Phase Transformations in Nano-structured Bainitic Steels

by

Khushboo Rakha
B.Tech. Metallurgical and Materials Engineering
Indian Institute of Technology, Roorkee
(IIT Roorkee)

Submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy (Engineering)

Institute of Frontier Materials
Deakin University
December, 2016
I am the author of the thesis entitled:

**Phase Transformations in Nano-structured Bainitic Steels**

submitted for the degree of

**Doctor of Philosophy (Engineering)**

This thesis may be made available for consultation, loan and limited copying in accordance with the Copyright Act 1968.

'I certify that I am the student named below and that the information provided in the form is correct'

Full Name: **Khushboo Rakha**

Signed: [Signature Redacted by Library]

Date: 6/12/2016
DEAKIN UNIVERSITY
CANDIDATE DECLARATION

I certify the following about the thesis entitled

Phase Transformations in Nano-structured Bainitic Steels

submitted for the degree of

Doctor of Philosophy (Engineering)

a. I am the creator of all or part of the whole work (including content and layout) and that where reference is made to the work of others, due acknowledgment is given.
b. The work is not in any way a violation or infringement of any copyright, trademark, patent, or other rights whatsoever of any person.
c. That if the work has been commissioned, sponsored or supported by any organisation, I have fulfilled all of the obligations required by such contract or agreement.
d. That any material in the thesis which has been accepted for a degree or diploma by any university or institution is identified in the text.
e. All research integrity requirements have been complied with.

'I certify that I am the student named below and that the information provided in the form is correct'

Full Name: Khushboo Rakha

Signed: [Signature Redacted by Library]

Date: 6/12/2016
A father’s goodness is higher than the mountain;

A mother’s goodness is deeper than the sea.

- Japanese Proverb

I would like to dedicate my thesis to my wonderful parents:

Dr. Naresh Kumar Rakha

Mrs. Sangeeta Rakha
Acknowledgements

I would like to express my sincere gratitude towards my principal supervisor, Professor Peter Hodgson for always being an inspiration and for providing a great deal of support, guidance and encouragement during this work. I am indebted to my co-supervisors Dr. Hossein Beladi and Dr. Ilana Timokhina for their constantly available advice, guidance and help in all aspects of this study.

I would like to gratefully acknowledge Dr. Klaus-Dieter Liss of ANSTO, Australia; Dr. Dierk Raabe of Max Plank Institute, Germany and Dr. Xiangyuan Xiong of Monash University, Australia for their very supportive collaborations.

I greatly appreciate the support of the Deakin Advanced Characterisation Facility, especially, the trainings and help provided by Dr. Andrew Sullivan, Dr. Mark Nave and Rosey. I would also like to sincerely thank all the technical staff at IFM, Mr. Lynton Leigh, Mr. Rob Pow, Mr. John Vella and Mr. Alex for their constant help and ever smiling faces.

I highly value the friendship, technical help and support provided by my colleagues Dr. Saurabh Kabra, Subrata, Qi, Vadim, Satyaveer, Debasis and Aditya. I would like to specially thank my colleague and friend Shahriar Reza for his help in making samples for TEM and APT and constant support.

I would also like to acknowledge the generosity and support of the wonderful ladies I met at Deakin University specially Marilyn, Helen, Sandy, Leanne, Jasjeet, Pragati, Liyuan, Toktam and Mrunali.

I owe my deepest gratitude to my family and friends in India, specially my brother Sugandh, who always believed in me, sometimes more than I believed in myself. I would also like to convey my special regards to my Bhabhi, for her constant love and motivation.

Thank you Almighty for blessing me with this wonderful life!

Signature Redacted by Library

Khushboo Rakha
Abstract

The ongoing industrial quest for high performance and fuel efficiency has encouraged scientists to explore novel microstructures in steels. The aim is to achieve a high strength to weight ratio together with good ductility. A new generation of steels have been designed to transform into nanoscale bainite and retained austenite at low temperatures of 200°C - 350°C. The microstructure consists of very fine laths of bainite with a controlling scale of ~ 20 - 40 nm, hence the name ‘nanobainite’. This class of steel has been reported to offer a notable strength/toughness ratio of ~ 2.5 GPa/40 MPa m\(^{1/2}\) with a ductility of up to 30%. These very strong bainite steels have been formed by alloying with silicon to avoid the formation of cementite and its harmful effects on toughness.

The aim of the work presented in this thesis, was to comprehensively understand the phase transformation behaviour, to be able to control the characteristics of nanostructured bainite. A substantial amount of research in the last few decades has revealed a significant amount of information about the mechanism of nanobainite formation. However, there remain some unresolved issues, which are holding up further development of this nanostructured steel. Two of these, carbon redistribution during phase transformation and formation of bainite from plastically deformed austenite have been taken up systematically in this thesis.

The evolution of low temperature bainite transformation has been monitored using in situ neutron diffraction. This study provides strong evidence of carbon redistribution in bainitic ferrite and retained austenite during the transformation. The fact that there is no carbon partitioning prior to the onset of bainite transformation, has been confirmed by direct observation. Atom probe tomography (APT) was further employed on the fully transformed microstructure to study the carbon distribution at the atomic level. APT revealed the existence of carbide particles even with the addition of 1.5 mass% silicon. Transmission electron microscopy (TEM) further confirmed the existence of strain fields around the bainite laths causing carbon segregation at the interface boundary, which was also observed through APT.
In the next section, the role of plastic deformation in the mechanical stabilisation of austenite was studied. A series of thermo-mechanical schedules were applied to obtain different microstructures by changing the ausforming parameters, i.e. ausforming temperatures and deformation strains. It was established that while a small amount of strain stimulated the bainite transformation, higher strain values mechanically stabilised the austenite and thus retarded the transformation. An increase in the ausforming temperature resulted in a decrease in the critical amount of strain that could stimulate bainite formation. The morphology of bainite formed subsequent to ausforming was also studied in details through TEM.

Further, a TWIP steel with a similar stacking fault energy to the nanobainite steel, was deformed to understand the mechanism of austenite stabilisation at the substructure level. TEM of the TWIP steel confirmed the existence of twins, dislocation pile ups and sharp dislocation walls when a strain larger than the critical strain was applied. The advance of glissile interfaces, which is essential to displacive transformations can be rendered sessile by the accumulation of dislocation debris and other strong defects.

To complete the understanding of the effect of austenite conditioning on the phase transformation mechanism, the changes in the crystallography of the transformed bainite were studied. A back-calculation approach was employed to determine the effect of prior austenite grain size and thermo-mechanical treatment on the orientation relationship of the product bainite to the parent austenite. A decrease in the austenite grain size weakened the variant selection, while it did not affect the orientation relationship between the parent austenite and product bainite phase. Variant selection became stronger with an increase in the deformation strain. An increase in the deformation strain caused a progressive change in the orientation relationship, which was attributed to the dislocation substructure formed due to ausforming, which divides a prior austenite grain into several sub-grains, locally having different orientations.
Table of Contents

Acknowledgements ........................................................................................................... V

Abstract ................................................................................................................................. VI

Table of Contents .................................................................................................................. VIII

List of Figures ......................................................................................................................... XIII

List of Publications .................................................................................................................. XIX

Chapters

1 Introduction ......................................................................................................................... 1

1.1 Research objectives ....................................................................................................... 3

1.2 Research outline ............................................................................................................. 4

2 Literature Review ................................................................................................................. 6

2.1 Introduction ................................................................................................................... 6

2.2 Advanced High Strength Steels (AHSS) ......................................................................... 7

2.3 Bainite ............................................................................................................................ 10

2.3.1 Transformation mechanism ....................................................................................... 11

2.3.2 The $T_0$ concept (Incomplete reaction phenomena) .................................................. 13

2.3.3 Role of alloying elements ......................................................................................... 14

2.4 Low temperature bainite .............................................................................................. 17

2.4.1 Steel design .............................................................................................................. 18

2.4.2 Stability of retained austenite ................................................................................... 19
2.5 Unresolved issues ........................................................................................................... 21
  2.5.1 Carbon redistribution in nanostructured bainite ........................................ 21
  2.5.2 Transformation from plastically deformed austenite ............................ 23
  2.5.3 Crystallography of nanobainite ................................................................. 26
2.6 Summary ....................................................................................................................... 27
3 Experimental Methodology ......................................................................................... 28
  3.1 Introduction ............................................................................................................... 28
  3.2 Alloy Design .......................................................................................................... 28
  3.3 In situ Neutron Diffraction ................................................................................. 30
    3.3.1 Rapid Sample Quencher (RSQ) ................................................................. 30
    3.3.2 WOMBAT (High intensity diffractometer) ............................................. 32
    3.3.3 Analysis methods ....................................................................................... 33
  3.4 Atom Probe Tomography ..................................................................................... 35
    3.4.1 Sample preparation ..................................................................................... 36
    3.4.2 Data acquisition ......................................................................................... 36
    3.4.3 Data analysis ............................................................................................... 37
  3.5 Transmission Electron Microscopy ..................................................................... 37
    3.5.1 Sample preparation ..................................................................................... 38
    3.5.2 Imaging and analysis .................................................................................. 38
  3.6 Servotest (Thermomechanical treatment) ........................................................... 39
  3.7 Metallography and optical microscopy ............................................................... 42
4 In situ study of phase transformations through Neutron Diffraction .... 47

4.1 Introduction................................................................. 47

4.2 Experimental methods ................................................... 48

4.3 Results............................................................................. 51

4.3.1 In situ Neutron Diffraction........................................... 51

4.3.2 Atom Probe Tomography............................................. 62

4.3.3 Transmission Electron Microscopy................................ 64

4.4 Discussion....................................................................... 65

4.4.1 Evolution of bainitic ferrite ........................................ 65

4.4.2 Presence of carbides/clusters....................................... 67

4.4.3 Coherent grain size and micro-strain............................ 68

4.5 Summary......................................................................... 69

5 Effect of ausforming on transformation kinetics and characteristics of nanobainite .................................................. 71

5.1 Introduction..................................................................... 71
5.2 Experimental methods ................................................................. 72
5.3 Results .......................................................................................... 75
  5.3.1 Microstructural evolution .......................................................... 75
  5.3.2 Kinetics of phase transformation .............................................. 80
  5.3.3 Transmission Electron Microscopy (TEM) ............................... 82
5.4 Discussion .................................................................................... 88
5.5 Summary ...................................................................................... 92

6 Effect of austenite conditioning on the crystallography of nano-structured bainite ................................................................. 94
  6.1 Introduction .................................................................................. 94
  6.2 Experimental procedure ............................................................... 95
  6.3 Approach .................................................................................... 98
  6.4 Results ........................................................................................ 101
    6.4.1 Effect of prior austenite grain size on variant selection and orientation relationship ................................................................. 105
    6.4.2 Effect of thermomechanical treatment on variant selection and orientation relationship ................................................................. 107
  6.5 Discussion .................................................................................. 110
    6.5.1 Effect of prior austenite grain size on variant selection and orientation relationship ................................................................. 110
    6.5.2 Effect of thermomechanical treatment on variant selection and orientation relationship ................................................................. 112
  6.6 Summary .................................................................................... 114
7 Conclusions and Future Work................................................................. 116

7.1 Conclusions...................................................................................... 116

7.2 Suggestions for future work.............................................................. 118

References .............................................................................................. 120
List of Figures

Figure 2.1: Global formability diagram, i.e. the strength versus ductility plot showing properties of existing AHSS and conventional steel grades .................. 9

Figure 2.2: Illustration of upper and lower bainite. Carbon partitioning and precipitation has been demonstrated [11] .................................................................................................................. 10

Figure 2.3: Illustration of the $T_0$ and $T_0'$ curve. $T_1$ is the temperature corresponding to the free energy curves [11] .................................................................................................................. 14

Figure 2.4: Interstitial carbon sites in face-centred cubic austenite [60]. ............ 16

Figure 2.5: Bright field TEM image of lamellar structure of bainite formed after isothermal holding at 200°C for 10 days [65] ........................................................................................................... 17

Figure 3.1: Rapid sample quencher; the setup includes the following parts: (a) Halogene lamps; (b) Liquid nitrogen flow; (c) Quartz tube; (d) Power supply; (e) Aluminium casing; (f) Thermocouple holding the sample; (g) Monochromatic neutron beam .................................................................................................................. 31

Figure 3.2: The high intensity powder diffractometer, WOMBAT ..................... 32

Figure 3.3: A representative Rietveld refinement fit for a particular scan ............ 35

Figure 3.4: Servotest thermo-mechanical treatment simulation unit (TMTS) and salt bath furnace .................................................................................................................. 40

Figure 3.5: Diagram of an axi-symmetric sample with thermocouple hole ......... 42

Figure 3.6: Example of point counting method used for the calculation of volume fraction .................................................................................................................. 43

Figure 4.1: Schematic diagram of heat treatment during in situ Neutron Diffraction .................................................................................................................. 49
Figure 4.2: Relative change in length of steel depicting phase changes in response to in situ heat treatment, as measured by a Dilatometer...................................................... 50

Figure 4.3: Integrated peak intensities for the 1st cycle of in situ heat treatment, illustrating the evolution of bainitic phase during isothermal holding.............. 51

Figure 4.4: First four peaks at different time intervals; t = 0 is the beginning of isothermal holding.......................................................... .................................................. 52

Figure 4.5: Azimuthally integrated peak intensities depicting the evolution of different phases during the complete cycle of in situ heat treatment. ............. 53

Figure 4.6: Volume fraction of bainitic ferrite over log scale of time, calculated from in situ neutron diffraction. The plot represents a typical Avrami equation. 54

Figure 4.7: Linear form of Avrami equation, with the constant ‘n’ as 1.7 depicting a nucleation controlled transformation mechanism.................................................. 55

Figure 4.8: Peak shift and peak asymmetry evident in γ-200 depicting enrichment of carbon in austenite phase and inhomogeneous distribution of carbon in untransformed austenite .......................................................... 56

Figure 4.9: Peak broadening and asymmetry in α-200 suggesting refinement in microstructure and internal stress. No peak position shift was observed in α-20057

Figure 4.10: Peak widths in terms of Full Width Half Maximum (FWHM) of first 10 peaks corresponding to ferrite and austenite phase at ~480 minutes from start of bainitic transformation .............................................................. 58

Figure 4.11: Phase fractions calculated through Rietveld fitting [110] ............... 59

Figure 4.12: Rietveld analysis of lattice parameter and lattice strain evolution of (a) ferrite phase, (b) austenite phase during phase transformation at 300°C. The windows represent the peak characteristics of α(200) and γ(200) at 360 min elapse of transformation, respectively.............................................................. 60
Figure 4.13: Micro-strain changes in both austenite and bainitic ferrite phase calculated through Rietveld Analysis of in situ Neutron Diffraction experiment. 61

Figure 4.14: Evolution of coherent grain sizes in both austenite and bainitic ferrite phases calculated through Rietveld analysis of in situ neutron diffraction experiment. ................................................................. 62

Figure 4.15: APT characterization of austenite and bainitic ferrite phases: (a) carbon atom map showing carbon distribution along the analyses needle, (b) corresponding 6.95 at.% iso-concentration surface, (c) carbon concentration profile along the z-axis of the needle analysed, (d) carbon concentration profile along the z-axis of the selected are in (a). .............................................................................................................. 63

Figure 4.16: Reconstruction of APT data using Integrated Visualization and Analysis Software (IVAS). Segregation of carbon atoms at austenite/bainitic ferrite interface is evident........................................................................................................ 64

Figure 4.17: Bright Field TEM images of (a) Bainitic ferrite colonies with retained austenite films and (b) Bainitic ferrite and retained austenite layers within the pack or colony. .................................................................................................................. 65

Figure 4.18: Schematic of the process of carbon rejection from supersaturated bainite. Here the austenite next to bainitic plates (red) are enriched in carbon and the remaining austenite phase away from the bainitic plates (pink) have carbon content close to the nominal composition ................................................................. 66

Figure 4.19: Progression in carbon content (in wt.%) with time in austenite phase calculated through the peak position changes in γ-200. ...................................................... 67

Figure 5.1: Schematic representation of the systematic thermo-mechanical treatment employed to study the effect of ausforming of nanobainite transformation. ........................................................................................................... 73

Figure 5.2: Evolution of the nanobainite microstructure with time after ausforming 30% at 570°C and isothermally holding at 350°C for different holding times as mentioned on each micrograph. ..................................................................................... 76

XV
Figure 5.3: Evolution of the nanobainite microstructure with increase in deformation strain after ausforming at 570°C and isothermally holding at 350°C for 12 hours. The amount of strain has been mentioned on each micrograph. .......... 78

Figure 5.4: Evolution of the nanobainite microstructure after ausforming at different temperatures with a deformation strain of 15% and isothermal holding at 350°C for 30 min. The ausforming temperature has been mentioned on each micrograph... 79

Figure 5.5: Plot of the volume fraction of bainite over the isothermal holding temperature (log scale) for samples ausformed at 570°C with different deformation strains................................................................. 80

Figure 5.6: Plot of the volume fraction of bainite formed after 60 minutes of isothermal holding over the deformation strain applied for 3 different ausforming temperatures of 350°C, 570°C and 850°C, respectively................................. 82

Figure 5.7: TEM bright-field (BF) images of lath bainitic ferrite (αb) and retained austenite (γ) for a sample ausformed at 570°C with 7% reduction and isothermally held at 350°C for 1 hour. The diffraction pattern represents a BCC structure, i.e. bainitic ferrite. ................................................................. 84

Figure 5.8: TEM bright-field (BF) image of lath bainitic ferrite, retained austenite and mechanical twins for a sample ausformed at 570°C with 15% reduction and isothermally held at 350°C for 6 hours. The diffraction pattern represents typical mechanical twins. ................................................................. 85

Figure 5.9: TEM micrograph of lath bainitic ferrite, retained austenite and carbide particles in bainitic ferrite for a specimen, ausformed at 570°C with 30% reduction and isothermally held at 350°C for 1 hour. The diffraction pattern evidences the existence of carbide. ................................................................. 86

Figure 5.10: TEM micrographs of TWIP steel deformed with 7% reduction at 300°C. The micrographs demonstrate the formation of stacking faults, dislocation cells and dislocation bands................................................................. 87
Figure 5.11: TEM micrographs of TWIP steel deformed with 15% reduction at 300°C. The micrographs demonstrate the formation of twins, dislocation pile up, interaction of dislocations and twins and formation of sharp dislocation walls. .. 88

Figure 6.1: Schematic representation of heat treatment to study the effect of prior austenite grain size on the variant selection and orientation relationship between the parent austenite and bainitic ferrite laths...................... 96

Figure 6.2: Prior austenite grain size (in µm) measured after austenitizing at three different austenitization temperatures. ............................................................... 97

Figure 6.3: Schematic of thermo-mechanical treatment conducted to investigate the effect of compression strain on the variant selection and orientation relationship. ................................................................................. 98

Figure 6.4: Band contrast map and IPF map (austenite phase in a selected grain), for a sample austenitized at 1000°C followed by isothermal holding temperature of 200°C for 10 days ................................................................. 102

Figure 6.5: EBSD data analysis for the grain selected in figure 6.4 to depict: a) IPF map in ND plane; b) Rolling direction and transverse direction; c) IPF colour coding and d) {001} PF map of the bainite variants for the selected prior austenite grain. ........................................................................................................ 102

Figure 6.6: (a) Histogram of summation of mutual misorientation angle (SMMA) versus austenite candidate variants in the prior austenite grain selected in figure 6.4; (b) The minimum SMMAs of 5 prior austenite grains; (c) The corresponding average of minimum SMMA of 5 grains for 5 known orientation relationships 104

Figure 6.7: Inverse pole figure map and pole figure of bainite phase for a given austenite grain transformed with an austenitizing temperature of 850°C followed by isothermal transformation at 200°C for 10 days..................................................... 106

Figure 6.8: Inverse pole figure map and pole figure of bainite phase for a given prior austenite grain transformed at an austenitizing temperature of 1200°C followed by isothermal transformation at 200°C for 10 days..................................................... 106
Figure 6.9: Average of minimum SMMA for five known orientation relationships in case of three different austenitization temperatures (i.e. prior austenite grain sizes).

Figure 6.10: Inverse pole figure map and pole figure for bainite phase in a given parent austenite transformed after austenitization temperature at 1000°C followed by deformation of 7% at 570°C and isothermal transformation at 200°C for 10 days.

Figure 6.11: Inverse pole figure map and pole figure for bainite phase in a given austenite grain transformed after austenitization temperature of 1000°C followed by deformation of 15% at 570°C and isothermal transformation at 200°C for 10 days.

