with stress = $d\theta/d\sigma_{true}$ where $\theta = d\sigma_{true}/d\varepsilon$

6.5.3 Void formation during ductile fracture: 06C03Nb steel

To examine the tensile fracture mechanisms of the intercritically annealed specimens, the specimens were polished up to the mid thickness and etched. The regions close to the fracture end, i.e. within 200 µm, is observed under the FEGSEM and is presented in Figure 6.31.This distance is somewhat arbitrary but was chosen based on the distance from fracture surface where no voids are visible. Examples of fine and coarse bainite samples before intercritical annealing are shown in Figure 6.31a and Figure 6.31b, respectively. Fine voids are observed at the M/A-bainite interface in the coarse bainite microstructure whereas relatively large sized voids are located at random regions in the fine bainite structure. The number of voids in the coarse bainite samples are higher in comparison to the fine bainite samples and was measured to be 700 per mm² and 450 per mm² in coarse and fine bainite, respectively. This is believed to be related to the higher fraction of M/A constituents in the coarse bainite compared to the fine bainite i.e. 6.5% vs. 2.5%, respectively. Upon intercritical annealing, qualitatively a large number of voids was observed near the fracture surface of the fine bainite IA 12 % M/A (Figure 6.31c) compared to the coarse bainite IA 12 % M/A (Figure 6.31d) specimen. The voids are located at the interface of M/A constituents and the bainite matrix, i.e. decohesion at the martensite-bainite interface. Cracking of M/A islands was not observed in any of these samples. Figure 6.31e and Figure 6.31f show the fine bainite IA 21% M/A and coarse bainite IA

21% M/A respectively, and very few voids are observed. The void density was quantified from these microstructures and is summarized in Figure 6.32. The overall change in void density is much smaller in the coarse bainite samples than for the fine bainite samples.



Figure 6.31: Voids on the secondary fracture surface of tensile specimens of 06C03Nb (a) Fine bainite and (b) coarse bainite before intercritical annealing (IA); (c) fine bainite + IA 12 % M/A, (d) coarse bainite + IA 12 % M/A, (e) fine bainite + IA 21 % M/A and (f) coarse bainite + IA 21 % M/A, observed in FEGSEM



Figure 6.32: Void density in the 06C03Nb steel microstructures as measured from tensile secondary fracture surfaces close to the fracture end (≤ 200 µm)

6.5.4 Discussion of tensile test results: 06C03Nb steel

It was shown in Section 6.4 that intercritical annealing of fine bainite and coarse bainite for 60 s at 725°C and 760°C increases the amount of M/A constituents to 12 % and 21 %, respectively. The effect of total M/A constituents on the yield strength and UTS are compared in Figure 6.33a and Figure 6.33b for the fine bainite and coarse bainite matrix, respectively. Noting that the fine and coarse bainite microstructure contained 2.5 % and 6.5 % of M/A constituents, respectively. Upon intercritical annealing at 725°C for 60 s, the fraction of M/A in the final microstructure increases to 12 %, however in both fine and coarse bainite, the yield strength changed only by ~1 % but UTS increased by ~7 %. Upon a further increase of M/A to 21%, the yield strength shows little change but the UTS increases linearly with the fraction of M/A in the rate of decrease of the work hardening with stress (d θ /d σ) as a function of M/A fraction is shown in Figure 6.34. The effect of M/A in fine bainite samples is more prominent in comparison to the coarse bainite samples before and after intercritical annealing.



Figure 6.33: Effect of intercritical annealing and M/A constituents of (a) fine bainite and (b) coarse bainite of 06C03Nb steel on yield strength and ultimate tensile strength



Figure 6.34: Change in the rate of decrease of work hardening with stress ($d\theta/d\sigma$) as a function of the total

M/A constituents present in fine and coarse bainite of 06C03Nb steel

Although these microstructures are complex, they can be simplified as a mixture of M/A particles in a bainitic matrix. Then the net yield stress (σ^{total}) of these microstructures can be expressed as:

$$\sigma_y^{total} = (1 - f^{M/A}) \times \sigma_y^{bainite} + f^{M/A} \times \sigma^{M/A}$$
(6.2)

where the fraction of M/A can be expressed as $f^{M/A}$, and the strength of bainite and martensite are $\sigma^{bainite}$ and $\sigma^{M/A}$ respectively. The strength of bainite can be estimated from the contributions of chemistry and microstructural features as also considered in Section 5.8 and Section 5.11.1:

$$\sigma_y^{bainte} = \sigma_0 + \sigma_{dis} + \sigma_{boundary} + \sigma_{ppt.} \tag{6.3}$$

where, σ_0 is the intrinsic strength of bainite due to lattice friction stress, $\sigma_{boundary}$ is the strengthening due to bainite boundaries, σ_{dis} is the dislocation strengthening and σ_{ppt} is the precipitation strengthening due to possible precipitation of Nb(C,N) precipitates during intercritical annealing.

The effect of intercritical annealing for 60 s at 725 - 760°C on the bainite matrix potentially includes i) precipitation strengthening due to the formation of Nb(C,N) precipitates (note that the Mo₂C are expected to be in solution in this temperature range from ThermoCalc TCFE7 database which predicts its dissolution temperature to be ~660°C) and ii) softening due to tempering i.e. recovery of the microstructure by annihilation of dislocations [257,258]. A simple calculation of the precipitation strengthening contribution using size of Nb(C,N) from TEM measurements by Ando [259] and fraction from ThermoCalc TCFE7database on the same steel with similar microstructure estimates a maximum 60 MPa increase in strength upon intercritical annealing. The individual effect of tempering of the bainite matrix at 725°C and 760°C during intercritical annealing was challenging to quantify as it interacts with precipitation hardening due to Nb(C,N) precipitates and phase transformation to austenite. The KAM analysis of strain induced misorientations in fine bainite samples in Section 6.4.1 indicate some changes to the internal structure of the fine bainite during the intercritical annealing: the decrease of KAM is most prominent in the sample which was intercritically annealed at 760°C for 60 s. Therefore, some softening in the microstructure due to tempering is possible in the fine bainite structure. On the other hand, the increase in volume fraction of M/A during intercritical annealing would increase the strength as has been well documented for dual phase steels. Further, it has been shown by Mazinani et al. [160] that martensite may yield in DP steels. However, the most challenging part here is to estimate the stress borne by the martensite particles. It is widely accepted that the strength of martensite can be correlated to its carbon content [144,167,168,170,260–262].

Thus, to estimate the strength of the M/A constituents, it is necessary to estimate the carbon concentration of martensite. For this purpose, it was assumed that the carbon content of the M/A is same as the carbon content of the parent intercritical austenite and that the austenite was in equilibrium with the surrounding ferrite. An analysis based on the Fe-C phase diagram using ThermoCalc with the TCFE7 database predicts that the carbon content in 12 % and the 21 % M/A is 0.51 and 0.26 wt.%, respectively, see Figure 6.35. This estimate is consistent with atom probe tomography measurements at the matrix-M/A interface as obtained by Li et al. [138]. They have measured in the ICCGHAZ of X100 steel containing Fe– 0.07C–0.25Si–1.94Mn–0.081Nb–0.28Cr–0.26Mo–0.014Ti and have shown that the intercritical M/A particles at the prior austenite grain boundaries were found to be notably enriched with C-0.49 wt.% and Mn-2.3 wt.%, however the carbon concentration was not related to the fraction of M/A for their cases.

A simple estimate of the yield stress for the martensite can be made using the data reported by Leslie on bulk martensite samples [165]. However, Leslie's data is only available until 0.4 wt.% carbon in martensite. Therefore, a linear extrapolation of Leslie's data has been done to obtain the martensite strength values up to 0.6 wt.% carbon as shown in Figure 6.36. Given the estimate of the carbon content, this would suggest that the yield stress for the martensite in the 12% and 21% microstructures is ~2000 and ~1300 MPa, respectively. Note that there is some uncertainty in the yield stress values for the 12% M/A case due to the extrapolation. Nevertheless, it would be expected that the yield stress of martensite would increase with an increase in carbon content.


