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**Department of Materials** 

# Effects of Niobium on Phase Transformations from Austenite to Ferrite in Low Carbon Steels

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### Abstract

Niobium is a widely used microalloying element in many steel products, e.g. plates, strip, sections and linepipe. Niobium has important effects on transformation behaviour, grain size refinement and precipitation strengthening during hot rolling and subsequent cooling, with even a low content of niobium having a strong effect on the transformation rate from austenite to ferrite. The purpose of this research was to accurately characterise and quantify the effects of solute niobium atoms and niobium carbo-nitride precipitates on phase transformations from austenite and ferrite, and to incorporate these effects into metallurgical models to predict the transformation behaviour and microstructure of niobium containing steels, which can benefit industry through their use of the models to optimise processing conditions.

In order to accurately investigate transformation kinetics and the effects of niobium, extensive analyses have been carried out. Isothermal transformations and continuous cooling using a wide range of cooling rates for steels with different niobium contents were carried out using a dilatometer, and the transformation kinetics were also recorded and analysed. The microstructure of the transformed samples was then characterised using a range of microscopy techniques including optical microscopy, field emission gun scanning electron microscopy (FEG-SEM), a dual beam system of focused ion beam (FIB) and FEG-SEM, and transmission electron microscopy (TEM) with energy dispersive X-ray analysis (EDX).

The results indicate that solute niobium atoms have a stronger refinement effect on the austenite grain size than niobium carbo-nitride precipitates. The refinement effect on austenite grains also reduces the ferrite grain size after transformations. Solute niobium atoms delay the isothermal transformation kinetics from austenite to ferrite and lower transformation temperatures during continuous cooling. The final microstructure after transformation is also affected by solute niobium atoms. During transformation from austenite to ferrite, both the nucleation rate and ferrite grain growth rate are delayed by the presence of solute niobium atoms. However, if solute niobium atoms precipitate as niobium carbo-nitride particles before transformation

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occurs, their effect on delaying the transformation is largely reduced. These effects were subsequently incorporated into an existing metallurgical model, and the new model developed in this research can successfully predict the kinetics of various kinds of transformations for the low alloy steels used in the work, and also other different steel types.

## **Publications**

Parts of this work are published as detailed below:

1 Li Wang, Sally Parker, Andrew Rose, Geoff West, and Rachel Thomson, "*Effect of niobium on transformations from austenite to ferrite in low carbon steels*", Journal of Iron and Steel Research, International, Volume 18, Supplement 1-1, 2011, Pages 208-212.

2 L. Wang, S.V. Parker, A.J. Rose, G.D. West, and R.C. Thomson, "Effects of Nb on isothermally reconstructive transformation kinetics in low carbon steels", in preparation for submission to Metallurgical and Materials Transactions A.

3 L. Wang, S.V. Parker, A.J. Rose, G.D. West, and R.C. Thomson, "Modelling of Nb influence on phase transformation kinetics from austenite to ferrite in low carbon steels", in preparation for submission to Metallurgical and Materials Transactions A.

4 L. Wang, S.V. Parker, A.J. Rose, G.D. West, and R.C. Thomson, "Effects of Nb on austenite and ferrite grain size in low carbon steels", in preparation for submission to Materials Science and Technology.

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## **1** Introduction

Low alloy steels are widely used for structural, transport and automotive applications, due to their low cost and high strength. In industry, low alloy steel is usually processed by hot rolling. Modelling has become an important tool to assist in research and development, and manufacturing of steels. Some thermodynamic and kinetic modelling software packages are already widely used to calculate transformation start and finish temperatures, and also phase diagrams. Recently, many researchers have focused on the development of models describing the microstructure and properties of steels after various treatments. Some of these models are applicable to practical steel types. With the help of these metallurgical models, the final microstructure, mechanical properties and transformation kinetics can be predicted, therefore less actual mill trials are required for optimising processing routes and hence the properties of steels, and the cost can be reduced. However, most of the models are empirical or semi-empirical models, and thus their applications are typically restricted to particular compositions or heat treatments. In order to extend these metallurgical models to more types of steels, some fundamental physical and metallurgical theories involving thermodynamics, nucleation and growth kinetics are utilised. However, the various alloying elements e.g. Mn, Si, Ni, Cr, Al, V, Nb, Ti, etc. all have different effects on transformation kinetics, and all of their effects should be studied separately and synergistically, and incorporated into metallurgical models to ensure that the models are comprehensive and accurate.