Figure 6.12: Average minimum SMMA for the five known orientation relationships at different strains transformed at 200°C.
List of Publications

1. On low temperature bainite transformation characteristics using *in situ* neutron diffraction and atom probe tomography

   Khushboo Rakha, Hossein Beladi, Ilana Timokhina, Xiangyuan Xiong, Saurabh Kabra, Klaus-Dieter Liss, Peter Hodgson


2. Growth of bainitic ferrite and carbon partitioning during the early stages of bainite transformation in a 2 mass% silicon steel studied by *in situ* neutron diffraction, TEM and APT

   I.B. Timokhina, K.D. Liss, D. Raabe, K. Rakha, H. Beladi, X.Y. Xiong, P.D. Hodgson

   *Journal of Applied Crystallography* 49 (2016) 399-414

3. *In situ* Neutron Diffraction study of nanobainitic steels in conjunction with Transmission Electron Microscopy

   K. Rakha, H. Beladi, S. Kabra, S. Metrustry, S. Pullen, I. Timokhina, P.D. Hodgson, K.D. Liss

   *TMS 2012*, Orlando, Florida

4. Effect of ausforming on phase transformations in low temperature, high strength nanostructured bainitic steels CAMS 2013, Sydney, NSW

   K. Rakha, H. Beladi, I. Timokhina, P.D. Hodgson

   *CAMS 2013*, Sydney, NSW
Steels have been argued to be one of the most important materials because of their abundance and wide range of properties, which can be controlled by changing the chemical composition and processing parameters. Steels are still the most successful of all materials, with 1.3 billion tonnes being consumed annually in improving the quality of life. The automotive industry has been demanding in recent times, advanced high strength steels (AHSS), because of three principle reasons: a) to reduce passenger car weight leading to the decreased fuel consumption and consequently to reduce environment polluting emissions; b) to improve vehicle safety by improved crash worthiness of the body and c) to face the strong competition from other light-weight metals and plastics [1, 2].

AHSS steels are broadly characterized as having a yield strength of generally more than 550 MPa and a tensile strength of more than 780 MPa. DP (Dual phase), TRIP (Transformation Induced Plasticity), complex phase and martensitic steels fall into this category. These usually consist of soft ferritic matrix containing islands of martensite, bainite or bainitic-austenitic islands [3, 4]. The drawback of present conventional high strength steels is that such high strength levels are generally achieved on the expense of ductility. This is a particular disadvantage in metal forming operations, which demand a significant amount of ductility.

A promising mechanism to achieve high strength without compromising ductility is through refinement of the microstructure through heat treatment. A recent class
of nano-structured bainitic steels has been formed by isothermal transformation at low temperatures ranging from 200-350°C. The benefit of the low transformation temperature is that the plates of bainite are extremely fine, only 20-40 nm thick, making the material very strong. These nano-structured bainitic steels are reported to offer an excellent strength-toughness combination of 2.3 GPa – 30 MPa m$^{1/2}$ with 30% ductility [5-7]. These notable properties are mainly due to the benefit of formation of nano-sized bainitic ferrite plates, in addition to a TRIP aided microstructure with retained austenite. These steels have incredible applications even outside the automobile industry such as construction, offshore, aero-space and defence applications [8].

Nano-structured bainite has been associated with the latest breakthrough technologies because of tremendous developments in its phase transformation theory. The carbon that is partitioned from bainitic ferrite during isothermal transformation, stabilises the residual austenite, enabling it to be retained at ambient temperature. Addition of silicon in concentration of about 1.5 wt% can be very beneficial. Silicon is generally present in steels as a result of the deoxidation reactions involved in the steelmaking process. However, it also retards the formation of cementite from austenite, making it possible to obtain a carbide-free microstructure of just bainitic ferrite and carbon enriched austenite [9]. Due to very low transformation temperature, carbon diffusion becomes very sluggish and hence the bainite transformation becomes a very slow process. Although, aluminium and cobalt have been added to the originally proposed composition to accelerate the kinetics, yet it takes several days for the completion of bainitic transformation at lower temperatures.

The morphology of the retained austenite is very important in nanobainitic steels. The phase can be present in the microstructure in two forms: blocky and film types. The best elongation behaviour has been observed when the austenite is in the form of films between the subunits of bainite rather than as blocks between sheaves of bainitic ferrite [10]. The blocky austenite tends to transform into martensite in the early stages of deformation and leads to early fracture. While the film austenite is fine in scale and stabilises by carbon enrichment. The absence of cementite reduces
the chances of cleavage or void nucleation. The films of austenite dispersed between the ferrite further fence the propagation of cracks.

Though much research has been done on bainite formation, there still remain some key issues that have not yet been subjected to a full quantitative treatment.

1. The theory of diffusion controlled growth rate cannot be applied to bainitic transformation because the quantified growth rate of individual bainite plates is much higher than expected from the theory of diffusion controlled growth \[11, 12\]. It is clear that bainitic ferrite is formed with a large supersaturation of carbon, but there remains a possibility of some interstitial diffusion during growth \[13\].

2. A better treatment of auto-catalytic nucleation is required. The existing kinetics theory is only capable of quantifying the bainite fraction received during the isothermal transformation of austenite in steels where the reaction is not accompanied by carbide formation. The formation of carbides cannot be ruled out even with the addition of silicon.

The result of defects induced by plastic deformation, on the kinetics and microstructure of bainite, is a subject which is not well comprehended yet. It has been established that displacive transformations are achieved by the progress of glissile interfaces, which can be rendered sessile by the accumulation of dislocation debris \[13\]. To complete the understanding of the effects of plastic deformation of austenite, it is important to also study the changes in orientation relationship and variant selection due to the ausforming treatment.

### 1.1 Research objectives

The overall objective of this study is to create a better understanding of the mechanism of phase transformation and to potentially improve the phase transformation kinetics through changing the austenite conditioning and application of deformation.
A great deal of advanced research in the field of nano-bainitic steels has revealed substantial information about the mechanism of the bainite transformation in steels. All the elements of the theory are useful in the designing of new alloys and interpretation of a variety of experimental data. The redistribution of carbon and the formation of bainite from the plastically deformed austenite remain the two major difficulties, which need to be understood through careful experimentation and interpretation [13].

The research questions have been enumerated below:

1. What are the morphological characteristics of retained austenite and ferritic bainite and their dependence on experimental parameters?

2. How is carbon partitioned between bainitic ferrite and remaining austenite during the phase transformation?

3. What is the nucleation and growth behaviour of transformation at the sub-structure level?

4. What is the effect of ausforming on the transformational kinetics, morphology and crystallography of thus formed bainite?

5. What are the optimal parameters for deformation to accelerate the kinetics of low temperature bainite transformation, particularly, in terms of austenitizing temperature, deformation temperature and amount of strain?

1.2 Research outline

In the present study, an attempt has been made to systematically address the research questions by the following framework:

1. Neutron Diffraction has been employed to monitor the in situ phase transformation during the formation of nanobainite at an isothermal temperature of 300°C [14]. The diffraction peak characteristics have been quantified to the volume fraction of different phases, lattice parameters, carbon redistribution in both phases and micro-strains evolved during the
phase transformation. Atom probe tomography (APT) was further employed to study the carbon distribution at the atomic level and to investigate the presence of carbides. Transmission electron microscopy (TEM) was also used to examine the morphology formed.

2. A systematic set of thermo-mechanical treatments were performed to study the effect of ausforming on the kinetics and morphology of bainite formation. Deformation strains varying from 7% to 60% were employed at different deformation temperatures to present a comprehensive analysis. Optical microscopy was used to calculate the volume fraction and establish the kinetics. Furthermore, TEM was employed to study the morphological features in the ausformed bainite.

3. A TWIP (Twinning induced plasticity) steel was used to study the austenite substructure formed due to ausforming with different amounts of strains [15]. Considering that the TWIP steel is fully austenitic at room temperature, it was deformed at a temperature of 300°C, which had the same stacking fault energy as that of nanobainite deformed at a temperature of 570°C. TEM was performed on the deformed TWIP steel to inspect the substructural features.

4. A recent back calculation method was employed to measure the orientation relationship between transformed bainite and parent austenite more accurately [16]. The back calculation method was also used to study the changes in the orientation relationship because of the austenite conditioning before bainitic phase transformation. The changes in variant selection due to austenite conditioning were also established.
2 Literature Review

2.1 Introduction

This thesis describes the characterisation of nanostructured bainitic steel, which is known to exhibit a very high strength (2.3 GPa), while maintaining notable toughness (30 MPa m$^{1/2}$) and ductility (30%), depending on the transformation temperature [5, 6, 17]. These high-silicon high-carbon steels consist of laths as fine as 20 nm, separated by thin films of austenite (~60 nm) [8]. On a coarser scale, the microstructure looks like wedge shaped sheaves of bainite and small blocks of residual austenite [18].

Advanced research in the field of nano-bainitic steels has produced substantial information regarding the formation of this nano-scale microstructure. The existing theory has been used successfully in the design of commercial steels. An example is a carbide free bainitic rail steel with remarkable wear resistance, rolling-contact fatigue strength and low temperature toughness [19]. While elements of the theory of low temperature bainite transformation have been in use, there remain some unresolved issues, which are holding up further technological advancements [13].

In general, to improve the industrial viability of nanobainitic steel, a systematic and comprehensive study is required to investigate the mechanism of transformation in terms of the following attributes:
1. Nature of transformation, displacive or diffusional.
2. Morphology of such formed bainitic ferrite and retained austenite.
3. Nucleation and growth behaviour of transformation at the micro-structural level.
4. Precipitation of carbide.
5. Effect of ausforming on transformation kinetics and nanobainite characteristic.

This review of literature describes the recent advancements in high strength steels in general and nanobainite in particular. In this chapter, a basic theory has been reported describing the transformation mechanism, morphology, crystallography, role of alloying elements, stability of retained austenite and the effect of ausforming on nanobainite. Here, a critical assessment of prior published literature has been presented and the gaps have been identified, which form the basis for the studies conducted in the following chapters.

2.2 Advanced High Strength Steels (AHSS)

Steels are well known to show a large variety of microstructures in response to temperature and deformation (thermo-mechanical) treatments. The exploitation of these microstructural features of steels to increase the strength and ductility has led to the development of Advanced High Strength Steels (AHSS).

Multiphase steels play an important role in the development of AHSS. These usually consist of two or more phases with relatively different mechanical properties thus giving a composite effect of high strength as well as good elongation. Multiphase steels, chiefly Dual Phase (DP) and Transformation Induced Plasticity (TRIP) steels account for more than 40% of steels used in the automotive industry because of possibly the best combination of strength and ductility [20].

Dual Phase (DP) steels are characterized by a microstructure consisting of 10-40% of hard martensite (or martensite-austenite) phase in a soft ferrite matrix, achieving
ultimate tensile strength (UTS) in the range of 500-1200 MPa [21]. The strength in this microstructure is controlled by the amount of martensite phase and the elongation is secured by size and distribution of the soft ferrite phase. TRIP-aided multiphase steels have been formed with a microstructure consisting of ferrite, retained austenite, bainite and sometimes martensite [22]. The retained austenite in these steels, transforms into martensite during deformation, resulting in the delay in the onset of necking [22-24].

Both DP and TRIP grades offer the kind of properties automotive manufacturers require [25]. TRIP grades exhibit a greater increase in energy absorption compared to DP grade of similar tensile strength at low and high strain rates. The TRIP grades demonstrate superior formability properties, offering solution to more complex shaped crash components. The increased uniform ductility of TRIP-aided steels is accredited to the process of plastic accommodation close to martensite plates [26]. Uniform elongation during plastic straining plays an important role in the significant improvement of ductility, because rapid transformation of austenite into martensite has been observed to be detrimental to ductility. Hence, the stability of retained austenite is the most important parameter to control in TRIP steels.

The bainite microstructure in TRIP steels is formed by quenching austenite or inter-critical austenite/ferrite to a temperature in the bainite region and isothermally holding there onwards. Along with bainitic transformation, the carbon partitions [27, 28] and, hence, enriches austenite located in the vicinity of bainitic ferrite. As a result, the austenite is stabilized and does not transform into martensite on cooling. The holding time and its variation in the bainite transformation temperature region has a strong effect on the stability of retained austenite, thus, affecting the final mechanical properties of steel [27].
Complex Phase (CP) steels also belong to the group of steels with high UTS, even higher than 800 MPa. Their microstructures are very similar to TRIP steels with addition of small quantities of Nb, Ti and V, promoting the precipitation strengthening effect. CP steels with bainite matrix have superior formability because of the hardness difference between bainite and martensite [29]. Another class of martensitic steels, provide the highest UTS of up to 1500 MPa. These require very critical criteria for chemical composition selection and processing technology design.

Mechanical twinning is one of the three modes by which steels can be deformed permanently at ambient temperature, without diffusion. Here, the crystal structure is maintained but the twinned region (region between two parallel twins) is reoriented in the process. Twinning Induced Plasticity (TWIP) steels, exploiting this particular property, show extraordinary ductility. TWIP alloys are austenitic throughout the mechanical deformation process and typically contain a large amount of manganese and some aluminium and silicon with nitrogen essentially as an impurity. The UTS of TWIP steels can be as high as 1100 MPa with an elongation of 60-95% [30]. These steels have high potential in the safety of automobiles by absorbing energy caused due to crashing.
2.3 Bainite

Bainite is a plate-shaped microstructure product of non-equilibrium transformation of austenite, which is formed at cooling rates fast enough to avoid the formation of diffusion-controlled transformation products (i.e. ferrite and pearlite), slowed down and typically isothermally treated to avoid the diffusionless transformation into athermal martensite.

Morphologically, bainite can be categorized into upper and lower bainite (Figure 2.2). Upper bainite consists of clusters of platelets of ferrite, which share identical crystallographic orientation and are closely linked to the parent austenite phase in which they grow. The standard bainitic ferrite plate usually measures to 10 µm (length) \( \times \) 0.2 µm (thickness) [11]. Elongated cementite particles cover the periphery of these plates. However, the steel carbon concentration determines quantity and continuity of the cementite layer. With the lowering of transformation temperature, some of the carbon precipitates within the ferrite plates as cementite leading to the lower bainite structure.

![Diagram of upper and lower bainite](image)

Figure 2.2: Illustration of upper and lower bainite. Carbon partitioning and precipitation has been demonstrated [11]
In general, the bainite transformation is a para-equilibrium reaction, in which the substitutional alloying elements are unable to partition, although carbon redistributes between phases until its chemical potential becomes uniform throughout [11]. The diffusion coefficient of carbon in ferrite is greater than that in austenite. The transition from upper to lower bainite depends on the comparison between the times required to decarburise or diffuse out carbon from supersaturated ferrite plates and the time required to precipitate cementite within the plates. If the decarburisation process dominates, upper bainite is predicted whereas relatively rapid carbide precipitation within the ferrite leads to the microstructure of lower bainite.

Products of austenite transformation, which take shape below the temperature of reconstructive transformations are termed as Widmanstatten ferrite, bainite and martensite. It is widely known that the bainite phase is seen at temperatures lower than that necessary for the formation of Widmanstatten ferrite. Surface relief induced by the transformation has been obvious in steels that have transformed into Widmanstatten ferrite or bainite. Besides, the decisive factor in the evolution of these intermediate displacive transformation products is the kinetics associated with the carbon partitioning. The ferrite normally contains much less quantities of equilibrium carbon as compared to that in the austenite.

2.3.1 Transformation mechanism

The thermodynamic conditions, that accompany growth, are the deciding factors for a nucleus to develop to bainite. In the event of unsustained diffusionless growth, the creation of Widmanstatten ferrite occurs rather than bainite. A stored energy in Widmanstatten ferrite of about 50 J mol\(^{-1}\) has been assumed [31], compared with that of bainite at around 400 J mol\(^{-1}\). The chemical free energy change must be sufficient so that it surpasses the stored energy for a transformation to occur. Higher levels of stored energy in bainite were rationalized on the basis of the lack of favourable strain interactions within the bainite sheaves [31].

High stored energy estimated in the bainite requires high growth rate, which has not been evident in the experiments. Thus, as a consequence, carbon super-saturation
in the bainitic ferrite bears ‘no conclusive evidence’ [32]. Oblak & Hehemann had earlier proposed that the bainite growth is fast, though, occurs in small steps [33]. Another theory advised that bainite forms, initially, as Widmanstatten ferrite plates followed by the formation of a mixture of the ferrite and the cementite in the inter-adjacent spaces [34].

At low temperatures, bainite is promoted over pearlite in eutectoid Fe-C alloys, not due to a martensite-like transformation mode, but is rather related to the high asymmetry in the Fe-C phase diagram [35]. Reducing the temperature leads to the increase in carbide formation, which may accelerate the edgewise growth. Precipitation of carbides takes place around the advancing bainite plate tips, which results in a shorter diffusion distance for carbon, away from the advancing tip [32].

Carbon diffusion at the austenite-bainite interface is believed to cause an increase in the free energy change, thereby facilitating the formation of bainite above the $M_s$ temperature [36]. Bhadeshia et al. suggested that bainite may grow by a martensite like growth mechanism, which is diffusionless and followed by, or along with, carbon partitioning into austenite [37], as illustrated in figure 2.2. Although the nature of bainite transformation in terms of “diffusion-controlled growth” or “diffusionless growth” is still debated, the overall kinetics are, indeed, agreed to be controlled by the diffusion of carbon. Similar models were also put forward by Muddle & Nie [38] and Saha et al. [39].

An in situ technique of TEM was later employed by Kang et al. to investigate the mechanism of bainite growth [40]. They reported that, in a number of alloys studied, a bainitic embryo is made of basic transformation units. These units are either a group of stacking faults or, in two dimensions, a series of parallelograms of different sizes. The thickening of these bainite embryos takes place through shear along the stacking fault planes or twinning planes. The bainite embryo is elongated by the formation of new transformation units at both tips of the bainite plate [41]. Three-dimensional morphology of bainite is like a convex lens. It is controlled by the diffusion of solute atoms during the transformation. As the growth rate is much lower than that of martensite, it is therefore, detectable.
2.3.2 The $T_0$ concept (Incomplete reaction phenomena)

Fully bainitic steels are devoid of allotriomorphic ferrite and almost free from athermal martensite. Thus, the structure is made of bainitic ferrite and may contain retained austenite and carbides. However, carbides are usually suppressed by alloying with Si and other elements like Al and P. Formation of carbides plays an important role in the mechanical properties achievable in different varieties of steel. Growth of bainite through a diffusionless mechanism has to take place at a temperature just below $T_0$, when the free energy of bainitic ferrite and adjacent austenite are the same [42], as shown in Figure 2.2.

To take into account the strain energy of bainitic transformation by shear mechanism, strain energy is added to the free energy curve, giving the $T_0'$ curve. During the isothermal transformation of austenite, the excess carbon in the bainite partitions into the remaining austenite, forcing the next plate to grow from the carbon-enriched austenite [11]. Upon reaching the $T_0'$ carbon content, the process stops, leading to the so-called ‘the incomplete reaction phenomenon’ [43]. It is important to note that this is valid only for carbide-free bainitic steels as carbide is a whole new different phase.
Figure 2.3: Illustration of the $T_0$ and $T'_0$ curve. $T_1$ is the temperature corresponding to the free energy curves [11]

The $T_0$ concept imposes a thermodynamic restriction on the extent of bainite formed and hence austenite is retained in form of blocky pools as well as thin films in between the bainitic laths (Figure 2.3). Quidort and Bonaziz proposed that the reduction in driving force through plastic straining leads to the stabilization of austenite phase resulting in the incomplete transformation [44]. Caballero and Bhadeshia studied the above theory and pointed out that the plastic straining should be taken per unit of bainitic phase rather than austenitic phase [45]. Hillert et al. argued that even if the diffusion-less growth of bainite has stopped, further transformation into Widmanstatten ferrite should still be possible [32].

2.3.3 Role of alloying elements

The temperature and transformation time play the most essential role in determining the phase fractions and the carbon content of the retained austenite. This further determines the mechanical properties [46-51]. The austenite volume fraction
decreases with time [52]. Extended holding causes carbide precipitation, thereby destablising the austenite. For the same holding time, the fraction of bainite transformed was greater when transforming at higher temperatures.

Silicon, when present in an amount greater than 1 wt.%, inhibits the carbide precipitation in austenite, thus leading to the enrichment of carbon in the austenite. Silicon hence enhances the stability of the residual austenite. Silicon has also been reported to reduce lower-bainite start temperature [53]. Limited use of silicon has been suggested because it harms the surface quality of steels. Thus, attempts have been made to substitute silicon with aluminium or phosphorus [54].

Mertens *et al.* later demonstrated the effect of aluminium in accelerating bainite transformation kinetics in comparison with Si [55]. Pichler *et al.* also recommended phosphorus as a substitute for silicon resulting in a significant improvement in strength [50]. However, it is uncertain how efficient the phosphorus is in preventing carbide precipitation [56]. Mo may also be effective as a ferrite solid-solution strengthening element, which inhibits the carbide precipitation [57].

### 2.3.3.1 Carbon

Austenite is a solid solution of carbon or other solute atoms in face-centred cubic structure. It is well established that carbon atoms occupy interstitial positions in the lattice. The atomic radius of carbon is 0.77 A.U. (atomic unit), while that of iron is 1.27 A.U. The austenite lattice parameter increases progressively with the carbon content, which occupies interstitial lattice positions [58]. In 1942, Petch [59] showed various possible interstitial sites in the face-centred cubic lattice using X-ray intensity measurements. He found that the centres of the unit cells and the midpoints of the cube edges can house the carbon atoms with the least amount of distortion (Figure 2.4). In 1% carbon steel, only 4.7% of these positions are actually occupied.
It is interesting to note that the interstitial arrangement of carbon atoms prevails irrespective of the source of carbon, that is, whether the austenite receives its carbon from cementite, graphite, or a carbon rich liquid phase.