Figure 6.35: Equilibrium compositional analysis of austenite using ThermoCalc 4.0 TCFE7 database



Figure 6.36: Estimation of strength of martensite as a function of its composition. Note that the solid line is from literature and the dashed line is the extrapolation (*Adapted from Leslie* [165]).

A simple estimate of load transfer to the martensite particles in the bainite matrix can be calculated using the analysis of Bao and co-worker's [263]. In this work, finite element calculations (FEM) were conducted for the stress on ellipsoidal particles embedded in an elastic - perfectly plastic matrix. Bao et al. showed that the FEM results for the flow stress of the composite could be analytically represented as:

$$\overline{\sigma}_0 = \sigma_0 (1 + \beta f) \tag{6.4}$$

where, $\overline{\sigma}_0$ is the flow stress of the two-phase model, σ_0 is the flow stress of the matrix and β is a factor related to the aspect ratio (AR) of the particles and *f* is its fraction in the microstructure. β can be expressed as:

$$\beta = 0.44 * AR + 0.69 * \frac{1}{AR} - 0.75$$
(6.5)

In the current case, the aspect ratio from our image analysis measurements of martensite islands was used and the flow stress of the matrix is estimated from the yield stress or the ultimate tensile stress of the bainitic matrix. Using Equation 6.5, this model has been used to estimate the stress in the martensite islands for different volume fractions, aspect ratios and matrix flow stresses assumption and are summarized in Table 6.8.

In the case of coarse bainite matrix with 12% martensite, the stress in martensite particles is estimated to be \sim 1300 – 1650 MPa which is lower than the yield stress of martensite based on the estimate from Leslie's data i.e. 2000 MPa. For coarse bainite with 21% martensite, the stress in the martensite is estimated to be \sim 1200 – 1525 MPa compared with the martensite flow stress of 1300MPa, suggesting that plastic yield of martensite islands is possible for this case.

Turning to the case of the fine bainite matrix, it is observed that for 12% martensite, the stress in the martensite islands is $\sim 1600 - 1900$ MPa compared to martensite yield stress of 2000 MPa, i.e. martensite remains elastic. On the other hand, for 21% martensite, the stress in martensite islands is $\sim 1300 - 1500$ MPa, the yield stress of martensite is ~ 1300 MPa suggests that martensite plasticity may be possible.

	Microstructure	Stress of bainite matrix (MPa)	Aspect ratio of M/A	Load transfer factor	Stress in martensite due to load transfer (MPa)	Yield strength of martensite from Leslie (MPa)
Lower bound calculation Using <u>vield strength</u> as stress in bainite	Coarse bainite + 12% M/A	559	2.8	2.34	1307	2000
	Coarse bainite + 21% M/A		2.5	2.15	1200	1300
	Fine bainite + 12% M/A	692	2.8	2.34	1590	2000
	Fine bainite + 21% M/A	082	2.1	1.91	1297	1300
Upper bound Calculation Using <u>UTS</u> as stress in bainite	Coarse bainite + 12% M/A	710	2.8	2.34	1660	2000
	Coarse bainite + 21% M/A	/10	2.5	2.15	1527	1300
	Fine bainite + 12% M/A	808	2.8	2.34	1890	2000
	Fine bainite + 21% M/A	000	2.1	1.91	1542	1300

Table 6.8: Maximum and minimum stresses on M/A islands in bainite matrix using load transfer model of Bao et al. on the 06C03Nb steel

This argument would be consistent with the observations on void density near the fracture surface summarized in Figure 6.32 and the observations that void nucleation occurs predominantly at the martensite-bainite interface (see Figure 6.31). In the case of the initial materials, the void density is higher in the coarse bainite compared to the fine bainite reflecting the higher M/A content, 6.4% vs. 2.8%. The reduction in void density is consistent with a higher true strain and true stress at failure in the fine bainite versus the coarse bainite ($\varepsilon_t^{fracture}$ 1.4 vs. 0.6 and $\sigma_t^{fracture}$ 1970 vs. 1086 MPa, respectively). The formation of 12% M/A after intercritical annealing results in a large increase in the void density for both fine and coarse bainite (Figure 6.32) and the commensurate drop in the true stress and strain to fracture (for fine bainite: $\sigma_t^{fracture} = 1550$ MPa and $\varepsilon_t^{fracture} = 0.95$; for coarse bainite: $\sigma_t^{fracture} = 1350$ MPa and $\varepsilon_t^{fracture} = 0.75$). Finally, in the case of 21% M/A after intercritical annealing, it is observed that the void density decreases

^{*}The yield strength of martensite is estimated using Leslie's data for 21% martensite and a linear extrapolation of Leslie's data for 12% martensite.

compared to the 12% samples for both fine and coarse bainite. This would be consistent with the estimates for stress in the martensite particles that suggest plasticity is possible, i.e. this would relax the stress at the martensite bainite interface and thereby reduce the rate of void nucleation. The result in terms of true stress and strain at fracture is that the true fracture stress and strain are almost unaffected. This line of reasoning is consistent with the results of Mazinani et al. [160] who studied void nucleation in dual phase steels and found that martensite plasticity was observed for higher martensite fractions. Nevertheless, a detailed study with digital image correlation (DIC) is suggested for future work to confirm this hypothesis.

In summary, the overall small changes in the yield stress shown in Figure 6.33a and Figure 6.33b can be explained by a decrease in yield stress of the bainite matrix due to tempering which is balanced by the increase in yield stress due to an increase in the fraction of M/A constituents, resulting in a negligible net change in the yield strength. However, the work hardening of the microstructure from the presence of hard M/A particles in a relatively soft bainite matrix increases the ultimate tensile strength in both coarse and fine bainite microstructure. The work-hardening and the ultimate tensile strength increases with decrease in temperature, due to lower dynamic recovery at low temperature.

6.6 Charpy impact toughness

6.6.1 Fine bainite + intercritical annealing: 06C03Nb steel

Figure 6.37 shows the results for the Charpy impact energy as function of test temperature for the four conditions considered in this work, i.e. fine bainite before intercritical annealing, 6 % M/A, 12 % M/A and 21 % M/A.



Figure 6.37: Charpy impact behaviour for 06C03Nb fine bainite before and after intercritical annealing (IA) tested at different temperature

The transition temperature (DBTT) in this study is defined as the temperature corresponding to 50% of the difference between upper and lower shelf energy. It can be observed that for the case of the fine bainite microstructure formed upon cooling at 50°C/s (after the first thermal cycle), the upper shelf energy is ≈ 270 J and the transition temperature is -55°C. As the volume fraction of M/A increases to 6 % (i.e. the decomposition product of the intercritical austenite from the second thermal cycle), the upper shelf energy increases to ≈ 300 J with a transition temperature of -45°C. The increase in the upper shelf energy is consistent with the higher yield and tensile stress and the increase in elongation for the sample with 6 % M/A, i.e. the energy absorbing capability is increased. However, in the case of 12 % M/A, a dramatic degradation occurs in the impact energy behaviour. The impact energy increases slightly from 10 J at -20°C to 31 J at 21°C (i.e. well below the industry rule of thumb of 50 J for low impact toughness). An impact

energy of 60 J at +40°C and 260 J at 100°C was recorded. As such, the DBTT was estimated to be 50°C. Finally, for the case of 21% M/A, the ductile-brittle transition temperature decreases to ~0°C and the upper shelf energy is ≈ 250 J.