Isothermal transformation and continuous cooling are two typical transformation methods for steels. For isothermal transformation, samples are first heated into the austenite phase, and then quenched to a temperature and held for some time for transformation, and finally quenched to room temperature. For continuous cooling, samples are first heated to a high temperature for austenitisation, and then continuously cooling to room temperature. For isothermal transformation, the isothermal holding temperature is the major factor which affects the final microstructure. For continuous cooling, the cooling rate is the major factor affecting

the final microstructure. In carbon steels, ferrite, pearlite, bainite and martensite are typical microstructural constituents which can be present, and have different transformation characteristics and mechanical properties. Generally, isothermal holding at a high temperature or slow cooling results in ferrite and pearlite. A fast cooling rate results in martensite. A moderate cooling rate or holding at a moderate temperature results in bainite, which can be 'upper' or 'lower' bainite.

Niobium is one of the most important micro-alloying elements in steels. It is a ferrite stabilising element, but it also has a strong tendency to form carbides. Therefore, there are two typical forms present in steels: solute niobium atoms and niobium carbide precipitates. The presence of niobium has a significant effect on the kinetics of the transformation from austenite to ferrite, and thus the holding time and temperature during an isothermal transformation should be adjusted according to the niobium content. The transformation start and finish temperatures during continuous cooling is also affected by the presence of niobium. It can also affect austenite grain growth, which in turn has an indirect effect on the subsequent transformation kinetics. In addition, solute niobium atoms and niobium carbide precipitates each have different effects on the transformation kinetics. After transformation, the final microstructure, grain size, strength and hardenability may all be affected by niobium. These effects are ascribed to solute drag, grain refinement and precipitation strengthening. In addition, even a small amount of niobium (e.g. 0.03 wt. %) can result in a significant improvement in the mechanical properties of steels. However, to date these effects have not been fully understood, and current metallurgical models require further development to incorporate the effects of niobium.

Solute niobium atoms, niobium carbide particles, and the austenite grain size all have an effect on the transformation from austenite to ferrite, and therefore their effects should be studied separately for a complete understanding. The effects of niobium on austenite grain growth have been characterised to make sure that all the samples have the same initial austenite grain size. Then samples were isothermal transformed or continuously cooled, in order to investigate the effects of solute niobium atoms on transformation behaviour. Some samples underwent a

precipitation heat treatment before transformation, to make the solute niobium atoms precipitate as niobium carbide particles, and then the effects of niobium carbide on transformation behaviours could also be studied. Advanced microscopy techniques have been utilised to study the mechanisms of the effects of niobium on transformations. All of these effects have then been incorporated to develop a new metallurgical model to predict the transformation behaviour of steels alloyed with niobium.

This thesis is organised into eight chapters as follows. Chapter 2 presents a literature review covering basic knowledge of steel metallurgy, and a brief introduction to pre-existing phase transformation models, together with an overview of previous research about the effects of niobium in steels.

Chapter 3 introduces the experimental procedure used in this research. The chemical compositions of the materials used in the research are described in detail. A brief description of the instruments and all of the operation parameters of the experimental techniques used in the research are explained in this chapter, including thermodynamic calculations, sample preparation, dilatometry, various microscopy techniques, and methodologies for microstructure quantification.

Chapter 4 discusses the results from thermodynamic calculations of the materials used in the research, using which phase boundary temperatures of the materials have been obtained. Therefore, temperatures for heat treatments e.g. austenitisation, precipitation and isothermal transformations can be determined. Some pre-existing models have also been utilised to predict the transformation behaviours of the materials, and the results from the different prediction methods compared and discussed.

In Chapter 5, the austenite grain size as a function of austenitisation temperatures or holding times has been characterised for materials with different niobium contents,

and then the effects of niobium on austenite grain growth have been investigated. After transformation from austenite to ferrite, the resulting ferrite grain size as a function of niobium content has also been analysed.

Chapter 6 describes all the dilatometry experiments in which the effects of solute niobium atoms and niobium carbide precipitates on transformation kinetics have been investigated. Various analytical microscopy techniques have then been used in order to understand the transformation mechanisms.

Chapter 7 proposes a modified phase transformation model for niobium containing steels based on a pre-existing metallurgical model and the experimental data obtained in the previous chapters. The new model has been proven to be successful by accurately predicting a variety of transformations kinetics for the materials used in the research, and additionally for some additional steels of interest to the sponsors, Tata Steel, but which were not a part of the experimental programme.

Chapter 8 presents the conclusions of the research and gives some suggestions for the further work.

The aims of the research were to:

- Study the effects of solute niobium atoms and niobium carbonitride precipitates on austenite grain growth, and also the effects on subsequent ferrite grain size after transformation;
- Study the effects of solute niobium atoms on the transformation rate during isothermal transformation and continuous cooling, and their effects on final microstructure;
- 3. Study the effects of niobium carbonitride precipitates on the transformation rate during isothermal transformation and continuous cooling, and their effects on final microstructure;

- 4. Study the mechanisms of the effects of Nb on transformation kinetics;
- 5. Incorporate the effects into a metallurgical model of phase transformations to develop a complete model to describe the effects of niobium on the transformation from austenite to ferrite.