The following equation describes the effect of alloying additions on the lattice parameter of austenitic Ni-Cr alloys using X-ray diffraction technique [61]:

\[
a_\gamma = 3.5770 + 0.033C + 0.00095Mn + 0.0002Ni + 0.0006Cr + 0.0056Al + 0.0031Mo + 0.0018V \quad \text{Equation 2.1}
\]

where C, Mn, Ni, Cr, Al, Mo and V represent the weight per cents of carbon, manganese, nickel, chromium, aluminium, molybdenum and vanadium, respectively. The lattice constant, \( a_\gamma \), is given in Å. Thus, it can be inferred that the lattice parameter of austenite varies by 0.0330 \times \text{wt.\% of C}. This inference can result in very accurate measurements of carbon concentration of different regions of the same phase (carbon enriched and carbon depleted).

A study of the effect of isothermal bainitic transformation temperature, on retained austenite fraction in a C-Mn-Si-Al-Nb-Ti TRIP-steel was conducted through X-ray diffraction [3]. In this study, the positions of austenite peaks with highest diffraction intensity were used to determine the lattice constant of austenite. This
parameter was then used to calculate the concentration of carbon in the retained austenite.

It is expected that carbon enrichment is greatest in the vicinity of the bainite plates, with distant blocky austenite affected little. Thus, it gives rise to the bimodal austenite parameters [62]. The changes in lattice parameter of both ferritic bainite and remaining austenite caused by the redistribution of carbon can be monitored accurately using neutron diffraction methods. The only previous study [63] of bainitic transformation behaviour studied by simultaneous neutron diffraction discusses the observation of broadening and peak shift, supporting earlier synchrotron experiments by Stone et al. [64].

2.4 Low temperature bainite

This thesis describes the characterisation and development of a promising new bainitic steel. This bainite, which forms isothermally at low temperatures (200°C – 350°C), exhibits remarkable mechanical properties with strength up to 2.5 GPa and a toughness up to 30 MPa m\(^{1/2}\) [6]. The excellent mechanical properties result from a highly refined microstructure, leading to a nanoscale microstructure, which is also TRIP-aided because of the retained austenite.

![Figure 2.5: Bright field TEM image of lamellar structure of bainite formed after isothermal holding at 200°C for 10 days [65]](image-url)
Embrittling carbides are suppressed by the addition of silicon. At isothermal transformation temperature of 200°C, bainite plates are reported to have widths of 20-50 nm (Figure 2.5) compared to the usual width of 0.2 to 0.5 µm in conventional bainitic microstructures. Blocky retained austenite, which limits the toughness, could be avoided by maximizing the volume fraction of bainite [66].

Transformation at low temperatures not only results in a high-volume fraction of bainite, but also leads to a notable strength by introducing a high number of defects such as dislocations and stacking faults in the microstructure. A high dislocation density results in a supersaturation of carbon in the bainite phase, leading to a remarkable hardness, which is resistant to harsh heat treatments [67].

2.4.1 Steel design

In 2006, Caballero et al. used thermodynamic and kinetics models to design steels with an optimum bainitic micro-structure consisting of a mixture of bainitic ferrite, carbon-enriched retained austenite and some martensite [68]. Using these models, a set of seven carbide-free bainitic steels were proposed for manufacturing. Except for the steel with the highest content of alloying elements, all the grades presented the same micro-structure composed of carbide-free upper bainite and retained austenite, after the hot-rolling and a two-step cooling. The tensile strength ranged from 1600 to 1950 MPa, while keeping a uniform elongation equal to 4% and a total elongation over 10%. Regarding toughness at room temperature, they match quenched and tempered martensite steels.

Cementite is responsible for the limited application of conventional bainitic steels. However it has been proved that cementite precipitation during bainite formation can be suppressed by the judicious use of silicon in medium carbon steels [68]. Thus, thermodynamic and kinetic models were used to design steels with an optimum bainitic microstructure consisting of a mixture of bainitic ferrite, carbon-enriched retained austenite and some martensite. In 2008, Caballero reported that experimental results on the temporary cessation of bainitic ferrite formation in medium- and high-carbon, high-silicon, manganese-alloyed steels confirm that the incomplete reaction phenomenon can be explained in terms of the diffusionless
growth of bainite subunits [69]. Carbon partitions into the remaining austenite just after the transformation. The bainite reaction stops as soon as the austenite carbon content reaches the $T_0$ value. Using local electrode atom probe tomography, it was evident that carbon is distributed non-uniformly.

Recently a theoretical design has been successfully applied to design the steels with a microstructure consisting of a mixture of the bainitic ferrite and the retained austenite [4]. Using thermodynamic and kinetic models, a set of four carbide-free bainitic steels were designed and manufactured following a thermo-mechanical treatment consisting of hot rolling and two-step cooling. The designed steels presented significant combination of strength and ductility, with tensile strength ranging from 1500 – 1800 MPa and total elongation over 15%. However, a carbon content of 0.3 wt.% is still high for in-use properties such as weldability. In this sense, a reduction in the average carbon content of advanced bainitic steels was proposed. Improved bainitic steel with a carbon content of 0.2 wt.% reached a combination of strength and ductility comparable to those in TRIP assisted steels.

### 2.4.2 Stability of retained austenite

The high strength obtained by refining the microstructure in bainitic steels is complemented with a respectable ductility because of the TRIP effect. TRIP property is shown by microstructures containing retained austenite and when they are subjected to mechanical loading, the retained austenite transforms to martensite, giving a serration in the stress-strain curve and necking in the physical structure. The stability of austenite plays the most important role to produce the TRIP effect and hence in enhancing the mechanical properties. Various experimental studies have proved that austenite films with high carbon content are much more stable in comparison with blocky austenite when tested for deformation toughness [24, 70-72]. The TRIP effect was firstly observed in fully austenitic steels with sufficient Ni and Mn to maintain the $M_S$ temperature below room temperature [73].

Ni is considered to be an expensive element. The use of such elements was proposed to be eliminated by studying the potential of bainite in TRIP aided carbide-free steels. Here austenite is enriched in carbon as a result of the transformation [27, 74-].
For any steel composition, the volume fraction, chemical stability and morphology of the retained austenite play a crucial role in the TRIP effect. A higher volume fraction of retained austenite is expected to contain a lower carbon concentration, whereas a much lower retained austenite content may be so rich in carbon that it does not transform at all on applying stress [78]. Thus, an optimum amount of retained austenite and an optimum carbon concentration in the retained austenite is required to eliminate low stable and over-stable austenite and obtain the best possible mechanical properties.

In 1983, Bhadeshia and Edmonds found an austenite stability parameter as the ratio of retained austenite and athermal martensite formed during final quenching to room temperature [72]. They stated that the stability of austenite is greater in bainitic steels due to its size being finer than that achieved in the plain carbon-steels. Lately carbon, manganese and chromium are being used as austenite stabilizers to achieve the TRIP effect in bainitic steels. Quite recently silicon has been found to act as an austenite strengthener besides suppressing carbide precipitation in austenite [79].

The retained austenite stability in a TRIP steel has been reported to improve the ductility of carbide free bainitic microstructures, consisting of a bainitic ferrite matrix and a mixture of austenite and martensite, the TRIP effect [10]. The role of microstructural parameters, such as the amount, morphology and composition of retained austenite, amount and size of martensite and morphology of bainitic ferrite matrix, on the ductility behaviour of advanced bainitic steel sheets was examined. Their results showed that bainitic microstructures formed along with coarse and blocky bainite morphology have shown higher uniform elongation values than those obtained by air cooling with the typical bainite morphology consisting on thin and long parallel bainite plates. Further to above study, an analysis of the microstructure-property relationships in thermo-mechanically processed multiphase steels with different amounts of phases was conducted [80]. They have shown that the strengthening is not only due to the retained austenite volume fraction but is significantly affected by the volume fraction of other phases and the interaction between phases during deformation.
In the former studies of TRIP-aided steels, the high ductility was known to be due to transformation of the retained austenite to martensite during deformation. Although a recent work emphasises the contribution of micro-constituents other than austenite in the overall deformation behaviour [23, 28, 81, 82]. Rodriguez inferences that the strain at first concentrates in the softest phase during deformation [83]. Once the soft constituents have strain-hardened, only then harder phases/constituents will deform plastically. The strain, because of martensite, is cushioned by the soft phases and therefore, the explosive transformation and autocatalytic process is inhibited and reduced. On the other hand, mean stress in the austenite is reduced because of the presence of hard phases and hence, the strain-induced martensite transformation is delayed. However, the transformation process becomes more progressive, which ultimately is good for ductility.

2.5 Unresolved issues

The theory of “incomplete reaction phenomena” as proposed by Hehemann and co-workers [84] has formed the basis for the further development and exploitation of the bainite phase. Some prominent research over the last few decades has revealed a significant amount of reliable data leading to the design of novel alloys. In case of low temperature bainite, there are several important issues, which need a full quantitative treatment. The following unresolved issues have been reported to be among the most urgent [13] and have been taken up systematically in the subsequent sections of this thesis.

2.5.1 Carbon redistribution in nanostructured bainite

While the effect of transformation temperature on microstructure and variant selection has been well established [8, 85, 86], there is an acute need to establish the \textit{in situ} transformation mechanism for further development of such steels. The postulated mechanism could be different from the conventional bainitic transformation as the size of bainitic ferrite laths is close to the simulated critical bainitic nuclei size [87]. The isothermal bainitic transformation of nanostructured steels has been previously investigated using \textit{in situ} X-ray and neutron diffraction techniques, though the results have not been consistent [7, 63, 64]. Babu \textit{et al.} [7]
showed that the austenite diffraction peaks split before the onset of bainitic transformation, suggesting carbon partitioning in the austenite phase prior to the onset of bainitic transformation. However, Stone et al. [64] did not observe the splitting of diffraction patterns before the onset of bainitic transformation. Later, Koo et al. [63] also observed the peak broadening and peak shift following the onset of bainitic transformation using in situ neutron diffraction, however, the peak split could not be identified due to the low resolution of the employed technique.

Neutron diffraction was firstly used to investigate the stability of retained austenite in TRIP steel by Zrnik et al. [88]. In situ neutron diffraction analyses proved to be effective in the investigation of the isothermal austenite transformation kinetics and in the evaluation of the volume fraction of the transformed ferrite. The progress of ferrite formation during the isothermal transformation of the conditioned austenite at different temperatures was monitored. The stability of retained austenite under the straining was studied from in situ mechanical tests. It was revealed that the electron diffraction method is convenient for investigating the untransformed retained austenite volume fraction during the sequential tension test.

The above-mentioned technique of neutron diffraction is very useful to monitor the bulk properties of a material very thoroughly. Simple calculations can be done to find out the evolution of phases in terms of volume fraction, carbon content of phases and refining the microstructure. Effect of carbon content on the lattice parameter and hence the position of diffraction peaks has been described above.

In general, the bainite transformation is a para-equilibrium reaction in which the substitutional alloying elements are unable to partition, although carbon redistributes between phases until its chemical potential becomes uniform throughout [11]. It is expected that the carbon enrichment is the greatest in the vicinity of the bainite plates, with distant blocky austenite affected little. Thus, it gives rise to the bimodal austenite parameters [62]. The changes in lattice parameter of both ferritic bainite and remaining austenite caused by the redistribution of carbon can be monitored accurately using neutron diffraction methods. The only previous study [63] of bainitic transformation behaviour investigated by simultaneous neutron diffraction discusses the observation of broadening and peak
shift, supporting earlier synchrotron experiments by Stone et al. however, it lacks in the precise calculation of changes in the lattice parameter accompanying the redistribution of carbon in bulk and retained austenite.

It is important to note here that the lattice parameter of austenite is also dependent on substitutional solutes. Any changes in substitutional solute content could lead to corresponding changes in the lattice parameter. It is thus important to homogenize the material to minimize the presence of any solidification induced chemical segregation. The benefit of neutron diffraction over other techniques is that if such segregations occur they can be easily identified because the peak intensities come from bulk material [89].

In view of the ongoing debate over the mechanism of carbon redistribution in retained austenite and transformed bainite, there arises a need to monitor the in situ isothermal transformation. Neutron Diffraction has been reported to yield a good counting statistics because of the high penetration ability of neutrons providing a unique opportunity to obtain information from bulk material. To closely monitor the partitioning of carbon into different phases, specially just before and after reaching the isothermal holding temperature and at the onset of bainite transformation, the instrument used also needs a high temporal resolution. Further, Atom Probe Tomography (APT) can provide valuable information on the carbon distribution at the atomic level and to investigate the presence of carbides.

2.5.2 Transformation from plastically deformed austenite

To study the effect of small stresses on the kinetics of the bainite transformation, Shipway & Bhadeshia in 1994, conducted experiments in which bainite was allowed to grow under the influence of an externally applied stress of magnitude less than the yield strength of austenite [87]. They observed acceleration due to stress in the transformation kinetics by applying transformation strains along two orthogonal directions. This was prevalent particularly at high transformation temperatures, where the chemical driving force for transformation is relatively small. The effect of stress has been studied in much more detail after this finding and various contradicting statement have been made.
There are three different views on the effect of external stress or austenite conditioning through deformation on the kinetics of bainitic phase transformation and the final microstructure developed.

1. Acceleration of kinetics of bainitic transformation has been reported by various research groups [90-92]. It seems to be completely rational to think that the deformation will increase the dislocation density, hence producing more nucleation sites for bainite and increasing the kinetics of transformation.

2. Mechanical stabilization is also an important factor influencing the kinetics of transformation [93, 94]. As discussed earlier, the austenite stabilization is important to have the TRIP effect, which is responsible for the high ductility displayed by nanostructured bainite. It has been established that the deformation stress induced strain in the austenite phase rendering the transformation kinetics to become slower. This particularly occurs at higher temperatures of deformation.

3. The transformation is accelerated during the early stages and retarded during later stages. Bhadeshia stated in his review that kinetics of bainitic phase transformation is observed to be accelerated during the early stages due to the high density of lattice defects introduced by austenite deformation and retarded during final stages because of work hardening of austenite resulting in smaller amount of bainite [13, 87].

Further to above study, an analysis of the microstructure-property relationships in thermo-mechanically processed multiphase steels with different amounts of phases was conducted by Timokhina et al. [80]. They have shown that the strengthening is not only due to the retained austenite volume fraction but is significantly affected by the volume fraction of other phases and the interaction between phases during deformation.

The inconsistency in the existing reports on the effect of ausforming on the kinetics and characteristics of low temperature bainite has gained considerable attention. The transformation of plastically deformed austenite to bainite is important because
of the role of thermomechanical processing in the current industrial production of steels. The different experimental conditions employed in different studies is the major cause of the varying and incomparable results. A comprehensive and systematic study is thus required to resolve the debate on the effect of ausforming on bainite transformation. The key here would be to understand the interaction of defects induced by plastic deformation on kinetics and microstructure of bainite.

2.5.2.1 Effect of SFE on the deformation mechanism

Plastic deformation occurs by slip or twinning and the dislocations in slip bands or twin boundaries have been suggested to assist the nucleation of transformation products [95, 96]. The amount of dissociation of the partial dislocations and their mobility are defined by the SFE (Stacking Fault Energy) of the material.

\[
SFE = \frac{Ga^2}{16\pi r}
\]

Where, G is the shear modulus, \(\alpha\) is the lattice parameter and \(r\) is the separation distance between two partial dislocations. Thus lower the separation distance between twopartials, higher the SFE and vice-versa.

In general, when an fcc crystal with high SFE deforms at an elevated temperature, only slip occurs [97]. More than one deformation mechanism may also take place concurrently during deformation [98]. The steel composition and the alloying elements present have a significant effect on the SFE, which can be calculated using different models [15, 99-101]. Calculation of SFE through the thermodynamic approach proves that the deformation temperature has a great effect on the SFE [102]. The same composition can display all three deformation modes (slip, twinning and TRIP) at different deformation temperatures. The deformation temperature can affect not only the deformation mode but also the substructure formed as a result of the deformation mode [103].

It would be interesting to use a steel sample which is fully austenitic at room temperature (e.g. TWIP) to study the austenite substructure formed due to plastic deformation. Employing a TWIP steel and deforming it at a similar SFE and with
the same strain as the bainitic steel would reveal the thus formed austenite substructure. The features formed in the substructure would be valuable to understand the effect of ausforming on the characterises of thus formed bainite.

2.5.3 Crystallography of nanobainite

The crystallography of nanobainite steels has previously been studied in detail for microstructures formed at different isothermal holding temperatures. Further, Gong et al. [97] studied the effect of ausforming temperature on the variant selection in nanobainite steels. It was previously established that the transformed bainitic variants from deformed austenite are much lower in number than the theoretical variants according to the known orientation relationships (N-W, K-S, G-T, G-T' and P) [8, 104, 105].

Beladi et al. [8] used electron back scattered diffraction (EBSD) and transmission electron microscopy (TEM) to investigate the crystallographic nature of the bainitic laths formed at relatively low transformation temperature, where a nanostructured bainite is formed. The bainitic ferrite laths were found to be close to the Nishiyama-Wassermman orientation relationship with the parent austenite. Furthermore, the temperature showed a significant effect on the retained austenite characteristics and the variant selection of the bainitic ferrite laths. A decrease in the temperature generally refined the bainitic structure and weakened the variant selection.

Gong et al. [92] employed EBSD and TEM to examine the effect of ausforming on kinetics, morphology and crystallography of nano-bainite steel. Ausforming was found to accelerate bainite transformation at 573K. A characteristic microstructure consisting of bainite laths and retained austenite was observed in the ausformed bainite steel where strong variant selection takes place due to the operated slip system.

Though the crystallography of nanobainitic steel in a non-deformed condition has been well established the effect of austenite conditioning on the crystallography has yet to be studied. While a previous study reports [97] the effect of ausforming temperature on the orientation relationship and variant selection in nanostructured bainite, the effect of other austenite conditioning parameters is still an unexplored
area. Thus there is a need to study the effect of prior austenite grain size, deformation strain and strain rate on the orientation relationship and variant selection of thus formed nanostructured bainite.

2.6 Summary

It is evident from the review of existing literature that the theory for the bainite transformation is at a fairly advanced stage to be used in the design of novel steels. In view of the vast variety of potential applications of TRIP-aided bainitic steels and the numerous studies conducted to understand the mechanism of bainitic transformation, the following unresolved issues have been identified:

1. The carbon redistribution during the transformation of austenite into nanostructured bainite is yet to be fully developed into a theory. There exists a need to monitor the carbon partitioning during the isothermal phase transformation. Further, an atomic level study will be key to investigating the presence of carbides.

2. In view of the very slow kinetics of transformation, it is important to establish the optimum conditions under which thermomechanical processing can assist in the acceleration of the transformation. Thus, the transformation of plastically deformed austenite to bainite and its effects on the kinetics and microstructure is yet to be studied comprehensively, which are yet to be understood.

3. To complete the understanding on bainite transformation under different thermo-mechanical conditions, the crystallography of nanostructured bainite and effect of austenite conditioning on the orientation relationship and variant selection needs to be studied systematically.

In the present work, an attempt has been made to answer the above-mentioned unresolved issues.
3

Experimental Methodology

3.1 Introduction

This chapter deals with the description of the material and methods used in the current study. The main objective of this research was to investigate the evolution of nanostructured bainite and the effect of thermo-mechanical treatment on its evolution. For this purpose, the state of the art characterisation techniques were employed to monitor and analyse the evolution of phase transformations at such small scale. A brief overview of the alloy design has also been provided in this chapter. In the sequence of their usage in the following research, the characterisation techniques and corresponding instruments that have described in this chapter are neutron diffraction, atom probe tomography (APT), transmission electron microscopy (TEM), Servotest, metallography, hardness testing, X-ray diffraction, scanning electron microscopy (SEM) and electron back scatter diffractometer (EBSD).

3.2 Alloy Design

As previously mentioned in the literature review, the exploitation of fully bainitic structures has been attempted for long [5, 11, 62, 68, 106]. The design was based on shifting the $T_0$ curve to a higher carbon content by adjusting the content of substitutional solute elements. The motive in steel design here was to obtain a fully
bainite microstructure with high volume fraction of the stable retained austenite and nano-size of the bainitic ferrite and retained austenite layers.

The various bainitic steel compositions considered for this particular research are given in Table 2.1 [8, 13, 45]. Here, Carbon, Manganese and Chromium help to maintain a low Bs temperature and are austenite stabilizers (i.e. as required for the TRIP effect). Silicon inhibits the precipitation of cementite from austenite and is also an austenite strengthener, while Molybdenum increases the hardness penetration of steel, slows the critical quenching speed, and increases high temperature tensile strength. Cobalt and Aluminium were added to increase the free energy change on transformation of austenite to ferrite, and thus accelerate the formation of ferrite [106].