6.6.2 Coarse bainite + intercritical annealing: 06C03Nb steel

Figure 6.38 compares the Charpy impact behaviour of the coarse bainite microstructure before and after intercritical annealing. A similar trend is found as seen in fine bainite microstructures, i.e. the DBTT increases dramatically with 12% M/A before decreases with 21% M/A in the microstructure. Specifically, the coarse bainite microstructure obtained during the 1st thermal cycle had a ductile to brittle transition temperature of ~10°C and an upper shelf energy of 400 J. Upon intercritical annealing to form 12 % M/A, the maximum impact energy was recorded to be ~200 J at 100°C and the DBTT increases to 62°C. Finally, for the case of 20% M/A, the average impact energy was found to be 300 J at 100°C and DBTT is lowered to 40°C.



Figure 6.38: Charpy impact behaviour for coarse bainite before and after intercritical annealing (IA) to form

microstructures with 12 % and 21 % M/A in 06C03Nb steel

6.6.3 Summary of Charpy impact results

The Charpy impact energy results are summarized in Table 6.9. The DBTT increases dramatically in the 12% M/A sample of both fine and coarse bainite. However, the DBTT of the 21% M/A sample in fine bainite is better than that of the coarse bainite. This will be discussed in detail in Section 6.9 after presenting the fracture results. The change in DBTT and the upper shelf energies in the different microstructures upon intercritical annealing are compared in Figure 6.39 and Figure 6.40 for the coarse bainite and fine bainite initial structures, respectively. The DBTT increased with an increase in the M/A fraction upto 12 % and then the DBTT again decreased towards a lower temperature when the M/A increases further to 21 %. Note that the DBTT does not decrease for 6% M/A in the microstructure. The upper shelf energy also decreases with increase in M/A up to 12% and upon further increasing the M/A, the upper shelf energy increases.

Starting microstructure	Final microstructure	Lower shelf energy (J)	T95% Brittle (°C)	DBTT T50% Brittle (°C)	Upper shelf energy (J)
	Fine bainite	5 ± 0.5	-105	-55	270 ± 10
Fine bainite	IA - 6 % M/A	3 ± 0.5	-70	-45	291 ± 15
50°C/s	IA - 12 % M/A	3 ± 0.5	8	50	$257\pm28*$
	IA - 21 % M/A	4 ± 0.5	-65	0	$256\pm12^*$
Coarse bainite formed at 5°C/s	Coarse Bainite	3 ± 0.5	-30	10	400 ± 3*
	IA - 12 % M/A	4 ± 0.5	35	62	$221 \pm 8*$
	IA - 21 % M/A	4 ± 0.5	10	40	295 ± 5*

Table 6.9: Summary of Charpy impact test results of 06C03Nb steel (obtained from curve fitting)

*denotes data in the upper shelf energy range is obtained from one temperature i.e. $100^{\circ}C$

Mean and average of the deviations from mean value in Charpy results were calculated from three repeat tests at one temperature for each condition.



Figure 6.39: Effect of intercritical annealing on the ductile-brittle transition temperature (DBTT) of 06C03Nb



Figure 6.40: Effect of intercritical M/A in 06C03Nb on upper shelf energy (upper shelf energies of several

cases were assumed to be at 100°C)

6.7 Fractography upon intercritical annealing: 06C03Nb steel

6.7.1 12% M/A in the final microstructure: 06C03Nb steel

The intercritically annealed bainite forming 12% M/A in the final microstructure cases from both fine bainite and coarse bainite starting microstructures have shown the highest ductile-brittle transition temperature. Specimens broken near the lower shelf energy, the DBTT and the upper shelf energy were selected for the study of the fracture surfaces under the FEGSEM.

6.7.1.1 Fine bainite matrix

Figure 6.41a shows the fracture surface of the fine bainite + intercritically annealed (IA) 12% M/A sample tested at -20°C, having a Charpy impact energy of 7 J, i.e. near the lower shelf energy region. The notch is located at the bottom of the image. A very flat fracture surface with 100% brittle area is observed with negligible plastic deformation. Magnified images of the region close to the notch are shown in Figure 6.41b and Figure 6.41c. Typical river-line characteristics of brittle fracture are observed and they seem to originate from a particle (see Figure 6.41b). The fracture path appears to follow the prior austenite grain boundaries.

The same sample when tested at +40°C yields an impact energy of 47 J and the fracture surfaces are shown in Figure 6.42. This region is closest to the transition region. The fracture surface is ~50% brittle and ~50% ductile as determined from measurements on Figure 6.42a. Figure 6.42b shows regions of tears of ~50 μ m in size which is of size of the prior austenite grains. The region close to the notch is rough and brittle, which when magnified has shown instances of river lines originating from a point, Figure 6.42c. Small dimples are observed in the white regions showing instances of tearing in Figure 6.42d.



Figure 6.41: Fracture surface of 06C03Nb fine bainite + intercritical annealing IA 12% M/A, tested at -20°C i.e. from the lower shelf energy region, having a 7 J impact energy. The region close to the notch (marked in red) is magnified in (b) and (c).



Figure 6.42: Fracture surface of 06C03Nb fine bainite + IA 12% M/A, tested at +40°C, having an impact energy of 47 J (close to the DBTT region)

6.7.1.2 Coarse bainite matrix

For the coarse bainite starting microstructure and intercritical annealing to form ~12% M/A in the final microstructure, a 100% brittle and a flat fracture surface is observed in Figure 6.43a for a test at -20°C. (Note that a 5 J impact energy was recorded). The region close to the notch is magnified in Figure 6.43b and Figure 6.43c. It appears that the white lines show evidences of tearing and may be located at the prior austenite grain boundaries. The facets are measured to be ~55 μ m, i.e. similar to the PAGB. These kinds of white features were not observed in the same steel before intercritical annealing presented in Section 5.11.3 of the previous chapter.



Figure 6.43: Fracture surface of coarse bainite + IA 12 % M/A tested at -20°C, having an impact energy of 5 J (lower shelf energy region) (a) full fracture area, (b,c) magnified area near by notch marked in red box.

Figure 6.44 shows the fracture surface tested at 40°C resulting in an impact energy of 17 J. This was the sample closest to the transition region. A fracture area measurement on Figure 6.44a shows that the sample is 85% brittle. When magnified near the notch as shown in Figure 6.44b and Figure 6.44c, river line features of cleavage fracture are observed with signs of tearing at the boundaries, similar to what we observed until now. The river line features are similar to that of observed in the same steel before intercritical annealing.



Figure 6.44: Fracture surface of 06C03Nb coarse bainite and intercritically annealed to form 12% M/A (IA 12% M/A), tested at +40°C, having an impact energy of 17 J. (b,c) Magnified area of the region marked by red box near notch

6.7.2 21% M/A in the final microstructure: 06C03Nb steel

The samples with ~21% M/A constituents in the final microstructure have better impact properties and lower ductile to brittle transition temperature than 12 % M/A case (although practically still very high). The DBTT in the IA 21% M/A samples was measured to be 0°C for the fine bainite initial structure and 40°C for the coarse bainite initial structure.

6.7.2.1 Fine bainite matrix

Figure 6.45 show a series of fracture surfaces of the IA 21% M/A tested at -45°C, -20°C and 21°C having impact energies of 20 J, 61 J and 200 J respectively, i.e. representative of brittle region, transition region and ductile region. The fracture area measurements on these three images reveal a 95 %, 30 % and 15 % brittle fracture surface. The regions close to the notch as marked by red box are magnified in the bottom row of Figure 6.45. A cleavage fracture behaviour is observed at -45°C and -20°C whereas the sample tested at 21°C shows dimples which signifies ductile fracture behaviour and is consistent with the 200 J impact energy measurement.



Figure 6.45: Fracture surface of 06C03Nb steel cooled at 50°C/s and intercritically annealed to form 21% M/A (LB-IA 21% M/A), tested at (a,d) -45°C (b,e) -20°C and (c,f) +21°C with impact energies of 20 J, 61 J and 200 J respectively. Notch is located at the bottom side of the images.