## **2 Literature Survey**

#### 2.1 Introduction

Steel is one of the most widely used materials in the world, due to its high strength, good toughness, good formability, and relatively low cost. The variety of properties of steel results from the different microstructural features present after transformation from austenite to ferrite. Niobium is a ferrite stabiliser but has a strong trend to form carbides. Therefore, it has a powerful effect on microstructural evolution during transformation from austenite to ferrite. Niobium is usually used as an important micro-alloying element in many steel products. However, solute niobium and niobium carbonitride precipitates in steels might have different effects on transformation kinetics such as nucleation and grain growth. In addition, the mechanical properties may be affected due to grain refinement and precipitation strengthening. The effects are complex, and may be vary with niobium content, transformation temperature, and cooling rate. Transformation models have been developed to predict the microstructural features and properties of steels. Current phase transformation models are typically based on fundamental physical and metallurgical principles of phase transformations, and some thermodynamic and kinetic theories are also utilised. It is important to incorporate the effects of niobium into current phase transformation models.

#### 2.2 Physical metallurgy of steels

#### 2.2.1 Iron carbon phase diagram

Pure iron has a melting point of 1538°C. It is quite weak, with a yield stress of less than 50 MPa [1]. For industrial applications, steels with much better mechanical properties are widely used. Steels are iron and carbon alloys, but other elements are often added to improve mechanical or physical properties [1, 2]. The phases present in steels are determined by the carbon content and the temperature as indicated by the iron-iron carbide phase diagram shown in Figure 2.1.

From Figure 2.1 it can be seen that with decreasing temperature, pure iron has three allotropes:  $\delta$ -ferrite with a body centred cubic (BCC) structure,  $\gamma$ -austenite with a face centred cubic (FCC) structure and  $\alpha$ -ferrite with a body centred cubic structure [1]. At high temperature,  $\delta$ -ferrite is present, but it transforms to  $\gamma$ -austenite at 1390°C, and  $\gamma$ -austenite transforms to  $\alpha$ -ferrite at 910°C. The maximum solubility of carbon in austenite is 2.14 wt. % at 1147°C, while the maximum solubility of carbon in  $\alpha$ -ferrite is only 0.022 wt. %. The large difference in carbon solubility between austenite and ferrite results from the crystal structures of the two phases. The interstitial holes in an FCC structure are much larger than the holes present in BCC materials, therefore more carbon atoms can be dissolved in austenite. When steels transform from austenite to  $\alpha$ -ferrite, the large difference in carbon solubility leads to the formation of carbide, or a supersaturated solid solution, depending on the cooling rate [1]. The eutectoid reaction occurs at 723°C for 0.76 wt. % carbon content:

$$\gamma \rightarrow \alpha + Fe_3C$$

If the carbon content is less than 0.76 wt. %, pro-eutectoid  $\alpha$  is formed on the prior  $\gamma$  grain boundaries. If the carbon content is more than 0.76 wt. %, pro-eutectoid cementite (Fe<sub>3</sub>C) is formed.

From Figure 2.1, there are some important boundaries at phase fields [3]:

A<sub>1</sub>: The eutectoid temperature. In addition, this is also the minimum temperature at which austenite can still be present.

A<sub>3</sub>: The  $\gamma / (\gamma + \alpha)$  phase boundary. This is the maximum temperature at which ferrite can be generated during cooling.

 $A_{cm}$ : The  $\gamma$  / ( $\gamma$  + Fe<sub>3</sub>C) phase boundary; the maximum temperature at which cementite can be generated during cooling.

 $A_1$ ,  $A_3$ , and  $A_{cm}$  are affected by alloying elements and cooling or heating rates. Letters c, e, or r are used to describe the conditions of heat treatment as follows:

 $Ac_1$ ,  $Ac_3$ , and  $Ac_{cm}$  are the boundaries during heating.

Ae<sub>1</sub>, Ae<sub>3</sub>, and Ae<sub>cm</sub> are the boundaries at equilibrium.

Ar<sub>1</sub>, Ar<sub>3</sub>, and Ar<sub>cm</sub> are the boundaries during cooling.



Figure 2.1: Iron-iron carbide phase diagram [1].