Table 3.1: Chemical compositions of alloys forming low temperature nanostructured bainite

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Co</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.79</td>
<td>1.59</td>
<td>1.94</td>
<td>1.33</td>
<td>0.30</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.98</td>
<td>1.46</td>
<td>1.89</td>
<td>1.26</td>
<td>0.26</td>
<td>0.09</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>0.83</td>
<td>1.57</td>
<td>1.98</td>
<td>1.02</td>
<td>0.24</td>
<td>-</td>
<td>1.54</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>0.79</td>
<td>1.49</td>
<td>1.95</td>
<td>0.97</td>
<td>0.24</td>
<td>-</td>
<td>1.60</td>
<td>0.99</td>
</tr>
</tbody>
</table>

On the basis of preliminary kinetic analysis, Alloy 4 was chosen for subsequent studies of low temperature bainitic phase transformations. Alloy 4 transforms in the shortest time (1 to 10 days) while maintaining low Bs (385°C) and Ms (155°C) temperatures [106]. A cast slab with an initial thickness of 40mm was hot-rolled in a deformation temperature range of 1473-1273 K through successive passes to obtain a final thickness of approximately 12 mm. Cylindrical samples of height 15 mm and diameter 10 mm (typical samples used for axi-symmetric compression testing) were machined from the hot rolled slab (Fig. 3.4). These samples were then sealed into stainless steel bags and homogenized at 1250°C for 8 hours in a tube.
furnace with flow of Argon gas. These samples were used for the neutron diffraction studies, thermo-mechanical testing and subsequent characterisation.

3.3 *In situ* Neutron Diffraction

The use of neutrons is known to yield a very good counting statistics since a larger volume of the sample can be monitored because of the high penetration power of neutrons. The high intensity powder diffractometer WOMBAT, of Australian Nuclear Science and Technology Organization (ANSTO) was employed for the *in situ* study of the kinetics of bainite transformation. This work was inspired by the need to verify prior observations [7, 63, 64] using an instrument with higher temporal resolution to cope up with subtle changes during the isothermal heat treatment. The specific heat treatment was achieved using a Rapid Quencher, which was specially designed for these experiments as described below. The analysis was performed using softwares IGOR and GSAS for single peak fitting and Rietveld refinement as explained in section 4.3.

3.3.1 Rapid Sample Quencher (RSQ)

To perform the specific heat treatment required for a bainitic microstructure, it was important to avoid the formation of pearlite/ferrite through a cooling rate faster than 5°C/s [4] and then maintain a stable heating to hold the temperature isothermally at 250-350°C for long durations. The rapid quencher was thus designed at Bragg Institute of ANSTO by the sample environment team. The RSQ achieved temperatures upwards of 800°C through use of Infrared Heating Lamps. The maximum heating rate recorded was 84.2°C/min. Through the use of a liquid nitrogen diffuser the RSQ was capable of quenching at a rate as high as 31.7°C/s. The liquid nitrogen was introduced into the system via an injection ring specifically designed for this application with a focal point just below the sample, allowing a high flow rate of liquid nitrogen to cool the sample. This system was efficient enough to quench the sample to as low as -196°C, and through use of PID control and cryogenic switches, the RSQ could quench down and maintain virtually any temperature above ambient for a prolonged period of time.
This was a first-case ever of a rapid quencher in the neutron sample environment community (Fig. 3.1) [14]. This first prototype of a rapid quencher was excellent in background noise reduction but had a limitation on the maximum power, which it could withdraw. Thus, the maximum reachable temperature was only 820°C. An induction heating coil was also studied as an alternative to achieve higher temperatures. The temperature was monitored throughout the experiment using two thermocouples embedded in the sample. Thermocouple holes of diameter 1.5 mm and depth 2.5 mm were drilled in both flat ends of the cylindrical specimen described in section 3.2. The sample was then hung using a thermocouple wire in between the two heating lamps and the height was adjusted using a neutron camera, according to its position in WOMBAT. The thermocouple was attached to a Eurotherm unit, which was later controlled remotely through the WOMBAT system.

Figure 3.1: Rapid sample quencher; the setup includes the following parts:
(a) Halogene lamps; (b) Liquid nitrogen flow; (c) Quartz tube; (d) Power supply; 
(e) Aluminium casing; (f) Thermocouple holding the sample; (g) Monochromatic neutron beam
3.3.2 WOMBAT (High intensity diffractometer)

WOMBAT is the first instrument on the thermal guide TG1 at the OPAL reactor at the Bragg Institute of ANSTO (Fig. 3.2). A germanium monocrystal was used as a monochromator and the wavelength used was 1.49Å. The position-sensitive detector (PSD) on WOMBAT gives a continuous coverage of 120° over 2D space with Full Width Half Maximum (FWHM) position resolution of about 1.5 mm [107]. The position-sensitive detector consists of eight 15° curved panels with a radius of curvature of 700 mm and a height of 200 mm. It routinely measures to a 1-minute time resolution and measurements to 100 ms are possible, which is a very fast acquisition rate compared to other such facilities.

![Figure 3.2: The high intensity powder diffractometer, WOMBAT](image)

In the present case, the calibration of detector position was done using Al2O3 and LaB6 standard specimens. The position of the sample in the rapid quencher was determined using a neutron camera in between the detector and the beam. Two in
situ cycles of heat treatment were run as described in section 4.2. The neutron diffraction data were constantly monitored and recorded using PSD for the whole cycle with a time resolution of 60 seconds per scan.

3.3.3 Analysis methods

3.3.3.1 Single peak fitting method

First all ten (α and γ) peaks were fitted simultaneously from later times to earlier times, until some α peaks disappeared in the background. Then, some α peaks were set to zero and the fit parameter held for fitting basically γ alone. In a second trial, only the first 3 peaks were considered for fitting in a similar way and the procedure was followed consistently down to where the γ peak vanishes. Basically, the single peak fitting was performed from where the γ phase formed to the end using voigt function employing IGOR Pro software.

The valuable fit parameters are position, area (intensity), width (FWHM - Full Width Half Maximum) for each peak. Essentially, the ratio of the areas under each peak provides the phase fractions, the position includes thermal expansion, chemistry (Vegard’s law) and elastic strain offset (if any), and width gives information about strain distribution and coherent lattice volume size.

The integrated intensities of α-110 and γ-111 were used in direct comparison method to obtain the volume fractions of the 2 phases [108]. The peak position $G_{\text{hkl}}$ in reciprocal space is a valuable parameter denoting total strain $\varepsilon = -\Delta G/G$, which includes: thermal expansion $\varepsilon_T$, chemical shifts $\varepsilon_c$ (Vegard’s law) and elastic strain offset $\varepsilon_e$. At a constant temperature, carbon concentration ($\chi_c$) is a linear function of $\varepsilon_c$ [89, 108], given by:

$$\Delta \chi_c = 76.25 \varepsilon_c \text{ (mass\%)}$$  \hspace{1cm} \text{Equation 3.1}

Equation 1 was derived from the following equation by Onink [89]:

$$a_T = (0.36308 + 0.0037C) \ [1+ (24.9-3C) \times 10^{-6} \times (T-1000)]$$  \hspace{1cm} \text{Equation 3.2}
where $a_γ$ is the lattice parameter of austenite in nm, $C$ is the atom percent of carbon and $T$ is the temperature in degree kelvin.

Peak broadening was also evaluated and the instrument function (instrument broadening) was obtained using FWHM from LaB$_6$ calibration sample. Assuming the peak shapes are Lorentzian, Willamson-Hall [109] plot was used to separate broadening due to crystallite size and lattice micro-strain. It was established that the broadening in $γ$ phase is essentially due to micro-strain and carbon redistribution and in $α$ phase is due to size effects though micro-strain plays some role too. FWHM values of $α$-200 and $γ$-200 were evaluated to calculate the carbon distribution, strain distribution and coherent lattice volume size.

3.3.3.2 Rietveld method

Rietveld refinement is a tool that helps to model a full powder diffraction profile based on the crystal structure data, specimen and instrument effects. This is achieved by introducing certain functions that describe typical phenomena in powder diffraction experiments and by fitting the corresponding parameters afterwards [110]. The parameters are varied using a least-squares procedure, to minimize the difference between the calculated and the experimental powder diffraction pattern.

A drawback of the powder diffraction technique is that the diffraction peaks grossly overlap, thereby preventing proper determination of the structure. Multiphase Rietveld analysis virtually separates these overlapping peaks to accurately determine the structure. Another advantage of Rietveld Quantitative Analysis is that all reflections in the pattern are included for calculation and this method also reduces the effect of texture since all reflection types are considered.

The method relies on the simple relationship:

$$W_p = \frac{S_p(ZMV)_p}{\sum S_i(ZMV)_i}$$

Equation 3.3

Where $W$ is the relative weight fraction of phase $p$ in a mixture of $n$ phases, and $S$, $Z$, $M$, and $V$ are the Rietveld scale factor, the number of formula units per cell, the
mass of the formula unit (in atomic mass units) and the unit cell volume (in Å³), respectively [111].

Here, the diffraction patterns are collapsed along the Debye-Scherrer rings to one dimension and subsequently Rietveld fitted. A representative Rietveld fit for the present work is given in Figure 3.3. Calibration substance LaB₆ was used to obtain an accurate instrument function, which was then used to refine phase fractions, lattice parameters, together with the peak profile parameters delivering coherent grain size and micro-strain. During the course of structural refinement, all refinable parameters were refined to arrive at a solution to ideally reach the minimum.

![Rietveld refinement fit](image)

Figure 3.3: A representative Rietveld refinement fit for a particular scan

### 3.4 Atom Probe Tomography

Atom probe tomography (APT or 3D Atom Probe) is the only material analysis technique offering extensive capabilities for both 3D imaging and chemical composition measurements at the atomic scale [112]. In the present study, the detection of carbon segregation (and segregation of other elements) in nano-bainitic steel and quantification of the detected particles were accomplished by APT. APT
analysis is a unique technique not only for reconstructing of the 3-D image of carbon segregates but to acquire quantitative information regarding their shape, size and the exact chemical composition [113]. There are several important features of APT including: (i) a high level of spatial resolution (<0.3 nm) can be achieved in all three directions, (ii) compositional imaging of the nano scale buried or subsurface features can be achieved three-dimensionally and (iii) there is high analytical sensitivity. Basically, the characterization of the nanostructure by atom probe tomography involved three steps: (i) sample preparation (ii) data acquisition and (iii) reconstruction and data analysis.

3.4.1 Sample preparation

Atom probe needle specimens were cut using the wire-cut method. Electro-polishing was achieved in two stages. In stage 1, a standard electro-polishing procedure was used to prepare the atom probe tips using 33% nitric acid in methanol [65]. A circuit was set up between a gold ring fixed into brass block and the needle sample clamped in tweezers. The sample was moved in and out of the electrolyte solution in the gold ring (electrode) to sharpen the end of the needle. The needle was taken out of the electrolyte solution when it was properly sharp. Similarly, in the second stage, atom probe tips were prepared using 2% perchloric acid in butoxy-ethanol at 16 V. The time between the second stage electro-polishing and entry to the vacuum chamber of the atom probe was kept to a minimum level to avoid oxidation [112].

3.4.2 Data acquisition

APT data acquisition was carried out at the Monash Centre for Electron Microscopy. For APT analyses, the Oxford nano-Science 3DAP in ultra-high vacuum (10^{-8} Pa) was used. A pulse repetition rate of 20 kHz and a pulse fraction of 0.2 were employed. The sample temperature was 80 K. In APT, atoms are progressively removed from the surface of a sharp tip specimen by the process of field evaporation. By the application of a high DC voltage (~2-11 kV), a very intense electrostatic field was produced at the apex of the specimen tip, having a radius of curvature of a few tens of nanometres. The atoms were subsequently field
ionised and then evaporated layer by layer towards a position-sensitive detector, where their chemical identity was determined by time-of-flight mass spectrometry. The evaporated volume was then reconstructed in three dimensions, using an inverse projection reconstruction algorithm and the sequence of detected events [112]. The result was a tomographic data set, typically spanning some hundreds of nanometres in depth and containing the spatial coordinates and elemental identities of tens to hundreds of millions of atoms with near atomic resolution.

### 3.4.3 Data analysis

Data analysis was done using both Position Sensitive Atom Probe (POSAP) software and Integrated Visualization and Analysis Software (IVAS). The most critical step in atom probe analysis is the characterisation or ranging of the mass spectrum to associate all the significant peaks to corresponding elements. 3D atom maps can be then constructed and viewed using both POSAP and IVAS softwares [114]. Some important information that can be demonstrated through atom probe analysis:

1) Iso-surface construction to reveal interface boundaries and segregation areas;
2) Matrix compositional analysis;
3) Particle statistics, size and composition;
4) Proximity histogram for a particular iso-concentration surface;
5) 3D mapping and compositional analysis for selected area that can be cropped from the initial 3d image.

The results obtained through atom probe analysis of nano-structured bainite will be demonstrated and discussed in section 4.4. Atom probe proved to be a very valuable technique in the present study.

### 3.5 Transmission Electron Microscopy

TEM is an analytical tool allowing visualisation and analysis of specimens in the realms of micro-space and nano-space. It enables the investigation of crystal structures, crystallographic orientations and chemical compositions of phases,
precipitates and contaminants through diffraction pattern, X-ray and electron-energy analysis. Transmission electron microscopy approach is used to produce images from a sample by exposing the sample to electrons within a high vacuum, and detecting the electrons that are transmitted through the sample [115]. TEM was used herein to study the morphology of the different phases formed, to reveal the austenite substructure and to determine the dislocation density for different microstructures.

3.5.1 Sample preparation

Thin foils for transmission electron microscopy (TEM) were prepared from samples with different processing conditions. The samples were sliced (2-3 slices from each sample) from the middle of the samples, in the longitudinal (tensile) direction using Accutom-50. Each thin slice was first ground to 0.18mm using 600 grade silicon grit papers and then to 0.12mm using 1200 grit silicon paper. Then 3mm diameter discs were prepared from the ground specimen using a shear punch. The discs were then ground to 0.06mm using 1200 grit silicon papers. The discs were further electro polished in 5% perchloric acid in methanol using a twin jet Tenupol unit, operating at 35V. Liquid nitrogen was used to cool the polishing solution to -45°C.

3.5.2 Imaging and analysis

Transmission electron microscopy (TEM) examination was carried out using a Philips CM20 transmission electron microscope operating at 200 kV. The conventional electron microscopy was conducted with a condenser aperture of 100μm nominal diameter and a nominal beam diameter of 55nm. The observations were made in both the bright and dark imaging mode, while selected area electron diffraction (SAED) patterns were recorded from areas of interest. The measurements for bainitic lath size and dislocation density was done using point intercept method. SAED patterns were analysed by comparing with standard patterns of fcc and bcc iron and Fe₃C carbide.
3.6 Servotest (Thermomechanical treatment)

To study the effect of ausforming on the morphology and kinetics of low temperature bainite formation, (Servotest, TMTS 500kN) was employed at Geelong Technology Precinct, Deakin University (Fig. 3.4). The Thermo-Mechanical Treatment Simulator (TMTS) is a complex metal forming simulation system. The system offers the ability to perform high rates of heating and cooling as well as very high deformation rates. The machine can perform multiple deformation steps with heating or cooling sequences between each step, thereby simulating industrial hot-rolling processes. The system offers state of the art high speed compression testing on practically any material from room temperature up to 1200°C.

The test operations are divided into 3 major segments:

1. Furnace segments – terminate on time or sample temperature as specified.

2. Deformation segments – the form of the deformations may be chosen from the following:
   a. Constant true strain rate at 0.001 to 100/s (for 12mm sample height to specified final strain.
   b. User specified strain rate/strain profile from ASCII file.

3. FTTU segments – Linear or exponential heating and cooling using closed loop control of the induction heating and forced air/mist cooling from a thermocouple in the sample.
The different parts of Servotest TMTS include the following:

1. Preheat Furnace - it can heat up to 4 samples, to a maximum of 1200°C.
2. Hydrostatic Bearing Wedge Actuator – it provides the deformation profiles at up to 1m/s.
3. Fast thermal treatment unit (FTTU) – with induction heating and forced air/mist and water cooling to simulate inter-stand temperature profiles.
4. Test furnace – to provide the environmental temperature during deformations.
5. Annealing furnace – for post-test heat treatment of the 4 samples up to 750°C.
6. Manipulator (Robot) – to transfer the samples between the process stations above.
7. Quench tank – when required the manipulator will drop the sample into the tank.
8. Digital control system (PULSAR) – it programs and controls the whole TMTS.
9. Hydraulic power supply – to power the test machine and manipulator.
10. Compressed air supply – for FTTU.

A salt bath furnace was used for prolonged isothermal heat treatment at temperatures of 200°C to 350°C. The salt bath furnace was placed next to the Servotest machine (Fig. 3.4) for direct quenching to the required temperature after the required thermo-mechanical treatment. The salt, AS-140 has a melting point of around 140°C with a working temperature of 150-500°C. Small baskets were made to hold the samples individually in the salt bath for up to 10 days.

Cylindrical samples of height 15 mm and diameter 10 mm (typical samples used for axi-symmetric compression testing) were machined and homogenized (Fig. 3.5). Thermocouple hole of width 1.1mm was drilled into each sample for temperature control in the FTTU system. After that, the thermo-mechanical treatments were employed and their effects on the properties and microstructures have been discussed in Chapter 5.
3.7 Metallography and optical microscopy

Metallography is the study of the physical structure and components of metals using optical microscopy. Axi-symmetric samples were cut longitudinally after deformation or heat treatment using Accutom-50. A low cutting speed of 0.01 mm/s was employed to avoid any transformation due to the heat. The specimens were hot mounted using Polyfast, such that they can be further used for SEM characterisation. Rough grinding was done using 240, 600 and 1200 grade silicon grit paper. Polishing was done on Struers Tegrapol automated polishing unit using 9 µm, 3 µm and 1 µm diamond colloidal suspension. The specimens were cleaned using ultrasonic cleaner in between each step to avoid contamination. The polished samples were etched in 4% nital solution (48 ml ethanol and 2 ml nitric acid).

Images were taken with 500X and 1000X magnification using DP70 microscope. Point counting method was used to measure the volume fraction of bainitic ferrite in a matrix of austenite/martensite (Fig. 3.6). 20 images were analysed for every condition and the average value of volume fraction was calculated with standard deviation and error. The volume fraction data were further used to determine the kinetics of phase transformation in different deformation conditions as described in chapter 5.
3.8 X-Ray Diffraction

X-ray diffraction relies on the dual wave/particle nature of X-rays to obtain information about the structure of crystalline materials. In the present study, Panalytical XPert Powder was employed to characterize bainitic ferrite and austenite phases. Samples, which were prepared and etched for metallography, were repolished using 1µm diamond suspension to prepare for XRD analysis. A spot size of 3mm × 3 mm was scanned with 2θ angle ranging from 30°-120°. The operating parameters used were 50 volt and 40mA current and a copper target based X-ray tube.

As described in chapter 5, thermo-mechanical treatment involved deformation at different temperatures and strains followed by isothermal holding to obtain bainitic microstructure. Fully transformed samples (3 days of holding in salt bath furnace) were further analysed using the comparison method on X-ray diffraction results [108]. Only fully transformed samples were analysed because bcc ferrite, bainite and martensite essentially give the same diffraction peaks, distinguishable only by a slight difference in lattice size due to the differences in carbon content. Thus, it
was important to have only bainitic ferrite and retained austenite in the microstructure. The analysis for phase fractions and carbon content in retained austenite was conducted using a combination of pattern matching and manual indexing. Analysis was done on the same fundamentals as Neutron Diffraction Analysis as described in section 3.3.

### 3.9 Vickers Hardness

The Vickers hardness test method consists of indenting the test material with a diamond indenter, in the form of a right pyramid with a square base and an angle of 136 degrees between opposite faces subjected to a load of 1 to 100 kgf. The load was applied for 15 seconds. The Vickers hardness is the quotient obtained by dividing the kgf load by the square mm area of indentation. The advantages of the Vickers hardness test are that extremely accurate readings can be taken, and just one type of indenter is used for all types of metals and surface treatments.

The hardness of the fully transformed specimens after thermo-mechanical treatments with different parameters was measured using the Future-tech fm-700 Microhardness tester. Optical microscopy samples were used for hardness measurement. The mean of the two diagonals was used in the formula to calculate VHN. Vickers Hardness Number (VHN) was calculated by the following equation [116]:

\[
VHN = \frac{2P\sin(\alpha/2)}{d^2}
\]

Where, \(\alpha\) = face angle (136°), \(P\) = load, kgf and \(d\) = mean diagonal of the impression (mm)

In the present study 20 kgf load was used to determine the Vickers Harness and the hardness was plotted against strain applied during deformation and deformation temperature as described in chapter 5.
3.10 Scanning Electron Microscopy

LEO 1530 FEG SEM was used at IFM, Deakin University for both Imaging and Electron Backscatter diffraction. The LEO 1530 is a high resolution scanning electron microscope (SEM) that uses a Schottky-type field-emission electron source. A beam booster is used to optimise electron optical performance at all accelerating voltages. There are 4 detectors attached to this SEM:

1. High efficiency In-lens secondary electron detector
2. Everhart-Thornley secondary electron detector
3. Backscattered electron detector (Rutherford Type)

In the present study, in-lens secondary electron detector and backscattered electron detector (BSE) were used for imaging and selection of area to be scanned for EBSD. The Electron Backscattered Diffraction (EBSD) was used extensively in this study as described further.