6.7.2.2 Coarse bainite matrix

However, a very different behaviour is observed on the intercritically annealed samples which had coarse bainite as the initial structure. Figure 6.46 shows the fracture surface when the sample was tested at -20°C. A 5 J impact energy was recorded, and the fracture surface appears very flat and 100% brittle as measured from fracture area measurements. The magnified region close to the notch as marked by the red box in Figure 6.46b reveals large facets with river lines denoting cleavage fracture. The white boundaries as observed in previous cases are also found in this case, which appears to be continuous and of ~50 µm and possibly related to the prior austenite grain boundaries. The ductile to brittle transition temperature of this microstructure was measured to be 40°C. This IA 21% M/A microstructure when tested at 40°C reveals a 60% ductile and 40% brittle fracture area, shown in Figure 6.47a. The brittle surface region is magnified in Figure 6.47b. River-line features showing cleavage fracture is observed inside surrounded by boundaries of white ridges showing signs of tearing. The region close to the notch is magnified in Figure 6.47c. It reveals a completely ductile fracture surface.



Figure 6.46: Fracture surface of 06C03Nb steel cooled at 5°C/s and intercritically annealed to form 21% M/A (IA 21% M/A), tested at -20°C. The region close to the notch marked with red box is magnified in (b). Impact energy was recorded to be 5 J.



Figure 6.47: Fracture surface of 06C03Nb steel cooled at 5°C/s and intercritically annealed to form 21% M/A (IA 21% M/A), tested at +40°C. The region marked with red box are magnified in (b) and (c). Impact energy was recorded to be 143 J.

6.7.3 Summary of fracture surfaces

The fracture behaviour of the fine and coarse bainite microstructures was discussed in the Section 5.10. The fracture behaviour of those two samples upon intercritical annealing was shown in Section 6.7.1 and 6.7.2. The observations reveal that in both the cases of 12% and 21% M/A, a nearly continuous networks of white ridges are present, possibly consistent with the martensite at the prior austenite grain boundaries. Inside those ridges, river-line cleavage fracture surfaces are observed, similar to that observed in the samples before intercritical annealing. The fracture energy is significantly lowered after inter-critical annealing when the fraction of M/A is greater than 10%. No dominant fracture mechanism due to presence of M/A is found so far in the intercritically annealed samples with nearly continuous network of 12% and 21% M/A constituents.

6.8 Crack propagation in the intercritically annealed samples

The intercritically annealed samples that failed by cleavage fracture, i.e. at lower temperatures -20°C and -45°C, were chosen to examine the primary crack front and the secondary cleavage cracks (which did not propagate) beneath the fracture surface. The propagation paths of the secondary cleavage cracks were studied by FEGSEM on the cross-section of the impact tested specimens. A series of images has been shown and analyzed for statistical purposes.

6.8.1 Coarse bainite + intercritical annealing: 06C03Nb

Figure 6.48 and Figure 6.49 show the secondary cracks in the intercritically annealed coarse bainite samples with 12% and 21% M/A, tested at -20°C (note: more examples are shown Appendix C). Some of the cracks are found to be within the prior austenite grains (marked by blue arrows) similar to our observation on the coarse bainite sample before intercritical annealing in Section 5.10. However, in most of the cases, cleavage cracks are observed at the interface of bainite and M/A islands (marked by orange arrows) and this leads to cracking of M/A constituents in some cases (marked by yellow arrows). Further, it can be observed that there are cracks surrounding the M/A particles on one side forming a continuous crack path along the prior austenite grain boundaries (marked by orange arrows). Figure 6.49b also shows some instances of plastic deformation of the M/A islands in 21% M/A cases.

6.8.2 Fine bainite + intercritical annealing: 06C03Nb

Figure 6.50 and Figure 6.51 show the secondary cracks in the intercritically annealed fine bainite samples with IA 12% M/A and IA 21% M/A, taken from the low Charpy impact energy specimens i.e. tested at -20°C for 12% M/A and -45°C for 21% M/A. In the IA 12% M/A specimen, two kinds of features were observed: i) cleavage fracture of the M/A constituents (marked by yellow arrows) and ii) continuous fracture path along the M/A-bainite interfaces (marked by orange arrows) and iii) local plastic deformation of the bainite laths (see Figure 6.51a).



Figure 6.48: Secondary fracture surface of the Charpy samples as observed under FEGSEM upon polishing and etching 06C03Nb <u>coarse bainite + IA 12 % M/A</u> tested at -20°C, impact energy of ~5 J. (a,b) are examples of two regions. Arrows marked by orange indicate cracks at M/A-bainite interface, yellow indicate cracking of M/A and blue indicates cracks within bainite



Figure 6.49: Secondary fracture surface of the Charpy samples of 06C03Nb <u>coarse bainite + IA 21% M/A</u> tested at -20°C, impact energy of ~ 5 J. Arrows marked by <u>orange</u> indicate cracks at M/A-bainite interface, yellow indicate cracking of M/A and blue indicates cracks within bainite.



Figure 6.50: Secondary fracture surface of the Charpy samples of 06C03Nb fine bainite IA 12% M/A tested at -20°C, impact energy of ~ 7 J. Arrows marked by orange indicate cracks at M/A-bainite interface, yellow indicate cracking of M/A and blue indicates plasticity within bainite.



Figure 6.51: Secondary fracture surface of the Charpy samples of 06C03Nb fine bainite IA 21% M/A tested at -45 °C, impact energy of ~ 6 J showing plastic deformation in bainite and martensite (dashed lines)

6.9 Discussion of microstructure and mechanical properties relationship

The results from the tensile and Charpy impact tests on the intercritically annealed 06C03Nb steel and the corresponding analysis of the fracture surfaces can be rationalized and related to the microstructure as follows. The mechanical properties for the fine and coarse bainite samples before intercritical annealing were discussed in Section 5.11. The high strength and lower DBTT for the fine bainite microstructure was attributed to the distribution of bainite variants and the misorientation angles between them. In particular, the high density of high angle grain boundaries (HAGBs) is considered to make the stress for cleavage fracture more difficult as the cleavage cracks must change their propagation direction to remain in {001} plane as they cross each high angle boundary.

In contrast, the microstructures formed upon intercritical annealing of the fine and coarse bainite samples with 12% and 21% M/A constituents are much more complex. For the volume fraction of 10% or greater, the M/A constituents form a nearly continuous layer along the prior austenite grain boundaries, covering more than 80% of the PAGBs and whereas the bainitic matrix may have softened due to tempering.

6.9.1 Fine bainite – 12% M/A

In Section 6.5.4, it is estimated that the stress in martensite for the fine bainite (with 12% M/A) was 1600 – 1900 MPa, i.e. below the yield strength of martensite ~2000 MPa. Further, it appears based on the observation of secondary cracks below the fracture surface in Figure 6.50, that the fracture path predominantly follows the boundary between M/A and the bainitic matrix. The combination of a nearly continuous layer of M/A on the prior austenite grains and the high yield stress of the M/A produces a low energy path for crack propagation to occur. The stress incompatibility at the martensite-bainite interface has most likely led to debonding of the M/A from bainite matrix and therefore assisted in nucleation of cleavage cracks at the boundary or in the M/A islands. Thus, the high density of HAGBs in the bainitic matrix does not significantly contribute towards restricting the crack path as the M/A-bainite matrix interface provides a continuous crack path and is the primary reason for dramatic increase in ductile-brittle transition temperature.

6.9.2 Coarse bainite – 12% M/A

In the case of coarse bainite + 12 % M/A, there is also a nearly continuous layer of M/A on the prior austenite grain boundaries but in this case the coarse bainite matrix is also rather poor at restricting crack propagation with a high DBTT due a low density of HAGBs as discussed in Section 5.11. The crack propagation through bainite laths was observed in Figure 6.48. In addition, it was estimated in Section 6.5.4 that the stress in martensite is ~1200 - 1525 MPa, but the yield strength of martensite is ~2000 MPa. Therefore, the two factors: high stress incompatibility at bainite - M/A matrix interface and lack of HAGBs in bainite matrix led to a continuous path for cleavage crack propagation lowering the impact properties of these microstructures.