3.10.1 Sample preparation

Sample preparation for electron microscopy follows almost the same steps as sample preparation for optical microscopy with a few modifications. The hot mounting should be done in Polyfast resin to have a conducting medium. Polishing was carried out on Tegrapol automatic polishing unit using 9µm, 3µm and 1µm diamond suspensions followed by a 2 minute polishing with Struers colloidal silica suspension (OPS). The samples were thoroughly cleaned manually and ultrasonically in between each of the polishing step. It is very important not to over polish with OPS as silica particles can adhere to the surface and act as obstacles in microscopy. The edges of these mounted samples were connected with holding studs using silver paint. This was performed to increase the conductivity and avoid charging up of the sample, which can destabilize the electron beam during log scans and can result in significant beam drifts.
3.10.2 Electron Back Scattered Diffraction (EBSD)

All EBSD scans in this study were performed on Leo 1530 FEG-SEM, which was coupled with a Nordlys II EBSD detector and AZTEC data collection software from HKL Technology. EBSD scans were carried out for specimens prepared through different thermo-mechanical or simple heat treatment processes. These scans were further analysed using back-calculation method [16] giving valuable information about variant selection and orientation relationships (OR). This further enables to study the effect of deformation and prior austenite grain size on ORs, as presented in chapter 6. Selected area scans were collected using an aperture size of 60 µm, an accelerating voltage of 20 kV, a working distance of 8-12 mm and a spot size of 100nm. The collected scans were analysed using both HKL Channel 5 software and the TSL software on the Quanta System. The indexing efficiency decreased with an increase in the deformation, further analysis was carried out for the scans exhibiting an indexing of higher than 80%.

3.10.3 EBSD analysis

The HKL file was first exported into a Channel Text File (.ctf), which was then opened in the TSL software. Clean-up was achieved using a minimum confidence index (CI) of 0.2 in the TSL OIM software. A minimum misorientation angle of 10° was employed to average all orientation data belonging to a particular phase (i.e. bainitic ferrite or austenite). The different variants of bainite were clearly visible after this process. Single grains were cropped out from the scanned images, as we were interested in variants of bainitic ferrite transformed from a single austenite orientation (see Chapter 6). The misorientation angle of each unique bainitic lath was recorded and exported as a text file. A minimum of 7 variants was determined for the use of minimum summation of mutual misorientation angle (SOMMA) approach to find the prior austenite orientation and best suited orientation relationship [16]. Effect of both prior austenite grain size and deformation strain was studied on variant selection and orientation relationship. The results have been presented in chapter 6.
4.1 Introduction

In the present chapter, in situ neutron diffraction was employed to monitor the evolution of nanostructured bainitic ferrite during low temperature isothermal heat treatment of austenite. The aim of the study was to elucidate the transformation mechanism and microstructural features of nanostructured bainite at relatively low temperatures. Previously, the partitioning of carbon in austenite prior to the beginning of bainite transformation [7, 63, 64] has been a topic of debate.

Babu et al. [7] had reported austenite diffraction peak splitting before the onset of bainitic transformation, which suggests that carbon partitions in the austenite phase before the onset of bainitic transformation. Peak splitting was not observed using in situ synchrotron studies by Stone et al. [64], suggesting a homogenous distribution of carbon in austenite before the start of bainitic transformation. Later, Koo et al. [63] studied the low temperature bainitic transformation using in situ neutron diffraction. However, the peak split could not be identified due to the low resolution of the employed technique.

In the present study, in situ neutron diffraction was employed using the high-intensity powder diffractometer, WOMBAT [107] at the OPAL reactor of the
Australian Nuclear Science and Technology Organization (ANSTO). Neutron diffraction is especially useful to obtain universal data from a bulk sample and is less sensitive to the surface decarburization during heating, as compared to the traditional X-ray diffraction technique. Here, the neutron diffraction peak characteristics have been quantified through both single peak fitting and Rietveld analysis to reveal the evolution of phase fraction, carbon redistribution, structure refinement and micro-strain development.

Further, atom probe tomography (APT) was employed to study the carbon redistribution at the atomic level and to confirm the presence of carbides in bainitic phase. APT helped to investigate the microstructural features in more detail and their effect on the mechanical properties of nanostructured bainite. Complementary to the neutron diffraction results, the structure refinement and dislocation was also studied using transmission electron microscopy (TEM).

4.2 Experimental methods

The chemical composition, and B₅₇ and M₅₆ temperatures of the alloy used in this study are described in section 3.2. Data collection was carried out by a position sensitive detector on WOMBAT. WOMBAT is an instrument with a high temporal resolution to cope up with subtle changes during the isothermal heat treatment, especially just before and after reaching the isothermal heat treatment temperature (section 3.3.2). All diffraction data were calibrated and expressed in reciprocal space, \( Q = \frac{4\pi}{\lambda} \sin \left( \frac{2\Theta}{2} \right) \), where \( 2\Theta \) is the scattering angle measured by the instrument. The temperature was monitored throughout the experiment using two thermocouples embedded at each end of the sample. The specimen was hung using a thermocouple wire in between the two heating lamps. The thermocouple was attached to a ‘Eurotherm’ temperature regulator, which was later controlled remotely through the WOMBAT system software. The neutron peak characteristics were quantified using single peak fitting and Rietveld analysis as a function of time. These characteristics were linked to changes in lattice parameter, volume fraction and carbon content, which further provide the evidence of carbon partitioning during transformation.
The heat treatment, as shown schematically in Figure 4.1, was performed using a rapid quencher (section 3.3.1). A cylindrical sample was austenitized by heating to 820°C at the rate of 5°C/s and retained at the same temperature isothermally for 30 min, followed by rapid cooling to 300°C, at a rate of 25°C/s under liquid nitrogen flow. The sample was then held isothermally at 300°C for over 12 hours. It is worth mentioning here that the temperature fluctuations at 300°C did not influence the result as the temperature drop (277°C) was still higher than the M_s temperature, and the time for temperature stabilization was much less than the incubation time for the bainitic phase transformation. The time resolution used for acquisition of data was 13 s per scan, which was much faster than previous studies [7, 63, 64].

![Figure 4.1: Schematic diagram of heat treatment during in situ Neutron Diffraction](image)

As explained in section 3.3.1, the rapid quencher had a maximum attainable temperature. Thus, dilatometry test was performed on the same composition to determine the temperature at which ferrite completely transforms to austenite. The dilatometry test was performed at the Department of Metallurgical and Materials Engineering, IIT Kharagpur, India. The dilatometry results display the relative change in length of steel depicting phase changes in response to in situ heat
treatment, Figure 4.2. It is evident that for this specific alloy, complete austenite phase is present above 820°C ($A_3$).

In the first in situ heat treatment cycle, the sample was austenitized at 810°C and further isothermally held at 350°C to facilitate the bainite transformation (Fig. 4.3). The rapid quencher could heat the sample to only 810°C, where ferrite phase could not fully transform into austenite phase. Therefore, some residual ferrite was present in the microstructure after austenitization. This can be seen in the integrated peak intensities of first 10 peaks over time. Thus, only the second heat treatment (Fig. 4.1) was analysed further for studying the evolution of nano-structured bainite from austenite phase. The possibility of presence of ferrite phase after austenitization at 820°C for 30 minutes cannot be nullified, but as no ferrite peak could be deciphered, the ferrite fraction was assumed to be less than 1%.

Figure 4.2: Relative change in length of steel depicting phase changes in response to in situ heat treatment, as measured by a Dilatometer
4.3 Results

4.3.1 In situ Neutron Diffraction

The peak characteristics at different time intervals during the in situ isothermal heat treatment process have been presented in this section. The detailed peak characteristics of $\gamma$-111, $\alpha$-110, $\gamma$-200 and $\alpha$-200 peaks were analysed using single peak fitting method to reveal microstructural parameters (Fig. 4.4). Peaks $\gamma$-111 and $\alpha$-110 were used to measure the kinetics of transformation and peaks $\gamma$-200 and $\alpha$-
200 were employed to determine microstructural characteristics through the peak shift, peak broadening and asymmetry. Further Rietveld analysis was undertaken to accurately determine the phase characteristics.

Figure 4.4: First four peaks at different time intervals; \( t = 0 \) is the beginning of isothermal holding

4.3.1.1 Peak intensity

Using reciprocal space \( Q \) as the independent variable, azimuthally integrated peak intensities of first 10 peaks were plotted against time and temperature profile in Figure 4.5, to present an overall picture of the evolution of different phases during the second heat treatment cycle. The initial diffraction pattern at room temperature
consisted of peaks, corresponding to ferrite phase only. Upon heating, ferrite (α) peak positions shifted towards lower scattering vectors. This phenomenon occurred due to an increase in the lattice size because of the thermal expansion.

On further heating to 820°C, a narrow γ-111 peak first appeared at 700°C and became stronger at the expense of α-110, which gradually diminished as shown in Figure 4.5. On rapid cooling, there was a sudden shift in γ-111 to a higher Q value due to the thermal contraction (i.e. a reduction in the lattice size). The start of isothermal holding treatment at 300°C has been taken as the zero time for further reference. It took 16.7 minutes for α-110 peak to reappear and become detectable (presence of <5% ferrite phase), which marked the onset of bainitic transformation after reaching the isothermal holding temperature.

Figure 4.5: Azimuthally integrated peak intensities depicting the evolution of different phases during the complete cycle of in situ heat treatment.
The kinetics of phase transformation was determined by the volume fraction evolution of bainitic ferrite with time. Initially, $\alpha-110$ was fitted using a voigt function. Further, the area under the curve (intensity) over the peak intensity of 100% ferrite was plotted over time (Fig. 4.6). This plot represents a typical Avrami Equation $[1-f = \exp(-kt^n)]$ and thus Avrami exponents, $k$ and $n$, were calculated using the linear form of Avrami equation as depicted in Figure 4.7 [117]. The exponent ‘$n$’ was calculated and was observed to be 1.7. The transformation kinetics was identified as nucleation-controlled since the observed value of parameter ‘$n$’ was less than 2 [118]. The volume fraction of bainitic ferrite at the end of transformation was 66%.

![Figure 4.6: Volume fraction of bainitic ferrite over log scale of time, calculated from in situ neutron diffraction. The plot represents a typical Avrami equation.](image)
4.3.1.2 Peak shift in $\gamma$-200

Careful examination of $\gamma$-111 and $\gamma$-200 revealed that as the isothermal treatment progresses, austenite peaks become wider and asymmetric, with the average position shifting towards smaller scattering vectors (or lower 2-theta values). In Figure 4.8, the shift in peak position of $\gamma$-200 is attributed to the changes in lattice size. As the bainitic transformation continues, carbon is rejected from the newly formed bainitic laths and thus, the remaining untransformed austenite becomes enriched in carbon. The asymmetry in $\gamma$-200 is attributed to the occurrence of more than one population of austenite with different carbon contents during transformation as discussed in the following sections. As apparent in Figure 4.8, the asymmetry increased with time. It is important to note here that at around 12 hours from the start of transformation $\gamma$-200 became symmetric again suggesting a uniformity in carbon content and hence completion of bainitic transformation. Carbon content of enriched austenite at the end of transformation, calculated from peak position changes using Equation 3.2, was $1.4 \pm 0.2$ mass% ($6.03 \pm 0.9$ at.%).
Figure 4.8: Peak shift and peak asymmetry evident in γ-200 depicting enrichment of carbon in austenite phase and inhomogeneous distribution of carbon in untransformed austenite

4.3.1.3 Peak broadening

After elapse of 33 minutes, the observed ferrite peaks were much broader than those observed at room temperature (Fig. 4.9). The peak intensities and shape of ferrite peaks became almost constant at around 12 hours from the start of the experiment. The peak broadening is in the Lorentzian component of the Voigt function, which depends on the coherent grain size and heterogeneous strain, giving rise to peak broadening [108]. Austenite and ferrite peak broadening have been reported in previous studies [7, 63, 64] and attributed to the refinement in the microstructure. Here, an attempt has been made to quantify the peak broadening in terms of size
and strain effects (Fig. 4.10). Full width half maximums (FWHM) from a LaB₆ calibration sample were taken as instrumental function. For the ferrite phase, there was a constant offset of α-200, with respect to the instrumental function suggesting a dominating size effect on the FWHM. The peak broadening was quantified to a very fine size of $2\pi/\Delta G \approx 182$nm. Comparing γ-200 and the LaB₆ instrument function, the FWHM of γ-200 was proportional to the scattering vector G, thus a strain broadening of $\varepsilon = -\Delta G/G = 12 \times 10^{-3}$ was calculated. In case of austenite, carbon content gradient mentioned in the above section also contributed to the peak broadening.

Figure 4.9: Peak broadening and asymmetry in α-200 suggesting refinement in microstructure and internal stress. No peak position shift was observed in α-200
4.3.1.4 Rietveld analysis

Quantitative Rietveld results are displayed in Figures 4.11, 4.12 (a & b), 4.13 and 4.14, showing phase fractions, lattice parameters, micro-strains and coherent grain sizes, respectively, for both ferrite and austenite phases. The phase transformation seemed to be sluggish at the beginning and then went off after 20 mins and finally reached an equilibrium mass% phase fraction of $\alpha/\gamma = 71/29$ (Fig.4.11). Lattice parameter evolution of both $\alpha$ and $\gamma$ phases are depicted in Figure 4.12 (a & b). As $\alpha$ lattice strain rose quickly to its constant value of $2.4 \times 10^3$, $\gamma$ lattice strain evolved pretty much in the same way as the phase fractions, approaching asymptotically $7.1 \times 10^3$. It is suggested that the peak shift was due to the change of carbon content (i.e. as soon as bainitic ferrite starts forming; carbon diffuses to the remaining austenite). Based on the equation proposed by Onink et al. [89], the change in the carbon content of the remaining austenite was calculated using the changes in the lattice parameters of the remaining austenite. An increase in the carbon content of the retained austenite, was calculated to be 3.3 at.%, that led to the peak shift. It is very interesting to note here that the $\gamma$ peak shape, which was asymmetric at the beginning of transformation, became symmetric towards the completion of transformation. The $\gamma$-200 peak asymmetry, after 360 min of isothermal hold is
shown in Figure 4.12(b). The asymmetry of the $\gamma$-200 peak confirmed a gradient of carbon content or gradient in lattice parameter of the remaining austenite. The latter symmetry of the austenite peak is attributed to the homogeneous redistribution of carbon in the remaining austenite.

Figure 4.11: Phase fractions calculated through Rietveld fitting [110]
Figure 4.12: Rietveld analysis of lattice parameter and lattice strain evolution of (a) ferrite phase, (b) austenite phase during phase transformation at 300°C. The windows represent the peak characteristics of $\alpha(200)$ and $\gamma(200)$ at 360 min elapse of transformation, respectively.

Non-uniform strain leads to systematic shifts of atoms from their ideal positions, thus causing peak broadening. This type of micro-strain can arise from point defects, plastic deformation at the atomic level or poor crystallinity. It was suggested that during bainite transformation, $\alpha$-layers contained a considerable amount of tetragonality [119], so that micro-strain of $\alpha$-Fe quickly raised from 0 to $5 \times 10^{-3}$ (Fig. 4.13). The radical changes in micro-strain, i.e. $\alpha$-Fe rising to $5.25 \times 10^{-3}$ after 33 minutes is coincidental with the changes in phase fractions as evident in figures 4.11 and 4.13. The observations for micro-strain changes for austenite phase were less straightforward. As bainitic transformation progresses, the inter-phase strain is plastically accommodated by the austenite next to bainite. The dislocation density is thus increased manifold in $\gamma$-Fe. This is evident from Figure 4.13 that while micro-strain in austenite was relatively stable till 40 minutes at around $1 \times 10^{-3}$, there was a considerable increase in micro-strain to $5.25 \times 10^{-3}$ to
accommodate the increase in the volume fraction of bainitic laths, which are incoherent with the austenite matrix. This was accompanied with a relaxation of micro-strain in austenite from $5.25 \times 10^{-3}$ to $4.8 \times 10^{-3}$ and a time constant of about 100mins. In general, a strong increase in lattice size is usually associated with a strong decrease of micro-strain [111], thus a relaxation of micro-strain in austenite phase takes place due to the carbon enrichment, which increases the lattice parameter.

![Graph showing micro-strain changes](image)

Figure 4.13: Micro-strain changes in both austenite and bainitic ferrite phase calculated through Rietveld Analysis of *in situ* Neutron Diffraction experiment.

Peak broadening was also used to measure the average coherent crystallite sizes for both bainitic ferrite and austenite phase. Within the first 40 min, coherent α grain sizes evolved from 20 nm monotonically to 50 nm, and then remained stable throughout the experiment (Fig. 4.14). In contrast, the average coherent crystallite size for austenite decreased from 50 nm to 20 nm at the beginning of the bainite transformation, further progressively increasing to 30 nm. These Rietveld calculations were further related to TEM observations in section 4.3.3.
4.3.2 Atom Probe Tomography

The bainitic ferrite and retained austenite phases at the end of the heat treatment were also characterised by APT on the basis of compositional analysis. A volume of $11.13 \times 11.13 \times 113.40 \text{ nm}^3$ was analysed using position-sensitive atom probe analysis, POSAP software (Fig. 4.15). The composition of retained austenite was calculated using the matrix calculation method for a selected box in the austenite phase [112]. An average carbon content of $6.95 \pm 0.1 \text{ at.}\%$ in the austenite film was directly comparable to the neutron diffraction results for the carbon content calculation. The average carbon content in the super-saturated bainitic ferrite phase was found to be approximately $0.5 \text{ at.}\%$ and the carbon atoms were distributed unevenly in this acicular microstructure. The iso-concentration surface at $6.95 \text{ at.}\%$ carbon gives a clear picture of bainite/austenite and bainite/carbide interface (Fig. 4.15b). The presence of scarce carbides and Fe-C clusters were also detected inside the bainitic ferrite laths. Figure 4.15a shows plate shaped $\text{Fe}_3\text{C}$ carbide containing $\sim 656$ ions in the bainitic ferrite phase with a thickness of $\sim 2 \text{ nm}$ and diameter $3.71 \text{ nm}$. Figure 4.15d shows the carbon composition profile of the selected box with the particle. The carbon content of retained austenite depends on both the volume fraction of each phase and the presence of carbide and clusters.
Figure 4.15: APT characterization of austenite and bainitic ferrite phases: (a) carbon atom map showing carbon distribution along the analyses needle, (b) corresponding 6.95 at.% iso-concentration surface, (c) carbon concentration profile along the z-axis of the needle analysed, (d) carbon concentration profile along the z-axis of the selected area in (a).

A more recent analysis method, Integrated Visualisation and Analysis Software (IVAS) was further used for better statistics and precise detection of carbon redistribution (Fig. 4.16). The average thickness of bainitic ferrite lath measured from APT, appeared to be 80±10 nm, but APT data is quite localized and Transmission Electron Microscopy revealed more accurate measurements. As evident from Figure 4.16, carbon atoms are segregated at the interface between austenite phase and bainitic ferrite phase. The proxigram across inter-phase boundary established that no other substitutional element was segregated at the inter-phase boundary and only carbon content increased at the interface within 2-4nm layers of the boundary. This segregation seemed to be because of carbon...
trapped at dislocations at these inter-phase boundaries. Inside the matrix, the carbon content was quite homogeneous in both austenite and bainitic ferrite phase.

![Figure 4.16: Reconstruction of APT data using Integrated Visualization and Analysis Software (IVAS). Segregation of carbon atoms at austenite/bainitic ferrite interface is evident.](image)

4.3.3 Transmission Electron Microscopy

The microstructure, after 2 days at 300°C, mainly consisted of lamella structure with the layers of bainitic ferrite and retained austenite (Figs. 4.17a&b). Figure 4.17a shows a colony of bainitic ferrite with retained austenite films. Well-developed bainitic ferrite packets with different orientations were observed in the final microstructure after a holding time of 744 minutes. Further magnification revealed bainitic ferrite and retained austenite layers formed inside the colonies or packs (Fig. 4.17b). The layers within each pack were oriented in the same direction. The bainite colonies grew from the prior austenite grain boundaries and had different orientations within the prior austenite grain. Tangles of dislocations were also observed at the bainitic ferrite/austenite interface, which were associated with the stress accommodation in the matrix during bainitic ferrite plate growth. The average thickness of the bainitic ferrite and retained austenite layers were 118 ± 40 and 60 ± 20 nm, respectively. Some carbide particles were also identified by diffraction in the microstructure by TEM.
Figure 4.17: Bright Field TEM images of (a) Bainitic ferrite colonies with retained austenite films and (b) Bainitic ferrite and retained austenite layers within the pack or colony.

4.4 Discussion

In the present neutron diffraction study, the accelerated data acquisition rate of 13 sec/scan assisted in minutely detecting any precursor events taking place in the austenite phase before the onset of the bainitic phase transformation. No peak shift or peak broadening was noted in $\gamma$-111 or $\gamma$-200 before the initiation of the bainitic phase transformation, suggesting no carbon partitioning taking place during the incubation time in the current experiment. This contradicts the results reported by Babu et al. [7]. Here, we also aimed to understand the carbon redistribution between the bainitic ferrite and remaining austenite, during in situ bainitic transformation and the microstructure in detail.

4.4.1 Evolution of bainitic ferrite

At the early stages of the bainitic transformation, two populations of austenite started to coexist in the microstructure: one adjoining the ferrite phase with higher carbon content and the other far from the transformed ferrite with the carbon content close to the parent austenite (Fig. 4.18). As the bainitic ferrite grows with non-equilibrium concentration of carbon, the carbon tends to partition into the residual
austenite near the newly formed bainite, where it has a lower chemical potential. The diffusion rate of carbon in austenite is slower than in ferrite at such low isothermal holding temperatures. This leads to the essential differences in the carbon content of different areas of remaining austenite. Along with shift in austenite peak due to the carbon enrichment, the peak asymmetry is also evident in Figure 4.8, due to the presence of two populations of austenite. The peak asymmetry and occurrence of more than one population of austenite is more clearly evident through the Rietveld analysis (Fig. 4.12b). Because of a wider range of carbon content in the austenite, the peak also becomes wider, increasing the FWHM. The increase in the FWHM can also be attributed to the refined size of the new population of austenite and the strain induced in austenite because of the shear transformation in bainite. It is not peculiar to note here that at around 744mins from the start of the transformation, γ-200 becomes symmetric again (Fig. 4.8), suggesting a uniformity in the carbon content and hence the completion of the bainitic transformation. An important inference from these observations is the simultaneous occurrence of bainitic ferrite growth and carbon redistribution within retained austenite.

Figure 4.18: Schematic of the process of carbon rejection from supersaturated bainite. Here the austenite next to bainitic plates (red) are enriched in carbon and the remaining austenite phase away from the bainitic plates (pink) have carbon content close to the nominal composition.
4.4.2 Presence of carbides/clusters

The changes in peak position and thus the lattice parameter of $\gamma$-200 were quantified to a final carbon content of 1.37 wt.% [120] in the austenite phase (Fig. 4.19). It has been established in the previous studies that the bainitic ferrite formed at an isothermal holding temperature of 300°C has maximum carbon content of 0.27 wt.% [4]. Following the law of mixtures for a volume fraction of 66% bainitic ferrite (Fig. 4.6), the remaining 34% austenite must have 1.8 wt.% of carbon. To account for the missing carbon (1.8 wt.% > 1.37 wt.%) and following previous studies [65, 69], atom probe tomography was carried out on the final microstructure formed after the in situ neutron diffraction experiment. It was initially speculated that this excess carbon either precipitates in the bainitic ferrite or austenite phase, or otherwise the bainitic ferrite somehow retains the excess carbon in its structure because of tetragonality.

Figure 4.19: Progression in carbon content (in wt.%) with time in austenite phase calculated through the peak position changes in $\gamma$-200.

Atom probe tomography revealed the existence of scarce carbide in the bainitic ferrite phase (Fig. 4.15). This carbide could have formed concurrently during the progress of transformation, which can be termed as auto-tempering [121] or through...
ageing over time [9]. Initiation of carbide formation might not be proven yet but the unfavourable effects are quite evident in the mechanical properties.

It has been well established now through various studies that the presence of Si prevents cementite formation in austenite phase but does not invalidate the formation of carbides and clusters in the ferrite phase [65]. This is speculated to be due to the dislocation annihilation in the bainitic ferrite after long isothermal treatment [2]. The excess carbon is expected to partly segregate to the ferrite plate dislocation network or to form small carbides [69]. Si may slow down the kinetics of dislocation recovery, which would be more effective in the conventional TRIP steels, where the bainitic transformation is completed within 30 minutes. However, the prolonged nanobainitic transformation mostly leads to the formation of carbides/clusters as the time of transformation is long enough to recover the dislocation substructure.

The carbon content of retained austenite was also compared by APT and an average value of 6.95 at.% matched the result obtained by the neutron diffraction, further supporting the existence of carbon in cluster and carbide form. The key factor affecting the stability of austenite is the carbon content of retained austenite and, unless we can control the carbon content of austenite, it would be very difficult to control the properties of nanostructured bainitic steel. Thus, it is important to find the true value of carbon content in different phases to be able to design and exploit this promising new nanostructed material.

4.4.3 Coherent grain size and micro-strain

A very valuable inference from this study, which can be used for further neutron diffraction studies is the quantification of the FWHM values of the α-200 peak to the refinement of the microstructure and micro-strain development. When compared to the instrument function, the lath size was expected to be 182 nm, assuming that the broadening was only due to refinement while internal stress did not play any role. With the TEM images revealing the true size of the bainitic laths to be ~120 nm, this difference can be directly attributed to strain due to the dislocation density, as the bainitic transformation is primarily a displacive
transformation. Rietveld analysis put more light on the micro-strain evolution during the heat treatment. This strain is considered to be due to the presence of dislocation tangles formed in the microstructure. There can be two strain components across the bainitic/retained austenite interface that can cause the formation of the dislocation tangles; i) one originates from the shape change during the bainitic plate formation, ii) the other is volumetric strain arising from difference in atomic density on the plane. Hence, the growth of the bainite plate is accompanied by the formation of dislocations around the bainite plate. APT markedly confirmed the segregation of carbon to the dislocations in austenite (Fig. 4.16), which is in good agreement with the TEM data, showing the strain fields around the bainitic ferrite plate. Since many dislocations were attached to the interface boundary due to the plastic deformation, fast diffusion of carbon along such dislocation sinks are expected, so that the carbon can be transported away from the interface into the austenite matrix during isothermal holding, leading to the homogeneous redistribution of carbon.

4.5 Summary

*In situ* neutron diffraction has been employed to monitor the evolution of nanostructured bainitic ferrite during very low temperature isothermal heat treatment of austenite. This has been done to throw more light on the much argued transformation mechanism of nanostructured bainite. The peak characteristics have been quantified to the changes in volume fraction, lattice parameter and lattice strains using both single peak fitting methods and Rietveld analysis. Complementary investigations have been performed using APT and TEM to verify and understand the results obtained from the *in situ* Neutron Diffraction. It was found that:

1. There is no splitting or broadening of austenite peaks before the onset of bainitic transformation inferring that there is no partitioning of carbon in austenite during the incubation period, resolving a former debate [7, 63, 64] stating carbon partitioning as a precursor event to bainite nucleation.

69
2. In the early stages of transformation, remaining austenite adjoining the newly formed bainitic ferrite laths is enriched in carbon while austenite phase away from such plates has lower carbon content. This gives rise to the peak splitting and asymmetry in the neutron diffraction results. The presence of more than one population of austenite is because of the slow rate of diffusion of carbon at such low temperatures.

3. With the completion of bainitic transformation, carbon redistribution becomes homogeneous within the retained austenite. Thus the growth of bainitic ferrite and redistribution of carbon in austenite phase are simultaneous processes.

4. The kinetics of transformation has been plotted w.r.t. the evolution of bainitic volume fraction and the result has been depicted in terms of an Avrami equation with n parameter as 1.7 thus identifying the transformation is nucleation controlled process.

5. APT was employed to investigate the distribution of carbon and presence of carbides. Si may prevent carbide formation in the austenite phase but scarce amount of carbide was observed in the bainitic ferrite phase [14]. The prolonged low temperature bainitic transformation mostly leads to the formation of carbide/clusters as the time of transformation is long enough to recover the dislocation substructure.

6. Peak broadening in α-200 was further quantified in terms of size effect and compared with the TEM characterisation. A strong increase in lattice size is usually associated with strong decrease of micro-strain, thus a relaxation of micro-strain in austenite phase takes place due to the carbon enrichment, which increases the lattice parameter [122].
Effect of ausforming on transformation kinetics and characteristics of nanobainite

5.1 Introduction

The mechanism of phase transformation leading to the formation of nano-bainite has been vastly discussed [4, 11, 14, 123]. Bainitic steels are now in use for rails and automobile parts. One of the major difficulty that remains as a hurdle in further exploitation of low temperature bainite is to understand the effect of plastic deformation of prior austenite on bainite formation [13, 106]. This chapter describes a study which was conducted to comprehend the formation of bainitic ferrite from plastically deformed austenite and its effect on the kinetics of transformation as well as the microstructural evolution.

Effect of ausforming on the formation of nanostructured bainitic steels has been essentially studied in an attempt to accelerate the otherwise sluggish transformation. Al and Co have been previously added as alloying elements to increase the chemical driving force and thus accelerate the bainite transformation [5, 106]. The deformation of austenite, in circumstances where it does not recrystallize, alters its state in two respects. The total grain boundary surface per unit volume increases and the density of defects such as dislocations, shear bands and grain boundary steps also enhances. The overall stored energy of the austenite consequently increases on deformation.
Formation of bainite from mechanically deformed austenite has been a subject of debate. There are three very varied views. Freiwillig et al. [90] and Tsuzaki et al. [91] reported that austenite deformation accelerated the bainite transformation. Gong et al. [92], later confirmed that small amount of ausforming, accelerated the bainite transformation. Contrary to this, Yang and Larn [93, 94] stated that ausforming causes a retardation of bainite transformation similar to martensite deformation due to the mechanical stabilisation of austenite. However, Shipway et al. [87] and Bhadesha et al. [13] claimed that bainite transformation was accelerated during the early stages but was retarded in the final stages due to the work hardening of austenite.

The results of the earlier studies, reported above have been inconsistent and incomparable because of the different experimental conditions. Thus there arises a need to systematically resolve the debate on the effect of ausforming on the formation of nano-bainite. The current chapter, reports a comprehensive study, made to understand the effect of different ausforming parameters on the kinetic of transformation and morphology of nanostructured bainite.

### 5.2 Experimental methods

The composition, bainite start temperature ($B_s$) and martensite start temperature ($M_s$) of the bainitic steel have been described in section 3.2 of chapter 3. In the present chapter, a systematic approach was employed to study the effect of different thermomechanical parameters on the kinetics and morphology of nanobainite transformation. Axisymmetric samples were firstly thermo-mechanically treated using Servotest TMTS, further metallographic techniques were employed to reveal the microstructure and calculate the volume fraction of different transformed phases. Later, X-Ray Diffraction (XRD) was used to provide complimentary information regarding volume fraction of bainitic ferrite and retained austenite in fully transformed microstructures. Transmission Electron Microscopy (TEM) was further employed to study the ausformed bainite characteristics and examine the austenite substructure in TWIP steel with approximately equal stacking fault energy (SFE).
Axisymmetric compression samples (10 mm × 15 mm) were subjected to different thermo-mechanical treatments using Servotest TMTS 500 kN. The TMP apparatus, sample specification and salt bath have been described in section 3.6 of chapter 3. The samples were firstly homogenised at a temperature of 1250°C for 8 hr in an argon gas environment, followed by furnace cooling.

The parameters, which describe a specific ausforming treatment are: the austenitizing temperature, the deformation temperature, deformation strain, strain rate, the isothermal holding temperature and isothermal holding time. Figure 5.1 schematically describes the thermo-mechanical treatment employed through variation in the deformation temperature and deformation strain. The austenitizing temperature was kept at a constant of 1000°C and the isothermal holding temperature was held at 350°C employing a salt bath. The prior austenite grain size (PAGS) was measure to be 30 ± 5 µm by the linear intercept method [124]. The mean austenite size was estimated by counting the number of grains intercepted by straight lines long enough to yield at least 50 intercepts in total.

Figure 5.1: Schematic representation of the systematic thermo-mechanical treatment employed to study the effect of ausforming of nanobainite transformation.
To study the effect of deformation temperature on the bainite transformation, five different ausforming temperatures were used: 850°C, 570°C, 450°C, 350°C and 200°C (Fig. 5.1). The deformation strains applied at each of these temperatures were 0%, 7%, 15%, 30% and 60% to understand the effect of increasing strain on the austenite substructure and hence the subsequent bainitic transformation. The deformation strain rate was 0.1s⁻¹ for all the thermomechanical schedules. The samples were further held at 350°C for different time periods, to study the evolution of the microstructure after ausforming at different conditions. It was not possible to hold the samples at an elevated temperature for more than 1 hour in the induction furnace attached to the Servotest machine and thus a salt bath was employed for longer holding times of 6 hr and above.

All thermo-mechanically treated samples were cut longitudinally to reveal the microstructure from the central part of each sample. A standard metallographic sample preparation technique was employed as described in section 3.7. Optical micrographs were obtained using DP70 microscope and analysed to calculate the volume fraction of bainite using point counting method. Fully transformed samples (i.e. 3 days of isothermal holding) were further analysed using X-ray diffraction technique to obtain the volume fraction of bainitic ferrite and retained austenite as described in section 3.8.

Thin foils were prepared for transmission electron microscopy (TEM) to study the morphology of ausformed nanostructured bainite. In view of the results, it was important to understand the austenite substructure formed due to ausforming, before the formation of bainite. Thus, a TWIP steel having a fully austenitic microstructure at room temperature was selected to determine the austenite substructure. The composition of the TWIP steel used was 0.61C–22.3Mn–0.19Si–0.14Ni–0.27Cr (wt.%). To complement the results from ausforming of nanobainite at 570°C, the stacking fault energy (SFE) was calculated using the equation proposed by Curtze et al. [15]. The TWIP steel sample was then deformed at a temperature of 300°C at 7% and 15% strains bearing the same SFE value as for nanobainitic steel deformed at 570°C. TEM was further conducted on the deformed TWIP steel samples to reveal the austenite substructure. The sample preparation and imaging for TEM was followed according to the section 3.5.
5.3 Results

5.3.1 Microstructural evolution

Optical microscopy revealed, in general, the refinement in the microstructure due to deformation. Figure 5.2 represents the evolution of the microstructure with time, due to a deformation strain of 30% applied at a deformation temperature of 570°C and further held at an isothermal temperature of 350°C for different holding times. In vitro tests were conducted and interrupted at 30 min, 60 min, 6 hr, 12 hr, 24 hr and 3 days for each deformation temperature and each deformation strain as described in the experimental methods. The average volume fraction of bainite, appeared as elongated features, was calculated from 24 micrographs of each condition. Volume fraction of bainite gradually increased with time. After 3 days of isothermal holding, the microstructure at consisted of bainitic ferrite and stable retained austenite with no martensite. The volume fraction of bainite after 3 days was calculated to be 34.86% through XRD, which was in good agreement with the average volume fraction of 33.82±1.16% calculated using the ‘point counting method’ using optical micrographs. Only the fully transformed samples were subjected to X-ray diffraction, which gave phase fraction results comparable to the results from point counting method on optical micrographs. Similar calculations were done for all thermo-mechanical conditions and have been graphically represented in the next section.
Figure 5.2: Evolution of the nanobainite microstructure with time after ausforming 30% at 570°C and isothermally holding at 350°C for different holding times as mentioned on each micrograph.
To understand the effect of deformation strain on the evolution of the bainite phase, different strains were applied to the axisymmetric samples at different ausforming temperatures. Figure 5.3 depicts the evolution of the microstructure for a constant deformation temperature of 570°C and a constant isothermal temperature of 350°C; increasing the strain from 0 to 0.6 after a time interval of 12 hr. An increase in the strain resulted in refinement of the microstructure as evident in Figure 5.3. In the particular case of ausforming at 570°C, the deformation with a strain of 7% produced a higher volume fraction of bainite than an undeformed microstructure. An increase in ausforming strain to 15% at 570°C retarded the kinetics and produced a lower volume fraction of bainite as compared to the undeformed condition. On increasing the strain further to 22%, 30% and 60%, the volume fraction of bainitic ferrite at 12 hr interrupted time further reduced. This suggests that there was a critical strain below which the phase transformation was accelerated.

Figure 5.4 shows the microstructures formed in different samples after deforming each with 15% strain at different ausforming temperatures and further isothermally held at 350°C for 30 min. These microstructures consisted of bainitic ferrite laths with some adjoining retained austenite in a martensite matrix. As calculated and also evident in Figure 5.4, there was an increase in the volume fraction of bainite, when 15% of strain was applied at the deformation temperatures of 200°C, 350°C and 450°C. On the contrary, in case of the same amount of strain, isothermal holding time and temperature, the volume fraction of bainite decreased when the deformation temperatures were 570°C and 850°C. The bainite transformation had not initiated in 30 min holding, when a strain of 15% was applied at an ausforming temperature of 850°C. Thus the critical strain for acceleration of the bainitic transformation decreased with an increase in the deformation temperature. It can be deduced from the microstructural evolution that the phase transformation characteristics were significantly influenced by the thermo-mechanical parameters: i.e. strain and deformation temperature. The results for the effect of the thermo-mechanical parameters on kinetics of phase transformation have been plotted in the next section, followed by the study of the changes in morphology using transmission electron microscopy (TEM).
Figure 5.3: Evolution of the nanobainite microstructure with increase in deformation strain after ausforming at 570°C and isothermally holding at 350°C for 12 hours. The amount of strain has been mentioned on each micrograph.
Figure 5.4: Evolution of the nanobainite microstructure after ausforming at different temperatures with a deformation strain of 15% and isothermal holding at 350°C for 30 min. The ausforming temperature has been mentioned on each micrograph.
5.3.2 Kinetics of phase transformation

To study the kinetics of phase transformation, the volume fraction of bainitic ferrite was plotted over isothermal holding time for different thermo-mechanical conditions. The average volume fraction was calculated from the optical micrographs presented above. In figure 5.5, the volume fraction of bainite has been plotted against isothermal holding time (log scale) for different deformation strains applied at 570°C. The plots clearly follow Avrami type equations.

![Figure 5.5: Plot of the volume fraction of bainite over the isothermal holding temperature (log scale) for samples ausformed at 570°C with different deformation strains.](image)

It is evident from Figure 5.5 that as compared to the undeformed condition, a strain of 7% applied at 570°C accelerated the bainitic transformation with the fully bainitic microstructure formed within 12 hours. It is important to note here that the volume fraction of bainite at the cessation of the transformation was lower in case of 7% strain as compared to the undeformed condition due to the substructure introduced during ausforming. Further, when ausformed with strains of 15% and
higher, the bainite transformation was retarded with the transformation taking up to 10 days to complete. Thus, only very small amounts of strain assisted in the acceleration of nanobainite transformation while larger amounts of deformation strain caused retardation of the transformation process. Similar studies for the kinetics of phase transformation were made for different ausforming temperatures.

The maximum amount of strain resulting in the acceleration of the nanobainite transformation has been termed as the critical strain [125]. This critical strain was found to be dependent on the ausforming temperature. Figure 5.6 shows that for an ausforming temperature of 350°C, 15% strain lead to the acceleration of bainite transformation while the same amount of strain caused retardation of the phase transformation for ausforming temperatures of 570°C and 850°C. The data represented in figure 5.6 is from interrupted tests at 60 min of isothermal holding. It is evident from the results that the critical strain decreased with an increase in the ausforming temperature.
Figure 5.6: Plot of the volume fraction of bainite formed after 60 minutes of isothermal holding over the deformation strain applied for 3 different ausforming temperatures of 350°C, 570°C and 850°C, respectively.

5.3.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy was primarily used to study the morphological features of nano-structured bainite formed subsequent to ausforming. Further, TEM was also employed to study the austenite substructure formed due to the deformation of a TWIP steel, which has only austenite phase at room temperature.
The results of the TEM observations have been presented in this section. In the following TEM images (Figs. 5.7 to 5.11), the compression direction (CD) is nearly perpendicular to the beam direction.

The microstructure after 1 hour at 350°C subsequent to ausforming with 7% strain at 570°C, mainly consisted of a lamella structure with the layers of bainitic ferrite and retained austenite (Fig. 5.7). Bainitic ferrite and retained austenite were identified by the analysis of diffraction patterns. Further magnification revealed bainitic ferrite and retained austenite layers formed inside the bainite colonies or packs. The bainite colonies seemed to grow from the prior austenite grain boundaries as well as from inside the grain, amounting to shortening of the laths. The length of the bainitic laths varied from 6 µm to almost 21 µm. The average thickness of the bainitic ferrite layers was 250±40 nm. Dislocation debris was evident in both the bainite and the surrounding austenite. No carbide particles could be identified while scanning through this particular sample of 3 mm diameter by TEM.

The microstructure in Figure 5.8 was obtained from a specimen ausformed at 570°C with 15% reduction and further transformed at 350°C for 6 hours. The bainitic lath was evidently shorter in this particular condition reaching a maximum length of about 17 µm. The thickness of bainitic ferrite laths estimated from the TEM micrographs was 173±35 nm. It was interesting to identify twins in the austenite substructure, which were absent in the microstructure of 7% strain condition. A very high dislocation density was observed with curved and tangled dislocations at the bainite/austenite interface.
Figure 5.7: TEM bright-field (BF) images of lath bainitic ferrite (ɑₜ) and retained austenite (γ) for a sample ausformed at 570°C with 7% reduction and isothermally held at 350°C for 1 hour. The diffraction pattern represents a BCC structure, i.e. bainitic ferrite.
Figure 5.8: TEM bright-field (BF) image of lath bainitic ferrite, retained austenite and mechanical twins for a sample ausformed at 570°C with 15% reduction and isothermally held at 350°C for 6 hours. The diffraction pattern represents typical mechanical twins.