In summary, for the cases of 12% M/A in both fine and coarse bainite, it is proposed that the martensite islands are predominantly elastic and that the fracture path follows the martensite-bainite interface. This would be consistent with the similar impact energy results for both coarse and fine bainite with 12% M/A.

6.9.3 Fine bainite – 21% M/A

In case of the 21% M/A in fine bainite matrix, it has been estimated that the yield stress of the M/A would be substantially lower than the 12% case, i.e. 1300 MPa vs. 2000 MPa. Further, it was calculated using load transfer model that the stress in martensite was possibly ~1200 - 1525 MPa. Thus, it can be argued that plasticity in the M/A constituents is possible thereby reducing the stress concentration at the martensite – bainite interface reducing the probability of cleavage crack initiation. This would be consistent with the observations that the transition temperature decreases to 0°C compared to the case of 12% M/A.

6.9.4 Coarse bainite – 21% M/A

In the case of coarse bainite + 21 % M/A, the stress in the martensite was estimated to be ~1200-1525 MPa, however yield strength of martensite is ~1300 MPa which may suggest that plasticity in the M/A constituents is possible, similar to the fine bainite with 21% M/A samples. As argued earlier this would

reduce the stress on martensite-bainite interface, thereby delaying fracture at this interface, i.e. the DBTT now drops. However, in this case the possibility of martensite plasticity is more borderline than for the fine bainite matrix. Thus, one sees only a limited reduction in the DBTT from 62°C in 12% M/A to 40°C in 21% M/A sample (See Table 6.9).

6.9.5 Fine bainite - 6% M/A

Finally, the case of 6% M/A in a fine bainite matrix can be rationalized by the observation that the M/A particles only cover approximately 60% of the prior austenite grain boundaries, i.e. in this case, there is not a continuous crack path for fracture to occur along. Further, a substantial fraction (~40%) of the M/A is retained austenite in this microstructure. The retained austenite may be beneficial to the behaviour as is the case in TRIP steels. Thus, this microstructure shows no degradation of Charpy impact energy behaviour upon intercritical annealing from fine bainite.

6.10 The role of carbon content

Based on the results and discussion of the mechanical behaviour of the microstructures relevant to the heat affected zone, it was found that for regions where the thermal fields overlap in multi-pass welds, a network of M/A constituents from 5 to 20% can be formed. The DBTT of the material of this region has been found to be much higher than the base material. However, the mechanical properties of these M/A constituents are largely dependent on the local carbon concentration. Therefore, examining the effect of reducing the carbon content of the steel on the Charpy impact behaviour is of interest. The hypothesis is that a reduction in the bulk carbon content in the steel will also reduce the carbon content of the intercritical austenite. In turn, this will lower the yield stress of the martensite, reduce the stress concentration at the martensite-bainite interface and potentially reduce the nucleation of cleavage cracks or interfacial decohesion.

In the present work, a low carbon 03C09Nb steel was chosen for intercritical annealing. Note that the Nb content is higher (~0.09 wt.%) in this steel compared to 06C03Nb steel having (~0.035 wt.% Nb).

The equilibrium compositional analysis for ~ 12 and $\sim 21\%$ austenite in 03C09Nb steel are compared to that of the 06C03Nb steel in Figure 6.52. The local carbon concentration in austenite for 12 and 21% austenite are summarized in Table 6.10.



Figure 6.52: Equilibrium compositional analysis of austenite using ThermoCalc on the 06C03Nb steel and 03C09Nb steel

Table 6.10: C-content of intercritical austenite as obtained from ThermoCalc 4.0 using TCFE7 database

C I	wt.% C in austenite				
Sample	06C03Nb steel	03C09Nb steel			
IA- 12% austenite	0.51	0.15			
IA- 21% austenite	0.26	0.08			

It is observed that the carbon content in the 12 % austenite decreases from 0.51 wt.% to 0.15 wt.%. when the bulk carbon content of the steel decreases from 0.06 wt.% to 0.03 wt.%. For 21% austenite, the carbon content is even lower i.e. 0.08 wt.% in the 03C09Nb steel. The effect of the carbon content on the yield strength of martensite estimate is shown in Figure 6.53 and summarized in Table 6.11. It is observed that the strength of martensite which formed from 12 % intercritical austenite is 950 MPa in 03C09Nb steel vs. 2000 MPa in 06C03Nb steel. Our estimation of load transfer to the martensite using the Bao and coworker's model [263] (see Section 6.5.4) suggests that the stress in the M/A will be ~ 1200 - 1545 MPa using the yield stress and UTS, i.e. much greater than the strength of the martensite i.e. 950 MPa (see Table 6.12). Thus, the lower carbon martensite can potentially result in more martensite plasticity thereby reducing the stress incompatibility at the bainite-martensite interface. Thus, it is proposed that this could lower the ductile-brittle transition temperature compared to the 06C03Nb steel.



Figure 6.53: Estimation of strength of martensite as a function of its composition (Adapted from Leslie [165])

Table 6.11: Estimated yield strength of the intercritical M/A as obtained from Leslie's experiment [165]

Samular	Yield strength of martensite (MPa)					
Samples	06C03Nb steel	03C09Nb steel				
IA- 12% M/A	2000	950				
IA- 21% M/A	1300	750				

	Microstructure	Stress in the bainite matrix (MPa)	Aspect ratio of M/A	Load transfer factor	Stress in martensite due to load transfer (MPa)	Yield strength of martensite from Leslie (MPa)
Lower bound calculation using	Bainite + 12% M/A	647	2.8	1.9	1234	950
<u>yield</u> <u>strength</u> as stress in bainite	Bainite + 21% M/A	047	2.1	1.8	1159	750
Upper bound calculation using <u>UTS</u> as stress in bainite	Bainite + 12% M/A	810	2.1	1.9	1545	950
	Bainite + 21% M/A		1.9	1.8	1451	750

 Table 6.12: Maximum and minimum stresses on M/A islands in bainite matrix using load transfer model of

 Bao and co-workers on the 03C09Nb steel

*The yield strength of martensite is estimated using Leslie's data.

6.11 Intercritical annealing of 03C09Nb steel

The low carbon steel i.e. 03C09Nb steel was chosen to produce microstructures similar to the intercritically reheated coarse grain heat affected zone. The results after the 1st thermal cycle i.e. austenitizing treatment to produce coarse austenite grains which upon cooling at 50°C/s forms bainitic microstructures similar to CGHAZ were discussed in Chapter 5. The results after the intercritical annealing treatment will be the discussed as follows.

6.11.1 Microstructure characterization: 03C09Nb

The bainite microstructures obtained by cooling at 50°C/s were heated to 775°C and 805°C for 60 s followed by cooling at 50°C/s. The optical microscope images of the initial state and after intercritical annealing were obtained after LePera etching and shown in Figure 6.54. Figure 6.54a shows that before

intercritical annealing, the bright M/A constituents are randomly distributed in the bainitic microstructure. However, upon intercritical annealing at 775°C for 60 s, new austenite preferentially nucleates and grows at the prior austenite grain boundaries in a necklace fashion, and transforms to martensite upon cooling as shown in Figure 6.54b. Increasing the intercritical temperature to 805°C increases the total fraction and width of these grain boundary M/A constituents, as shown in Figure 6.54c. The M/A at the prior austenite grain boundaries are analyzed in a similar way like Section 6.4 and are presented in Figure 6.55. The results are summarized in Table 6.13.



Figure 6.54: LePera etched optical microstructures for 03C09Nb steel (a) as-austenitised bainite at 50°C/s, (b) intercritically annealed at 775°C for 60 s and (c) intercritically annealed at 805°C for 60 s.



Figure 6.55: Thresholded images to characterize M/A at prior austenite grain boundary in (a,b) IA 12 % M/A

and (c,d) IA 21% M/A of 03C09Nb steel

 Table 6.13: Microstructure characterization of bainite before & after intercritical annealing (IA) in 03C09Nb

 steel

Condition	Total M/A fraction (from dilation) (%)	Retained austenite from EBSD (%)	Fraction of M/A at PAGB (%)	Fraction of M/A within PAGs (%)	PAGB covered by M/A (%)	Size of GB M/A (µm)	Aspect ratio of M/A
Bainite before intercritical annealing	3.7 ± 0.7 *	0.2 ± 0.03	NA	NA	NA	$0.9 \pm 0.2*$	2.2 ± 1.0
IA 775°C-60s	12.1 ± 1.5	0.3 ± 0.05	7.5	4.6	84	1.3 ± 1.0	2.1 ± 1.1
IA 805°C-60s	20.5 ± 1.9	0.4 ± 0.04	13.5	7.0	88	1.8 ± 1.4	1.9 ± 0.8

*M/A fraction measured from EBSD (see Section 5.6)

The distribution of M/A constituents at prior austenite grain boundaries and inside bainite after intercritical annealing of 03C09Nb steel with bainite matrix are shown in Figure 6.56a with the results being comparable to that of 06C03Nb steel shown in Figure 6.15. The size of the M/A in grain boundaries are compared in Figure 6.57a for the two steels. It can be observed that the grain boundary M/A increases in fraction and size with the increase in degree of inter-critical annealing, a result as observed in 06C03Nb steel as well in Section 6.4.3. However, the size of the M/A is significantly smaller in the 03C09Nb steel compared to our previous results in 06C03Nb steel. More than 80% of the prior austenite grain boundaries are observed to be covered by the intercritical M/A in a necklace fashion in the both the steels, see Figure 6.57b.



Figure 6.56: Distribution of M/A in the microstructure in the as-austenitised state and after intercritical annealing 03C09Nb steel cooled at 50°C/s



Figure 6.57: Microstructure characterization of the intercritically annealed microstructures showing (a) size of the grain boundary M/A and (b) % prior austenite grain boundary covered by M/A in the 03C09Nb steel cooled at 50°C/s and 06C03Nb steel cooled at 5 and 50°C/s after both thermal cycles

6.11.2 Tensile behaviour upon intercritical annealing: 03C09Nb

The bainite microstructures of 03C09Nb steel with 12 and 21 % intercritical M/A were chosen for the tensile tests. Figure 6.58 shows the results from the tensile tests conducted on the 03C09Nb steel at ambient temperature before and after intercritical annealing. The results for the yield stress (YS), ultimate tensile stress (UTS) and uniform elongation are summarized in Table 6.14.



Figure 6.58: Tensile behaviour of 03C09Nb steel before and after intercritical annealing

	0.2% YS (MPa)	UTS (MPa)	Uniform elongation (%)	YS/UTS	True fracture stress (MPa)	True strain to failure
Bainite (50°C/s)	644 ± 8	810 ± 7	6.1 ± 0.5	0.79	1475 ± 65	1.10 ± 0.10
IA-12% M/A	697 ± 6	824 ± 3	7.3 ± 0.5	0.84	1650 ± 50	1.25 ± 0.08
IA-21% M/A	622 ± 12	745 ± 8	9.1 ± 0.9	0.83	1360 ± 95	1.26 ± 0.05

Table 6.14: Summary of tensile behaviour of 03C09Nb steel before and after intercritical annealing

Mean and average of the deviations from mean value in tensile results were calculated from three repeat tests for each condition

It is observed that the yield strength increases from 644 MPa to 697 MPa upon intercritical annealing to form 11% M/A and then decreased to 622 MPa for 21% M/A. Similarly, the ultimate tensile strength also increases for 12% M/A and then decreases for 21 % M/A. The uniform elongation increases gradually with increase in M/A. Finally, the ratio of yield strength and ultimate tensile strength also increases to 0.83 for 21 % M/A from 0.79 to 0.84, but then decreases to 0.83 for 21 %

M/A. The results of yield strength, UTS, uniform elongation and the YS/UTS ratio are compared to that of the 06C03Nb steel. The change in yield strength, UTS, uniform elongation and the YS/UTS ratio in both 03C09Nb and 06C03Nb steel are compared in Figure 6.59.

In 03C09Nb steel, the yield strength is observed to increase for 12% M/A and decrease considerably for 21% M/A, however in the 06C03Nb steel, the yield strength had no significant change upon intercritical annealing. The UTS in 03C09Nb steel, on the other hand, has only increased for 12 % M/A, but decreases significantly for 21 % M/A compared to the 06C03Nb steel where the UTS increased with increase in M/A. The uniform elongation also increases with increasing intercritical annealing for the 03C09Nb steel. Therefore, it is implied that there is no significant work-hardening in the 03C09Nb steel due to formation of intercritical M/A. This is also supported by the trend in the YS/UTS ratio in Figure 6.59c, which is observed to decrease in the 06C03Nb steel and increase in case of 03C09Nb steel upon intercritical annealing. Our simple estimate on the load transfer to martensite considering UTS of bainite and aspect ratio of M/A shown in Table 6.12 suggests that the stress in martensite is ~1545 MPa in 12 % M/A case and 1450 MPa in 21% M/A. Thus, the stress in martensite is above the estimated yield stress of martensite (950 and 750 MPa, respectively) and one would expect substantial martensite plasticity. This would also be consistent with the results of Mazinani et al. [160] who reported that for martensite carbon content below ~0.1wt.%, substantial martensite plasticity was observed. On the other hand, to form similar level of M/A constituents, the intercritical temperature in the 03C09Nb steel were 775°C and 805°C which were significantly higher than the annealing temperatures used in 06C03Nb steel i.e. 725°C and 775°C. This would suggest that intercritical annealing of 03C09Nb steel could result in further softening of the bainite matrix due to tempering.



Figure 6.59: Comparison of change in (a) yield strength, (b) ultimate tensile strength, (c) uniform elongation and (d) ratio of yield strength and UTS in the 06C03Nb steel and 03C09Nb steel

6.11.3 Void formation in tensile specimens: 03C09Nb

To examine the tensile fracture mechanisms of the intercritically annealed specimens, the specimens were polished up to the mid thickness and etched. The regions close to the fracture end were observed under the FEGSEM and are presented in Figure 6.60. Qualitatively, few voids are observed within 100 μ m from the fracture end in all the three specimens i.e. before and after intercritical annealing. No

voids are observed at the interface of M/A constituents and the bainite, suggesting that there is negligible decohesion at martensite-bainite interface. Considerable plastic deformation of the overall microstructure including the bainite matrix and M/A can be observed.



Figure 6.60: Secondary fracture surfaces of broken tensile specimen of (a) as austenitised bainite, (b) IA 12 % M/A and (c) IA 21 % M/A

The secondary fracture surfaces of the broken tensile specimen for the IA 12% M/A samples of the 03C09Nb steel were compared to that of the 06C03Nb steel with fine bainite matrix in Figure 6.61. Voids were observed at the M/A and bainite interface of the 06C03Nb steel with negligible deformation of the M/A islands whereas almost no voids were identified at the M/A-bainite interface for 03C09Nb case. Significant plastic deformation of both the bainite matrix and the intercritical M/A was observed which would suggest a low stress incompatibility between matrix and M/A constituents. The void density for the

03C09Nb steel before and after intercritical annealing is compared to that of the 06C03Nb steel in Figure 6.62 for the fine and coarse bainite matrices. The overall density of voids near the fracture end is significantly less in the 03C09Nb steel. Upon intercritical annealing forming 12 and 21% M/A, there is only a small increase in the void density compared to the 06C03Nb steel.