Figure 5.9 represents the TEM results obtained from a specimen ausformed at 570°C with 30% reduction and further isothermally transformed at 350°C for 1 hour. The bainitic laths were found to be much shorter with evident curving of the interface. The maximum length of the bainite laths reduced to about 3.6 μm. The
width of bainitic ferrite laths was measured to be 140±50nm. It is very interesting to note here that carbide particles were formed in the bainitic ferrite laths, which were identified by the diffraction pattern (Fig. 5.9). The carbide particles were uniformly distributed in the bainite phase throughout the microstructure. Another important feature of the microstructure observed with 30% reduction was the occurrence of dislocation walls along the bainitic ferrite/austenite interface.

Figure 5.9: TEM micrograph of lath bainitic ferrite, retained austenite and carbide particles in bainitic ferrite for a specimen, ausformed at 570°C with 30% reduction and isothermally held at 350°C for 1 hour. The diffraction pattern evidences the existence of carbide.

The variation in the kinetics of phase transformation and microstructural features with changes in the amount of strain and deformation temperature could be mainly because of the austenite substructure formed as a result of ausforming. The austenite substructure, in turn, is dependent on the stacking fault energy (SFE) of the particular steel composition at a particular temperature. Thus, to understand the austenite substructure formed due to ausforming, a TWIP steel (0.61C–22.3Mn–0.19Si–0.14Ni–0.27Cr wt.%), which remains fully austenitic at room temperature was used. The Curtze model [15] was applied for the calculation of stacking fault energies (SFE) of both nanobainite and TWIP steel. The SFE of nanobainite at
570°C was calculated to be 91.61 mJ/m$^2$ which corresponds to an SFE of 88.13 mJ/m$^2$ for the TWIP steel at 300°C. To study the effect of strain on austenite substructure the TWIP steel was deformed at 300°C corresponding to a deformation temperature of 570°C for nanobainite steel.

The TWIP steel was thermo-mechanically treated by uniformly heating to 1000°C and cooling down to 300°C to be deformed with 7% and 15% reductions. Figure 5.10 represents the TEM micrographs thus obtained from the TWIP steel specimen deformed with 7% reduction. The average austenite grain size was measured to be 34±21 µm. Interestingly, the microstructural features present due to the application of 7% strain were stacking faults, dislocation cells and dislocation bands (Fig. 5.10). On the contrary, as a result of the application of 15% reduction at 300°C, the TWIP steel displayed the formation of twins, dislocation pile up, interaction between dislocations and twins and most importantly the formation of sharp dislocation walls (Fig. 5.11). The difference in the austenite substructure formed under different conditions has been the key to the discussion on phase transformations in ausformed nanobainite.

![Figure 5.10: TEM micrographs of TWIP steel deformed with 7% reduction at 300°C. The micrographs demonstrate the formation of stacking faults, dislocation cells and dislocation bands.](image-url)
Figure 5.11: TEM micrographs of TWIP steel deformed with 15% reduction at 300°C. The micrographs demonstrate the formation of twins, dislocation pile up, interaction of dislocations and twins and formation of sharp dislocation walls.

5.4 Discussion

The in situ observation of study of the transformation mechanism of low temperature bainite transformation has been established through Neutron Diffraction as described in Chapter 4. A displacive and nucleation controlled mechanism of transformation was confirmed. The quantitative theory of nanostructured bainite has already been used to design carbide-free bainite rail steels [5, 19]. However, even after almost 2 decades of remarkable developments, there are yet some important issues, which require a full quantitative treatment. One of the most important unresolved issues is the formation of bainite from plastically deformed austenite. In view of the current large scale production of steels by thermomechanical processing, it is essential to understand the effect of different ausforming parameters on thus formed bainite.

The effect of ausforming on the kinetics of low temperature bainite transformation rate has previously been studied giving rise to differing views. An acceleration in the kinetics of phase transformation was reported and attributed to the increase in number of nucleation sites due to ausforming [90-92, 126]. However, opposing views stating a retardation in the rate of bainite transformation due to the mechanical stabilisation of austenite were reported by Yang and Larn [93, 94]. Later, Shipway et al. [87] and Bhadeshia et al. [13] claimed that the bainite
transformation at low temperatures was accelerated during the early stages but was retarded in the final stages due to work hardening of austenite.

Though, high-carbon bainite with similar composition was used in all these studies, yet, the ausforming parameters were quite different. An attempt has, thus, been made in the present chapter to systematically resolve the above debate through the study of austenite substructure formed subsequent to ausforming with a varied range of parameters. The current results reveal that the deformation parameters such as strain and ausforming temperature have a remarkable influence on the kinetics and morphology in the low temperature bainite. For example, for a particular deformation temperature, an increase in the strain after a particular limit, leads to the retardation of the bainite transformation and for a particular amount of strain, an increase in the deformation temperature retards the bainite transformation. It is, thus, important to understand the mechanism at the microstructural level to explain these results.

The deformation of austenite prior to the transformation affects both nucleation and growth processes at the substructure level. Firstly, the deformation increases the number of nucleation sites due to the serration of grain boundaries as a result of the intersection of slip lines with prior austenite grain boundaries [66]. The rule for nucleation of bainite in austenite is to reduce both boundary and strain (i.e. dislocation density) energies during the bainitic ferrite lath formation. Thus, it would be expected that the deformation increases the bainitic ferrite nucleation rate on prior austenite grain boundaries. Secondly, the growth of bainitic laths is limited due to the strengthening of austenite through the introduction of a dislocation substructure by deformation [127]. The dislocation substructure thus introduced, enables the mechanical stabilisation retarding the decomposition of austenite.

Through interrupted tests, it was shown that the volume fraction of bainite in the microstructure increased with time to a maximum limit when ausformed 30% at 570°C and isothermally held at 350°C (Fig. 5.2). Further, specimens ausformed at 570°C, using different amounts of strain (7%, 15%, 22%, 30% and 60%) were compared with the non-deformed condition (figure 5.3). The bainite laths had undoubtedly refined as the strain increases. An interesting finding is that while a
strain of 7% accelerates the kinetics of phase transformation, strains of 15% and above significantly retard the phase transformation, taking the time for completion to 10 days (Fig. 5.5). The volume fraction of bainite found in the fully transformed microstructure also decreases with the increase in strain demonstrating a higher stability in deformed austenite.

Transmission electron microscopy revealed that with the increase in deformation strain thus reducing the prior austenite grain size, the bainitic laths were significantly shortened. The substructure introduced during ausforming not only affected the size of the bainitic laths, but also caused curving of the austenite/bainite interface with the increase in strain. This must be due to dislocation debris on the active slip plane during ausforming [2]. The dislocation density increased manyfold with clear dislocation entanglements and dislocation walls visible. It was very interesting to find carbide particles, identified through diffraction patterns in the ausformed bainitic laths (with 30% strain). To understand these significant results, it was important to observe the state of the austenite substructure formed due to deformation prior to bainite transformation.

The dislocation substructure formed due to ausforming is dependent on the temperature and stacking fault energy of the material [1]. The stacking fault energy, at a particular temperature, is in turn dependent on the steel composition. There are different models to calculate the SFE of a steel at a particular temperature using the steel composition [15, 99, 102]. The equation by Curtze et al. [15] was found to be most inclusive and thus used to calculate the SFE of nanobainite at different temperatures. To fully comprehend the austenite substructure formed prior to transformation, a TWIP steel was chosen which is fully austenitic at room temperature and was deformed with 7% and 15% strain at 300°C. The TWIP steel had a nearly equal SFE at 300°C to that of nanobainite at 570°C.

Through TEM observations of TWIP steel specimens after deformation, it was interesting to observe that while a 7% strain produced quite visible stacking faults, dislocation cells and dislocation bands (Fig. 5.10), a higher strain of 15% results in the formation of mechanical twins, dislocation pile ups and sharp dislocation walls (Fig. 5.11). Displacive transformations involve the coordinated movement of
atoms. While minor defects such as dislocations can be incorporated into the lattice but interface movement cannot be sustained against strong defects causing mechanical stabilization in austenite prior to deformation. Displacive transformations are accomplished by the progress of glissile interfaces which can be rendered sessile by the accumulation of dislocation debris and other defects [13].

It is very important to note here that while a small amount of strain leads to acceleration in the bainite transformation, higher strains can lead to the mechanical stabilisation and thus retardation of the bainite transformation with decreased amount of bainite volume fraction at the termination of the transformation. The strain required to initiate stabilisation of austenite or the maximum strain, which can cause a faster transformation is termed at the critical strain. Chatterjee et al. [125] formed a model to calculate the critical strain by balancing the force, which drives the motion of the interface against the resistance of the dislocation debris and defects created by the deformation of the austenite. It was observed that the critical strain for stabilisation decreases as the deformation temperature increases (Fig. 5.6) as expected by the above stated model.

The effect of ausforming temperature on the bainite transformation has also been previously studied by Gong et al. [97], comparing ausforming of 15% strain at 300°C and 600°C followed by isothermal phase transformation at 300°C for a steel composition similar to the present study. It was reported that while the deformation at 300°C accelerated the bainite transformation, there was no significant change in kinetics in case of deformation at the higher temperature of 600°C. It was also shown that the dislocation substructure introduced by ausforming is much more effective than the external stress in accelerating bainite transformation

In the present study, Figure 5.4 displays that for the same amount of applied strain (15%), the transformation is accelerated when ausformed at 200°C, 350°C and 450°C. However, there seem to be a definite retardation when the ausforming temperature is increased to 570°C and further to 850°C. This is due to the decrease in the critical strain with an increase in deformation temperature. As discussed above, the features of the dislocation substructure formed after ausforming change considerably with the amount of deformation strain and stacking fault energy. This
difference in the dislocation substructure is due to the temperature dependence of the stacking fault energy; with low temperature ausforming causing an acceleration in the transformation.

5.5 Summary

The present chapter focused on the systematic study of the transformation kinetics and microstructural features in low temperature bainite after ausforming process. In view of the continuing debate, a comprehensive quantitative study was performed. Specimens were thermo-mechanically treated with varying deformation temperatures and deformation strains. Further optical microscopy and XRD revealed the volume fraction of different phases present, while transmission electron microscopy (TEM) was utilized to reveal the bainite characteristics. To understand the dislocation substructure leading to the stabilization of austenite, a TWIP steel was employed, which was fully austenitic at room temperature. From the results and observations made in the study, it can be inferred that:

1. While using 570°C as the ausforming temperature, a strain of 7% accelerated the bainite transformation while a strain of 15% slowed down the kinetics of transformation. The difference was caused due to the introduction of different dislocation substructures in austenite.

2. The morphology of bainite was established through TEM observations. In general, the shortening of bainite laths, increase in dislocation density, existence of twins and curving of the interface were observed. At higher strains, carbide particles where also observed in the bainitic laths.

3. The dislocation substructures were further studied using a TWIP steel. It was established that while a lower strain of 7% created stacking faults, dislocation cells and dislocation bands, a higher strain of 15% formed much stronger defects like dislocation pile up, twins and sharp dislocation walls. This evidences that the deformation substructure introduced during ausforming plays an important role in the mechanical stabilization of austenite.
4. The strain at which strong defects and sessile dislocation debris was introduced in the substructure was termed as the critical strain. The critical strain decreased with an increase in the deformation temperature due to the temperature dependence of the stacking fault energy of this steel.
Effect of austenite conditioning on the crystallography of nano-structured bainite

6.1 Introduction

In the previous chapter, the effect of austenite conditioning on the kinetics of transformation and morphology of nano-structured bainite has been discussed in detail. The variation in the transformation behaviour was shown to occur due to the introduction of different dislocation substructures in the deformed austenite. To complete the understanding of the effect of austenite conditioning on the phase transformation mechanism, the changes in the variant selection and orientation relationship have been described in this study.

In the present chapter, a recent back-calculation approach has been employed to determine the effect of prior austenite grain size and thermo-mechanical treatment on the orientation relationship formed following low temperature bainitic phase transformation. This approach was devised by Tari et al. [16] to back-calculate the initial ‘orientation’ of face-centred cubic (fcc) parent austenite phase from sets of variants of body-centred cubic (bcc) ferrite orientations present after the completion of phase transformation in each prior austenite grain employing the known orientation relationships.

In the particular case of nano-structured bainitic steel, some prior austenite is enriched with carbon and retained even at the cessation of the transformation [62].
Yet, two dimensional EBSD leads to the loss of information on all existing variants, which could have been observed through three-dimensional EBSD [128]. The back-calculation method is fairly accurate in determining the closest orientation relationship (OR) in case of a low number of observable variants as compared to the traditional matching method of orientation relationship determination. It requires at least 7 variants to be able to back-calculate the parent austenite orientation and the closest orientation relationship.

Previously, the effect of thermo-mechanical parameters on the crystallography of nanobainitic steels has been studied through the variation in the isothermal holding temperature [8] and the variation in the ausforming temperature [92], as discussed later. In this chapter the gap has been filled systematically by studying the effect of prior austenite grain size and applied strain on the crystallography of nano-structured bainite.

### 6.2 Experimental procedure

The composition, bainite start temperature (Bₜ) and martensite start temperature (Mₜ) have been thoroughly presented in section 3.2 of chapter 3. In the present chapter, the clustering approach devised by Tari et al. [16] has been employed to study the effect of ausforming on the orientation relationship between the parent austenite grain and the product phase bainite variants formed during phase transformation. A systematic methodology was employed to firstly comprehend the effect of prior austenite grain size by changing the austenitizing temperature and secondly to look at the effect of small strains on the variant selection and orientation relationship.

Axisymmetric compression samples (10mm × 15mm) were employed to conduct different thermomechanical treatments using Servotest TMTS 500kN. The TMP apparatus and sample specification have been described in section 3.6 of chapter 3. The samples were firstly homogenised at a temperature of 1250°C for 8 hrs in an argon gas environment, followed by furnace cooling.
Figure 6.1 schematically describes the heat treatment employed through 3 different austenitizing temperatures: 1200°C, 1000°C and 850°C. Each sample was isothermally held at 200°C for 10 days in a salt bath (described in section 3.11), followed by water quenching. The respective grain size for each austenitizing temperature was calculated using the standard intercept method via SEM (Scanning Electron Microscope) micrographs obtained though FSD (Forward Scatter Detector). The prior austenite grain size was 7.38±2.82 µm, 43.72±7.21 µm and 103.44±13.58 µm at 850°C, 1000°C and 1200°C, respectively, held for 180 s (Figure 6.2).

Figure 6.1: Schematic representation of heat treatment to study the effect of prior austenite grain size on the variant selection and orientation relationship between the parent austenite and bainitic ferrite laths.
In the previous chapter (Chapter 5), it has been established that in case of ausforming while a small amount of strain can accelerate the bainitic transformation, large strains cause the stabilization of austenite matrix, limiting the advance of bainite transformation. This led to a smaller bainitic ferrite fraction. It is also important to look at the effect of such strains on the bainite variants formed after phase transformation and their relationship to the parent austenite phase. To investigate the effect of strain, the thermomechanical treatment was performed using Servotest with three deformation conditions: 0% strain, 7% strain and 15% strain. The thermomechanical treatment has been schematically represented in Figure 6.3. Austenitization temperature was held at a constant of 1000°C for 180s followed by ausforming at 570°C where the samples were deformed at different strains. The samples were then transferred to a salt bath at 200°C and held for 10 days, similar to the basic heat treatment samples.

Figure 6.2: Prior austenite grain size (in µm) measured after austenitizing at three different austenitization temperatures.
Figure 6.3: Schematic of thermo-mechanical treatment conducted to investigate the effect of compression strain on the variant selection and orientation relationship.

The samples, after respective heat treatment and thermo-mechanical treatment were vertically sectioned and polished using standard mechanical polishing procedure followed by colloidal silica slurry polish. Electron Back Scattered Diffraction (EBSD) was performed on LEO 1530 enabled with Aztec data acquisition software. Post-processing was conducted using TSL OIM software as described in section 3.10 of Chapter 3 to extract out the orientations of atleast 7 bainite variants from each prior austenite grain. The extracted data was then processed using the following approach coded in Fortran95 programming language, using a personal computer with Linux Ubuntu 11.00 and 2GHz CPU.

6.3 Approach

A unique approach developed by Tari et al. [16] has been employed in this chapter to calculate the orientation relationship and parent austenite orientation from sets of variants of orientations in bainitic phase transformation products. In the course of bainitic phase transformation, the parent austenite phase orientation is inherited...
by the product bainite phase orientation via the Orientation Relationship (OR). There are a number of known orientation relationships (ORs): Kurdjumov-Sachs (K-S) [129], Nishiyama-Wasserman (N-W) [130, 131], Pitsch (P), Greninger-Troiano (G-T) and Greninger-Troiano’ (G-T’) [132]. In the current approach, all these five main ORs have been used to back transform each observed product bainite variant from a single parent austenite grain to the potential parent austenite orientations.

D. Qiu et al. have previously developed a near-coincidence-sites (NCS) method based on the orientation relationship generated by the O-line model between two phases, specially between bcc and fcc phases [133, 134]. In the particular case of ausforming the back-calculation method is better suited in determining the closest orientation relationship (OR) because of a low number of observable variants as compared to a non-ausformed microstructure.

Traditionally a transformation matrix $T$ defines the rotational part of the forward transformation. The transformation from parent fcc orientation to a product bcc variant can be represented by equation 1 [135].

$$g_{di} = TO_i g_p$$

(1)

Where, $g_p$ and $g_{di}$ are the orientations of the parent and product phases, respectively. $O_i$ is the fcc crystal symmetry operator, taken from the set of 24 elements for cubic crystals (i = 1, 2 .... 24). The five known orientations and the corresponding transformation matrices in terms of minimum angle and axis are given in Table 6.1 [104]. Because of the effect of the crystal symmetry in the austenite (fcc) phase, the K-S, G-T and G-T' ORs produce 24 distinguishable ferrite (bcc) variants and N-W and Pitsch ORs give 12 variants (Table 6.1).

In the present approach, each bainite variant was back-calculated to all possible austenite (fcc) variants as described in equation 2:

$$g_{pi} = T^{-1} Q_i g_{dj}$$

(2)

Here, $T^{-1}$ is the inverse of the orientation relationship, which is used as a transformation matrix to back-calculate from each bainite variant to the parent
phase. \( g_{dj} \) and \( g_{pi} \) are the orientations of the bainite and austenite phases, respectively. \( Q_i \) is the bcc crystal symmetry operator, which is same as \( O_i \) from equation 1 as both parent and product phase are cubic crystals with 24 elements.

Table 6.1: Orientation relationship between parent (fcc) and product (bcc) phases [104]

<table>
<thead>
<tr>
<th>Orientation Relationship</th>
<th>Parallelism</th>
<th>Minimum angle/axis</th>
<th>No. of variants</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pitsch (P)</strong></td>
<td>{100}( \gamma ) // {011}( \alpha ) &lt;011&gt;( \gamma ) // &lt;111&gt;( \alpha )</td>
<td>45.98°&lt;0.083 0.201 0.976&gt;</td>
<td>12</td>
</tr>
<tr>
<td><strong>Nishiyama-Wasserman (N-W)</strong></td>
<td>{111}( \gamma ) // {110}( \alpha ) &lt;112&gt;( \gamma ) // &lt;110&gt;( \alpha )</td>
<td>45.98°&lt;0.976 0.083 0.201&gt;</td>
<td>12</td>
</tr>
<tr>
<td><strong>Kurdjumov-Sachs (K-S)</strong></td>
<td>{111}( \gamma ) // {110}( \alpha ) &lt;110&gt;( \gamma ) // &lt;111&gt;( \alpha )</td>
<td>42.85°&lt;0.968 0.178 0.178&gt;</td>
<td>24</td>
</tr>
<tr>
<td><strong>Greninger-Troiano (G-T)</strong></td>
<td>{111}( \gamma ) // {110}( \alpha ) &lt;123&gt;( \gamma ) // &lt;133&gt;( \alpha )</td>
<td>44.23°&lt;0.973 0.189 0.133&gt;</td>
<td>24</td>
</tr>
<tr>
<td><strong>Greninger-Troiano' (G-T')</strong></td>
<td>{110}( \gamma ) // {111}( \alpha ) &lt;133&gt;( \gamma ) // &lt;123&gt;( \alpha )</td>
<td>44.23°&lt;0.189 0.973 0.133&gt;</td>
<td>24</td>
</tr>
</tbody>
</table>

To find the actual parent orientation from all possible back-calculated fcc orientations, the minimum mutual misorientation was calculated between all sets of possible fcc orientations back-calculated using each OR. Each set of back-calculated austenite orientations was then clustered by minimizing the sum of the misorientations between the members. The cluster with the minimum summation
of mutual misorientation angle (SMMA) among these clusters was taken as the actual parent orientation. This process is described systematically with verification by Tari et al. [16]. The confidence index was also calculated by referring to the SMMA of the next best cluster. For the present chapter, this approach has been used to identify the closest OR (i.e. the OR that yields a smaller SMMA than the other ORs is more favourable to be the closest OR) among all theoretical ORs for all thermomechanical conditions.