The low void density in the intercritically annealed 12% M/A in 03C09Nb steel is consistent with a higher true strain at failure (see Table 6.14) in the 03C09Nb steel vs. both fine bainite and coarse bainite 06C03Nb steel ($\varepsilon_i^{fracture} = 1.24$ in 03C09Nb steel vs. 0.95 and 0.75 in fine and coarse bainite of 06C03Nb steel, respectively). In the case of 21% M/A after intercritical annealing, the further decrease in void density in 03C09Nb steel is also consistent with relatively low void density in fine and coarse bainite of 06C03Nb steel. These results would offer further evidence for the hypothesis that plasticity of martensite reduces the stress at the martensite-bainite interface thereby reducing the void nucleation.



Figure 6.61: Tensile secondary fracture surface of IA 12% M/A of (a) 03C09Nb and (b) 06C03Nb steel with fine bainite matrix



Figure 6.62: Void density in the microstructures for three conditions as measured from tensile secondary fracture surfaces close to the fracture end (≤ 200 µm)

6.11.4 Charpy impact behaviour: 03C09Nb

Figure 6.63 illustrates the results for the Charpy impact energy as function of test temperature for the three conditions considered in this work for 03C09Nb steel, i.e. bainite before intercritical annealing, 12 % M/A and 21 % M/A and the results are summarized in Table 6.15.

It can be observed that for the case of the as-austenitised bainite microstructure of 03C09Nb steel, formed upon cooling at 50°C/s (after the first thermal cycle), the upper shelf energy is ~ 300 J and the transition temperature is +40°C. As the volume fraction of M/A increases to 12 %, the impact behaviour improved, i.e. DBTT decreases to 12°C. At 100°C, an average impact energy of 300 J was recorded, and this was considered as the upper shelf energy. Finally, for the case of 21% M/A, the ductile-brittle transition behaviour further decreases with an upper shelf energy of ~ 300 J and a transition temperature of -10°C.



Figure 6.63: Charpy impact properties of 03C09Nb steel before inter-critical annealing and after intercritical annealing to form 12 % and 21 % M/A

Table 6.15: Summary of C	harpy impact test results fron	1 03C09Nb steel (obtained f	from curve fitting)
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Final microstructure	0.2% YS (MPa)	Lower shelf energy (J)	T95% Brittle (°C)	DBTT T50% Brittle (°C)	Upper shelf energy (J)
Bainite (50°C/s)	644 ± 8	3.5 ± 0.5	0	35	$305 \pm 20*$
IA - 12 % M/A	697 ± 6	4 ± 0.5	-10	12	$310\pm5^*$
IA - 21 % M/A	622 ± 12	4.5 ± 0.5	-25	-10	$200 \pm 7*$

*denotes data in the upper shelf energy range is obtained from one temperature i.e. 100°C

Mean and average of the deviations from mean value in Charpy results were calculated from three repeat tests at one temperature for each condition.
6.11.5 Summary of the Charpy impact behaviour

The impact behaviour upon intercritical annealing of coarse and fine bainite of 06C03Nb steel and bainite of 03C09Nb steel to form 12% M/A and 21% M/A are compared in Figure 6.64a and Figure 6.64b, respectively and the DBTT results are summarized in Figure 6.65. It is observed that for the case of 12% M/A, the Charpy impact behaviour has significantly improved for the 03C09Nb steel reducing the ductile-brittle transition temperature. Moreover, the range of transition from ductile to brittle has also decreased in the low carbon steel. It was shown that for these three cases, more than 80% prior austenite grain boundaries are covered by intercritically formed M/A. It is proposed that the plasticity of martensite in the 03C09Nb steel and 06C03Nb steel with a fine bainite matrix, i.e. cases where it is proposed that martensite plasticity is likely. However, the results for the 06C03Nb steel with a coarse bainite matrix do not show a significant change in DBTT as the M/A fraction increases from 12 to 21%. This is the case where martensite plasticity is proposed to be borderline.



Figure 6.64: Variation in the impact behaviour of (a) 12% M/A and (b) 21% M/A upon intercritical annealing of a high carbon and a low carbon steel with bainitic microstructure



Figure 6.65: Comparison of the effect of inter-critical M/A on the ductile-brittle transition temperature for the 06C03Nb steel and 03C09Nb steel cooled at 50°C/s

6.12 Summary

Finally, it is worth emphasizing that the results for the DBTT of the low carbon steel for the asaustenitised microstructure are not promising (i.e. DBTT of $+35^{\circ}$ C compared to -55° C for higher carbon fine bainite matrix). This could be attributed to the relatively coarse bainite in this steel and the low fraction of M/A, i.e. lack of cleavage crack deflection sites.

In summary, reducing the bulk carbon content of the steel had positive effects on the DBTT for the intercritically annealed material but a negative effect on the as-austenitised bainite. For future work, it would be of interest to try to find a microstructure solution that combines the best features of various microstructures. It is proposed that the ideal microstructure would have i) a fine bainite matrix (perhaps by alloy additions such as Mo, Nb, Cr which suppress the transformation start temperature to lower temperatures and ii) a low carbon level to decrease the strength of intercritically formed M/A constituents.

Chapter 7: Summary and Future Work

7.1 Summary

The current work had the objective of relating the local mechanical properties in the heat affected zone (HAZ) to the processing history (i.e. the welding parameters) which controls the local microstructure. The heat affected zones of actual welds have a complex microstructure gradient with continuous as well as discreet microstructural features in different regions, especially in the regions where the thermal field of weld passes overlap. In this work, bulk microstructures relevant to the coarse grain heat affected zone (CGHAZ) and intercritically reheated coarse grain heat affected zone (ICCGHAZ) were produced in the laboratory. Detailed characterization of microstructures, mechanical properties (tensile and Charpy impact), fracture behaviour and crack propagation were conducted on those samples. The following key results can be summarized based on the discussion presented in Chapter 5 and 6:

Microstructures relevant to CGHAZ

- I. For a cooling rate relevant to GMAW (~50°C/s) after a thermal cycle with a peak temperature of 1300°C, the austenite grains transform to multiple Bain groups separated by high angle grain boundaries, leading to a fine bainite structure with < 3% M/A constituents. For a slower cooling rate relevant to SAW (~5°C/s), the austenite transforms to coarse bainite microstructures with predominantly one Bain group with different bainite variants separated by low angle grain boundaries (< 15°) and high fraction of M/A constituents (> 7%). The morphology of the bainitic microstructure is strongly dependent on the transformation start temperature, i.e. higher the cooling rate, lower is the transformation start temperature and finer are the bainitic plates for a given alloy composition.
- II. Fine bainite microstructure has excellent yield and tensile properties and superior impact properties (DBTT of -55°C) due to the high density of high angle boundaries which provide obstacles to dislocation motion and deflect cleavage cracks leading to a higher propagation stress.

- III. Coarse bainite microstructures with relatively high amount of M/A constituents (≥ 7%) have reasonably good yield and tensile properties (> 550MPa), good ductility and work hardening. However, it has poor impact properties (a DBTT of 10°C). It is proposed that the high DBTT results from a due to a lack high angle boundaries and M/A particles which can act as crack deflection sites resulting in a low resistance to cleavage crack nucleation and propagation.
- IV. Bainite with a coarse lath size as well as a low fraction of M/A (< 5%) has reasonably good yield and tensile properties (≥ 640 MPa) but has a high DBTT of ~35°C due to absence of sufficient high angle boundaries and M/A constituents to deflect or restrict crack propagation.

Microstructures relevant to ICCGHAZ

- V. Upon reheating the bainitic microstructures to the intercritical region, austenite forms on prior austenite grain boundaries and at the M/A islands in the bainite. Upon cooling, the intercritical austenite transforms to M/A constituents which are predominantly martensite (> 90%). For volume fraction of ≥10%, a nearly continuous film of M/A constituents is found on the prior austenite grain boundaries, covering >80% of the prior austenite grain boundaries. The carbon concentration of the M/A constituents was estimated for different volume fractions of austenite using thermodynamic calculations, i.e. carbon content can be as high as ~0.5 wt.% for ~10% M/A in a 0.06 wt.% C containing steel. These microstructures are relevant to cases where the thermal field of the second pass overlap with the first pass and the temperature lies in the intercritical region.
- VI. The yield stress of these intercritical M/A containing microstructures is only weakly dependent (1 3% increase) on the fraction of M/A constituents. It is proposed that this relates to the competing effects of tempering of the bainitic matrix (softening) and strengthening due to the introduction of the hard M/A constituents. The ultimate tensile strength increases almost linearly with the fraction of M/A, consistent with previous results in the literature on dual phase steels.

- VII. The ductile-brittle transition temperature increases significantly to 40°C and 62°C for volume fraction of ~ 10 12% M/A in the fine and coarse bainite matrices, respectively. Fracture was observed to occur predominantly on the boundary between hard, elastic M/A and the soft bainitic matrix. In the case of ductile fracture, void nucleation was observed at the interface of bainite-M/A constituents. In the case of ~ 21% M/A in 06C03Nb steel, some recovery in the DBTT was observed and the formation of voids in tensile ductile fracture was suppressed. This could be rationalized by plasticity of the M/A constituents i.e. the stress at the martensite-bainite interface would be relaxed and thereby reduce the rate of void nucleation, also consistent with literatures on martensite plasticity in dual phase steels. Qualitative evidence of martensite plasticity was observed.
- VIII. For the low carbon 03C09Nb steel, the size and aspect ratio of the M/A constituents are smaller than that of the high carbon 06C093Nb steel for similar fraction of M/A. The yield strength and the UTS are observed to decrease with increase in fraction of M/A, however, the DBTT decreases upon intercritical annealing with increase in fraction of M/A. Void nucleation is drastically reduced with extensive plastic deformation of the microstructure. This would be consistent with plasticity in the martensite i.e. the decrease in the bulk carbon concentration of the steel manifests as a decrease in the carbon content of the martensite and the commensurate decrease in the flow stress of martensite.

From industrial perspective

The results from this research work indicate that the CGHAZ and ICCGHAZ of GMAW has a better mechanical response in terms of yield/tensile strength and the DBTT than that of SAW due to its faster cooling rate resulting in finer bainitic microstructures. The presence of nearly connected 10-12 % M/A constituents in the intercritically reheated regions of the CGHAZ of the multi-pass welds significantly increases the DBTT due to continuous crack path between hard, elastic M/A and soft bainitic matrix. Further increase in the volume fraction of the M/A constituents improves the DBTT of these regions. It is proposed that the beneficial effects of martensite plasticity on tensile ductility and the DBTT could be improved by

decreasing the bulk carbon concentration of the steel such that the 10-12 % M/A constituents have a lower carbon concentration providing a possibility of plastic deformation of martensite under stress. The preliminary work from this thesis suggest that this is feasible, although, the addition of microalloying elements such as Nb, Mo and Cr is required to lower the transformation start in order to produce a fine bainite microstructure. Additional studies are needed to assess how practical this would be for the industry. Nevertheless, the results from this work, provide guidelines for future development of linepipe steels (in terms of chemistry) and pipeline constructors on the input of different welding parameters (such as using low heat input welding processes etc.) on the properties in the heat affected zone of the base pipe.

7.2 Scope for future work

Based on the knowledge generated from this work, the following suggestions are provided for future research in this field:

- I. Advanced characterization such as atom probe tomography coupled with nano-indentation can be performed on the intercritical M/A to obtain experimental results of the composition and strength of intercritical M/A. Digital image correlation techniques can be used during tensile deformation to examine the strain partitioning between the bainite matrix and the M/A constituents to provide direct evidence on whether martensite plasticity occurs.
- II. In the current work, the combined effect of high angle boundaries and M/A constituents on the DBTT could not be modelled satisfactorily. It is suggested that future research be focused on developing quantitative relationships to describe the DBTT as a function of the characteristic length scale of the microstructure and some parameter and some parameter characterizing the size, aspect ratio, fraction and composition of M/A constituents in the microstructures.
- III. Research could be focused on developing bainite microstructures having superior strength and impact properties for cooling rates between 5 - 50°C/s by lowering the carbon content (< 0.06 wt.%) and adding suitable alloying elements such as Nb, Mo, Cr etc. such that the bainite transformation start temperature is less than < 530°C where fine bainite is produced.</p>

IV. Using the current results and results from additional experiments proposed above, it would be useful to develop chemistry dependent models using both mean field and phase field approach for the CGHAZ and ICCGHAZ to allow for predictions of the microstructure for different thermal histories and cooling paths.

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Appendices

Appendix A : Thermal gradient in a specimen inside Gleeble chamber

Several thermo-couples were attached alongside the control thermocouple at the centre during the process of optimization of the heat treatment parameters for the two different geometries: thin long strip tensile geometry and thick full size Charpy geometry. Figure A.1 shows the thermal gradient of the specimens at 1300°C.



Figure A.1: Thermal gradient inside Gleeble chamber with (a) low force jaws for thin tensile and (b) high force jaws for thick Charpy specimen for a peak temperature of 1300°C

A negligible temperature gradient (\pm 5°C) was recorded in the region \pm 6 mm from the centre control thermocouple of the thin long strip tensile geometry, shown in Figure A.1(a). Therefore, it will be assumed that the austenite grain size and Nb content in solid solution is constant throughout the gauge of tensile sample as machined from the Gleeble heat treatment sample. For the thick full size Charpy geometry, the temperature gradient was measured at different free span i.e. 20 mm, 30 mm, 40 mm (distance between the jaws). The result shows that the temperature gradient is steeper as the free span decreases. Figure A.2 shows the cooling rate results for different free span lengths. The maximum cooling rate obtained decreases with the increase in free span.



Figure A.2: Maximum cooling rate obtained upon free cooling and temperature gradient in the Charpy

specimen at different free-span

Appendix B : Image thresholding on microstructures

The M/A constituents in the intercritically annealed samples were characterized from the LePera etched microstructures by applying a threshold such that the fraction obtained from image analysis matched the fraction measured from dilatometry analysis. The thresholded images are overlapped with the original microstructures and the boundaries of the M/A are shown in Figure B.1 and Figure B.2 for coarse bainite and fine bainite matrix of 06C03Nb steel, respectively. It is observed from these images that this methodology to characterize the intercritically formed M/A can minimize the errors in measurement of the size and fraction of M/A constituents located at the prior austenite grain boundaries.



Figure B.1: Thresholded image (by ImageJ) using fraction from EBSD for (a) and dilatometry for (b-e) for (a) coarse bainite before intercritical annealing; intercritical annealing at (b) 725°C for 1 s, (c) 725°C for 20 s, (d) 725°C for 60 s and (e) 760°C for 60 s of a 06C03Nb steel


Figure B.2: Thresholded image using fraction from EBSD for (a) and dilatometry for (b-d) for (a) fine bainite before intercritical annealing; intercritical annealing at (b) 710°C, (c) 725°C and (e) 760°C for 60 s of a 06C03Nb steel





Figure C.1: (a-d) Examples of secondary crack propagation through <u>coarse bainite + IA 12% M/A</u> upon Charpy testing at -20°C, impact energy of ~5 J. Arrows marked by <u>orange</u> indicate cracks at M/A-bainite interface, yellow indicate cracking of M/A and blue indicates cracks within bainite



Figure C.2: (a-f) Examples of secondary crack propagation through <u>coarse bainite + IA 21% M/A</u> upon Charpy testing at -20°C, impact energy of ~5 J. Arrows marked by <u>orange</u> indicate cracks at M/A-bainite interface, <u>yellow</u> indicate cracking of M/A and <u>blue</u> indicates cracks within bainite