6.4 Results

Following the austenite conditioning schematically represented in figures 6.1 and 6.3, fully bainitic structures were formed in all specimens after isothermal holding at 200°C for 10 days. A band contrast (BC) map was shown in figure 6.4 along with the corresponding inverse pole figure (IPF) map of the retained austenite of one selected grain. The IPF map of austenite phase showed only one orientation, confirming that the selected area contained only one variant of austenite and thus lies in a single prior austenite grain.

The IPF map in ND plane of BCC (bainitic ferrite) for the selected grain was shown in Fig. 6.5a, along with the pole figure of bainite (Fig. 6.5d). Packets containing bainite laths and retained austenite films can be easily identified. In the following sections, the change in the variant selection was recognized by comparing the transformed variants in case of the particular condition to the transformed variants in an undeformed sample austenitized at 1000°C. The prior austenite orientation and the closest OR were calculated from the observed bainite variants using the back-calculation approach as shown in figure 6.6.
Figure 6.4: Band contrast map and IPF map (austenite phase in a selected grain), for a sample austenitized at 1000°C followed by isothermal holding temperature of 200°C for 10 days.

Figure 6.5: EBSD data analysis for the grain selected in figure 6.4 to depict: a) IPF map in ND plane; b) Rolling direction and transverse direction; c) IPF colour coding and d) {001} PF map of the bainite variants for the selected prior austenite grain.
In figure 6.6(a), the summation of mutual misorientation angle (SMMA) for all known ORs was plotted using an in-house code written on the basis of the back-calculation approach presented above. The austenite candidate variants have been shown in an ascending order from the minimum SMMA to the maximum SMMA value for the selected grain shown above (i.e. Fig. 6.6a). For each grain, the austenite candidate corresponding to the minimum SMMA has been taken to represent the closest prior austenite orientation. Similar histograms were calculated for 10 to 15 grains from all microstructures produced through different thermomechanical conditions.

Figure 6.6b, shows the minimum SMMA of all five ORs for five prior austenite grains in a sample austenitized at 1000°C and transformed at the isothermal holding temperature of 200°C. It is interesting to note here that all grains do not follow the same orientation relationship. Thus, the average of minimum SMMA of 5-10 grains was taken to depict the closest OR for each TMP condition. For this particular condition, figure 6.6c shows the average of minimum SMMA of 5 grains for the five known ORs. This suggests that the OR is very close to G-T orientation relationship for this particular microstructure.

Similar results were presented in figures 6.4 through 6.6 obtained from microstructures produced through different thermo-mechanical treatments described in Section 6.3. The results have been reported in terms of the effect of parent austenite grain size and the effect of strain on the variant selection and orientation relationship in the following sections.
Figure 6.6: (a) Histogram of summation of mutual misorientation angle (SMMA) versus austenite candidate variants in the prior austenite grain selected in figure 6.4; (b) The minimum SMMAs of 5 prior austenite grains; (c) The corresponding average of minimum SMMA of 5 grains for 5 known orientation relationships.
6.4.1 Effect of prior austenite grain size on variant selection and orientation relationship

The three different austenitization temperatures; 850°C, 1000°C and 1200°C, produced prior austenite grain sizes of 7.38±2.82 µm, 43.72±7.21 µm and 103.44±13.58 µm, respectively (Fig. 6.2). It appeared that some of the variants were missing at austenitization temperature of 850°C for 180s followed by isothermal holding at 200°C for 10 days (Fig. 6.7). This suggested that there was a slight strengthening of variant selection compared to 1000°C (Fig. 6.5). An increase in the austenitization temperature to 1200°C further weakened the variant selection (Fig. 6.8). In addition, the average length of bainitic ferrite laths enhanced with an increase in the prior austenite grain size (i.e. austenitization temperature).

The back-calculation analysis revealed that the change in the prior austenite grain size (i.e. austenitization temperature) did not change the closest orientation relationship between the parent austenite and bainitic ferrite laths. Indeed, Greninger-Troiano (G-T) OR remained the closest orientation relationship within experimental error with a similar trend for all three grain sizes (Fig. 6.9). In other words, G-T OR revealed the minimum SMMA values for all grain sizes. By contrast, Pitch OR showed the highest SMMA values for all conditions. The other three ORs (i.e. K-S, G-T’ and N-W) had SMMA values between G-T and Pitch ORs (Fig. 6.9). It is important to note here that each prior austenite grain in a given microstructure may follow different orientation relationship, thus it is important to take an average and only suggest the overall trend.
Figure 6.7: Inverse pole figure map and pole figure of bainite phase for a given austenite grain transformed with an austenitizing temperature of 850°C followed by isothermal transformation at 200°C for 10 days.

Figure 6.8: Inverse pole figure map and pole figure of bainite phase for a given prior austenite grain transformed at an austenitizing temperature of 1200°C followed by isothermal transformation at 200°C for 10 days.
Figure 6.9: Average of minimum SMMA for five known orientation relationships in case of three different austenitization temperatures (i.e. prior austenite grain sizes).

6.4.2 Effect of thermomechanical treatment on variant selection and orientation relationship

Ausforming is known to promote the variant selection in bainitic microstructures [136]. Steel samples ausformed at 570°C displayed strong variant selection, revealing a decrease in the number of detectable variants within a prior austenite grain with an increase in strain (Figs. 6.10 and 6.11). In addition, the bainitic laths became much shorter in length with an increase in the strain. To use the backcalculation approach for determining the closest orientation relationship between parent austenite and bainitic ferrite laths accurately, at least seven bainitic variants are required for a given austenite grain, which became strongly difficult with increase in strain (e.g. for strains above 0.15) due to an enhanced variant selection.
The average of minimum SMMA for the five known orientation relationships in the specimens compressed with different amount of strains has been presented in Fig. 6.12. For a non-ausformed microstructure, G-T OR had the lowest average of minimum SMMA, signifying G-T to be the closest OR. Interestingly, the introduction of 7% strain led to an increase in the average of minimum SMMA for G-T OR, becoming comparable to K-S and G-T’ ORs. Though, the strain did not change the SMMA trend for Pitch and N-W OR, still showing the highest SMMA values. Similar trend was observed for a 15% strain, though the minimum SMMA for the K-S OR became slightly lower than those measured for the G-T and G-T’ ORs. This suggests that the strain led to the change in the OR from G-T OR towards K-S OR with an increase in the strain (Fig. 6.12).

Figure 6.10: Inverse pole figure map and pole figure for bainite phase in a given parent austenite transformed after austenitization temperature at 1000°C followed by deformation of 7% at 570°C and isothermal transformation at 200°C for 10 days.
Figure 6.11: Inverse pole figure map and pole figure for bainite phase in a given austenite grain transformed after austenitization temperature of 1000°C followed by deformation of 15% at 570°C and isothermal transformation at 200°C for 10 days.

Figure 6.12: Average minimum SMMA for the five known orientation relationships at different strains transformed at 200°C.
6.5 Discussion

The effect of austenite conditioning on kinetics of phase transformation and morphology of nanostructured bainitic ferrite was discussed in detail in the previous chapter. It was established that the displacive transformations achieved by the advance of glissile interfaces can be rendered sessile by the accumulation of dislocation debris [137]. Further, in the present study, an attempt has been made to understand the effect of austenite conditioning on the crystallography (i.e. variant selection and orientation relationship) of nanostructured bainitic steels. A new approach [16] has been employed to accurately determine the orientation relationship between the parent austenite and product nanobainite laths.

The crystallography of nanobainite steels has previously been studied in detail for microstructures formed at different isothermal holding temperatures [8, 65, 138]. Further, Gong et al. [97] studied the effect of ausforming temperature on the variant selection in nanobainite steels. It was previously established that the transformed bainitic variants from deformed austenite are much lower in number than the theoretical variants according to the known orientation relationships (N-W, K-S, G-T, G-T' and P) [8, 104, 105]. To fill the gaps and systematically understand the effects of austenite conditioning on the crystallography of transformed nanobainite, the effects of prior austenite grain size and ausforming strain have been discussed here.

6.5.1 Effect of prior austenite grain size on variant selection and orientation relationship

The parameters that affect the condition of austenite prior to phase transformation are austenitizing temperature, ausforming temperature, strain, strain rate and isothermal holding temperature. Beladi et al. [8] showed that with a decrease in isothermal holding temperature, the bainitic structure becomes finer and variant selection becomes weaker. The change in the variant selection mechanism from 350°C to 200°C was attributed to the fact that at lower transformation temperatures, it becomes more difficult to accommodate the plastic strain induced by shear.
transformation, giving rise to multi-variants resulting from the relaxation of internal stresses caused by transformation misfit strains [139].

The decrease in austenitizing temperature leads to a smaller austenite grain size (Fig 6.2). With refinement of the prior austenite grain, the grain boundary area and hence the number of possible nucleation sites increase. The effect of austenite grain size on the kinetics of isothermal bainite transformation has been studied previously [140]. It was reported that the rate of transformation accelerated with the refinement of austenite grain size in case the overall reaction is limited by a slow growth rate and an opposite trend was seen when the number of nucleation sites is the limiting factor [140].

It has been evidenced through *in situ* Neutron diffraction technique using Avrami Equation that the kinetics of nanobainite formation is nucleation controlled [14]. Thus, a reduction in the austenite grain size would typically reduce the total volume transformed, per nucleus, and retard the overall reaction rate limiting the growth. Further, from the present results, it is evident that with a decrease in grain size from 103.44µm to 7.38µm, there was strengthening of variant selection (Figures 6.5, 6.7 and 6.8). The smaller grain size provides a higher nucleation rate and limited growth for self-accommodation of transformation strain. Variant selection takes place to reduce the boundary energy and the strain energy produced during the nucleation of bainitic ferrite laths [86].

The back-calculation approach was applied in this study to more accurately determine the closest orientation relationship [16]. Beladi *et al.* [8] reported that for low temperature bainitic transformation, the bainitic ferrite laths were close to the N-W relationship with their parent austenite. Though, there was a significant effect of isothermal bainite transformation temperature on the retained austenite characteristics and the variant selection of bainitic ferrite laths. In other words, the variant selection became weaker as the bainitic transformation temperature was reduced. To utilize the back-calculation approach efficiently in this study, a very low transformation temperature of 200°C was, therefore, chosen to obtain the maximum number of variants possible [8].
It is clearly evident here that a decrease in the austenite grain size has no significant effect on the OR and the trend is very similar for all austenitization temperatures (Fig. 6.9). The G-T OR has also been previously reported for carbide free bainite [141]. Though the variant selection and kinetics are affected by the prior austenite grain size, it does not affect the orientation relationship between the parent austenite grains and the product bainite laths. This suggests that the prior austenite grain size does not change the nature of bainitic nuclei (i.e. orientation), though it mainly influences the effective nucleation sites (i.e. grain boundary area). In other words, the effective nucleation sites progressively increase with a decrease in the prior austenite grain size, enhancing the rate of nucleation (i.e. phase transformation kinetics). However, the growth of bainite became limited as the prior austenite grain size decreases, leading to formation of fewer bainitic variants (i.e. variant selection).

6.5.2 Effect of thermomechanical treatment on variant selection and orientation relationship

The effect of ausforming temperature on the variant selection and orientation relationship has been previously studied by Gong et al. [97], comparing ausforming of 15% strain at 300°C and 600°C followed by isothermal phase transformation at 300°C for a steel composition similar to the present study. It was reported that while the deformation at 300°C showed a strong variant selection, it became weaker in the case of deformation at the higher temperature of 600°C. The orientation relationship remained the same i.e. close to the N-W for both cases. A partial dislocation model was postulated to explain the variant selection mechanism. It was also reported that strong variant selection occurs for nanobainite transformation but it hardly takes place for the martensite transformation in the sample ausformed at 300°C. It has also been reported previously that for the martensite transformation the OR is closer to K-S for the same composition [97].

In the present study, less colours/orientations are found in the EBSD maps (reducing to one colour of bainite in one prior austenite grain) as the amount of deformation increases (0%→7%→15%→30%, Figs. 6.5, 6.10 and 6.11). Thus, the
deformation of the parent austenite results in morphological changes along with a crystallographic variant selection in the bainitic ferrite. The deformation of prior austenite has two contradicting effects on the formation of bainite variants [142]. First is the strengthening of austenite leading to the refinement of blocks and more self-accommodation, which is typically responsible for weakening of the variant selection. The second effect is the formation of planar dislocations on limited active slip planes inducing particular variants while assisting bainitic transformation. Bainite forms at a higher temperature than martensite. Thus, it has a lower driving force for self-accommodation. Unlike ausformed martensite, the ausformed bainite, therefore, shows a strong variant selection owning to the formation of dislocation boundaries with limited slip systems activated locally.

The current result reveals that deformation has a remarkable influence on the variant selection of bainite. For the non-ausformed state, the G-T OR is the closest OR but as strains of 7% and further 15% are applied, the trend progressively changes towards the K-S OR as more appropriately describing the relationship between the parent austenite and the product phase. It is important to understand the mechanism at the microstructural level to explain these results.

In general, the deformation causes a complexity (i.e. dislocation substructure formation) in the microstructure. At the substructure level, three events are taking place concurrently due to ausforming, which may change the orientation relationship. First event is the increase in the number of nucleation sites due to the serration of grain boundary as a result of the intersection of slip lines with prior austenite grain boundaries. A simple rule for the nucleation of bainite in austenite is to reduce both boundary and strain energies during the bainitic ferrite lath formation. Therefore, it would be expected that the deformation enhances the bainitic ferrite nucleation rate on prior austenite grain boundaries. Secondly, the growth of bainitic laths is limited due to the strengthening of austenite through the introduction of substructure by deformation. The dislocation substructure induced through deformation is discussed in chapter 5. The third event is the fragmentation of an austenite grain by deformation, which divides a given austenite grain into several small sub-grains, having slight different orientations locally as compared to
the original grain [127]. The extent of the difference in orientation depends on the strain and parent austenite grain orientation [143].

Here, the back-calculated austenite orientation is almost an average of all local sub-grain orientations. In the deformed state, a bainitic ferrite lath formed in a deformed austenite grain locally follows an OR with respect to the sub-grain region, which has slightly different orientation from the neighbouring sub-grain/s. This results in a change in the overall OR between the parent austenite and bainitic ferrite laths. As observed in the results the extent of orientation relationship changes enhances with an increase in the deformation.

### 6.6 Summary

The present study was undertaken to further understand the effect of austenite conditioning on crystallography of nanobainite. To fill the gaps in the previous literature, the influence of prior austenite grain size and ausforming strain on the variant selection and orientation relationship was studied. The samples were heat treated with or without deformation to obtain the required microstructures. Further, the EBSD technique was used to reveal the crystallography in different conditions. A new approach was employed to calculate the parent austenite orientation, by clustering into SMMA sets, and determine the closest orientation relationship among the five known orientation relationships. It was found that:

1. A decrease in the austenite grain size weakened the variant selection due to the self-accommodation of the transformation strain arising from the increase in the number of nucleation sites and limitation to the growth.

2. The back-calculation approach was used to more accurately determine the closest orientation relationship. For the three different austenite grain sizes, the G-T (Greninger-Troiano) was found to be the closest orientation relationship representative. A change in the austenite grain size did not affect the orientation relationship between the parent austenite and product bainite phases.
3. Strong variant selection was observed in the deformed samples. There was a decrease in the number of variants with increasing strain. Formation of dislocation boundaries on active slip planes appeared to be much more effective for a strong variant selection than the opposing weakening effect through austenite strengthening in the case of nanobainite.

4. Deformation enhanced the bainitic nucleation sites due to the serration of prior austenite grain boundaries. However, the bainitic lath growth became limited due to the presence of dislocation substructure in the prior austenite grain interior.

5. An increase in the deformation strain caused a progressive change in the orientation relationship between the parent and the product phase. The closest orientation relationship shifted from the G-T (Greninger-Troiano) OR for the non-deformed condition to the K-S (Kurdjumov-Sachs) OR for 15% strain. This significant result was attributed to the formation of dislocation substructure during deformation, which divides a prior austenite grain into several sub-grains, locally having different orientations.
Conclusions and Future Work

In the present study an attempt has been made to create a better understanding of the low temperature bainite phase transformation and the effect of plastic deformation of austenite on subsequently formed bainite. The high carbon alloy studied here displayed a useful combination of phases in the microstructures in both undeformed and deformed conditions essential for a fundamental study. The silicon, to some extent, suppressed the formation of cementite during isothermal transformation, and hence enabled some austenite to be retained.

7.1 Conclusions

_in situ_ neutron diffraction analysis led to the conclusion that there is no partitioning of carbon in austenite prior to the onset of bainite transformation resolving a former debate [7, 63, 64] stating the formation of carbon enriched and carbon depleted zones in austenite prior to the transformation. It has been shown through an instrument with high temporal resolution that carbon redistribution only occurs after the onset of transformation.

During the early stages of transformation, austenite adjoining the newly formed bainitic ferrite laths is enriched in carbon while austenite phase away from such plates has lower carbon content (i.e. close to the nominal composition) giving rise to more than one population of austenite because of the slow rate of diffusion of carbon at such low phase transformation temperatures. By fitting the kinetics plot
obtained from the evolution of bainite phase fractions to an Avrami equation, the transformation was established to be nucleation controlled. The diffraction peak characteristics were further quantified to coherent grain size and micro-strain verified using transmission electron microscopy (TEM).

Strikingly, atom probe tomography (APT) revealed the presence of carbide despite the high level of silicon in the composition. It was proposed that silicon may prevent carbide formation at the beginning of the transformation, however, the continued isothermal holding may lead to carbide/clusters formation with enough time the annihilation of the dislocation substructure (i.e. recovery). The formation of clusters and carbides needs to be studied in more details and has been added to the suggestions for the future work.

A comprehensive study of the effect of different ausforming parameters on the kinetics and morphology of bainite transformation revealed some interesting outcomes. A small amount of strain led to an acceleration in the kinetics, while, higher amounts of deformation strain slowed down the kinetics of transformation. With an increase in the deformation temperature, the critical strain required to stimulate the bainite transformation decreased. The critical strain reduced with an increase in the deformation temperature due to the temperature dependence of the stacking fault energy in this steel.

The morphology of bainite investigated through TEM, in general, revealed a shortening in bainite laths, an increase in the dislocation density, existence of twins and curving the interface due to ausforming treatment. At higher deformation strains, carbide particles were also observed in the bainitic laths. The dislocation substructure studied using a TWIP steel exhibited the presence of strong defects such as dislocation pile up, twins and sharp dislocation walls at higher strains, which cause hindrance to the advance of glissile interfaces hence hindering the growth.

A crystallographic examination was conducted through the electron backscattered diffraction (EBSD) technique to examine the effect of austenite conditioning on the variant selection and orientation relationship between the product bainite and parent
austenite. A recent back calculation approach was applied to determine the most suitable orientation relationship. A decrease in the austenite grain weakened the variant selection due to the self-accommodation in the grain. G-T (Greninger-Troiano) was found to be the closest orientation relationship and did not change with the change in the parent austenite grain size.

Strong variant selection was observed with an increase in the ausforming strain. Formation of dislocation sub-boundaries on active slip planes proved to be much more effective for a strong variant selection than the opposing weakening effect through austenite strengthening. The closest orientation relationship progressively changed from the G-T (Greninger-Troiano) OR for the non-deformed condition to the K-S (Kurdjumov-Sachs) OR with the amount of deformation strain. This noteworthy result was attributed to the formation of a unique substructure during deformation, which divides a prior austenite grain into several sub-grains, having different orientations locally.

7.2 Suggestions for future work

The work presented in this thesis is believed to provide a significant contribution towards the existing knowledge of phase transformations in nanostructured bainite. A research study, which starts with a particular research objective is always limited in its scope and thus gives way to the continuation of further research. There are a few potential areas of future study comprehended during this work:

1. Low temperature bainitic phase transformation has been studied extensively with regard to the effect of isothermal holding temperatures. However, the austenitization temperature has received much less attention, though it determines the size, static recovery and homogeneity of the austenite grains and therefore influences the kinetics, extent and chemistry of the subsequent phase transformation. Thus, the study of the effect of prior austenite grain size characteristics on low temperature bainite transformation kinetics using in situ neutron diffraction is proposed.
2. The scope of this study was limited to the identification of carbides through atom probe tomography (APT). It has been established that clusters and carbides do exist despite the addition of 1.5% silicon in the alloy. It is thus very important to conduct a quantitative analysis of the clusters/carbides present in the nanobainite microstructure through APT.

3. It is also evident that carbides formed during bainitic transformation form by a displacive mechanism without the partitioning of substitutional solute. A major gap in the experimental evidence is the measurement of shape deformation due to the carbide precipitation. Atomic force microscopy might prove as an aid to characterize the surface relief due to these incredibly fine carbide particles.

4. The recent back calculation method has proven to be more accurate than the direct comparison method to determine the orientation relationship between the product bainite phase and the parent austenite phase. It would be interesting to use this back calculation method to determine the effects of different heat treatment and thermo-mechanical treatment parameters on the orientation relationship.
References


54. Mahieu, J., *Contribution to the physical metallurgy or crash-resistant galvanized TRIP-assisted steel for automotive structures*. 2003, Ghent University.