#### 2.2.2 The austenite-ferrite transformation

For hypoeutectoid steels, pro-eutectoid ferrite will be formed when its temperature reaches Ar<sub>3</sub> during cooling. A fast cooling rate delays the transformation and decreases the Ar<sub>3</sub> temperature. In low alloy steels, allotriomorphic ferrite is nucleated before the eutectoid transformation, therefore  $\gamma/\alpha$  boundaries are preferential nucleation sites for pearlite nodules [4]. Formation of ferrite increases the carbon content in the remaining austenite until it reaches the eutectoid point.

The equilibrium weight fractions of ferrite and austenite present at a temperature between  $Ae_1$ , and  $Ae_3$  can be calculated by the lever rule. The weight fraction of ferrite is:

$$Wf_{\alpha} = \frac{x^{\gamma \alpha} - \bar{x}}{x^{\gamma \alpha} - x^{\alpha \gamma}}$$
 Equation 2.1

The weight fraction of austenite is:

$$Wf_{\gamma} = \frac{\bar{x} - x^{\alpha \gamma}}{x^{\gamma \alpha} - x^{\alpha \gamma}} \qquad \qquad Equation \ 2.2$$

where  $x^{\gamma\alpha}$  is the carbon content in austenite in equilibrium with ferrite,  $x^{\alpha\gamma}$  is the carbon content in ferrite in equilibrium with austenite, and  $\bar{x}$  is carbon content of the bulk steel.

At the Ae<sub>1</sub> temperature, the content of all pro-eutectoid ferrite can be calculated by the lever rule:

$$Wf_{proeutectoid \alpha} = \frac{0.76 - \bar{x}}{0.76 - 0.022} \qquad \qquad Equation \ 2.3$$

where 0.76 is the carbon content of the bulk steel at the eutectoid point, and 0.022 is the maximum carbon content in ferrite at the eutectoid point.

During the austenite-ferrite transformation there are four possible morphologies which can form: allotriomorphic ferrite, idiomorphic ferrite, Widmanstätten ferrite, and intragranular Widmanstätten ferrite plates, as shown schematically in Figure 2.2. Optical micrographs of the morphologies are shown in Figure 2.3. Allotriomorphic ferrite and idiomorphic ferrite are formed via a diffusional mechanism, but Widmanstätten ferrite and intragranular Widmanstätten ferrite are formed via a diffusional mechanism, but Widmanstätten ferrite and intragranular Widmanstätten ferrite plates are formed via a displacive mechanism [1, 5].



Figure 2.2: Schematic illustration of the four morphologies which can form during the austenite-ferrite transformation in steels: (a) allotriomorphic ferrite originates from austenite grain boundaries, and idiomorphic ferrite forms inside an austenite grain; and (b) primary Widmanstätten ferrite originates at austenite grain boundaries, and secondary Widmanstätten ferrite grows from allotriomorphic ferrite [6, 7].

The allotriomorphic is the first morphology to appear during slow cooling. It tends to nucleate at the austenite grain boundaries, and it has a high growth rate along the austenite grain boundaries but a low growth rate in the direction normal to the boundary plane. The allotriomorphic ferrite nucleates between at least two austenite grains and has a coherent orientation with one grain, but a random orientation with the other. There is a typical Kurdjumov-Sachs relationship between the allotriomorphic ferrite and the austenite grain [1, 5]:

$$\{1 \ 1 \ 1\}_{\gamma} // \{1 \ 1 \ 0\}_{\alpha}$$
  
 $\{1 \ -1 \ 0\}_{\gamma} // \{1 \ -1 \ 1\}_{\alpha}$ 

Idiomorphic ferrite is intragranular and typically nucleates on non-metallic inclusions where it forms equiaxed crystals and a defined crystallographic orientation relationship [1].



Figure 2.3: Optical microscopy images of the four typical morphologies of ferrite: (a) allotriomorphic ferrite and secondary Widmanstätten ferrite; (b) Intragranular idiomorphic ferrite; and (c) primary Widmanstätten ferrite [8, 9, 10].

At lower temperatures, interstitial atoms can still quickly diffuse between the phases, but diffusion of substitutional elements becomes difficult, and thus it is a displacive transformation mechanism. A different morphology, which is typically referred to Widmanstätten ferrite, can be formed via this transformation mechanism, and the transformation rate is controlled by the diffusion of carbon in the austenite ahead of the transformation front. Primary and secondary Widmanstätten ferrite grows from the austenite grain boundaries and the already formed allotriomorphic ferrites, respectively.

#### 2.2.3 Pearlite

Cementite (Fe<sub>3</sub>C) and  $\alpha$ -ferrite are formed via the eutectoid reaction. If the cooling rate is slow, e.g. cooling in furnace, a lamellar structure, which is composed of fine, alternating layers of cementite and ferrite, will be formed [2]. This microstructure is called pearlite, because it appears like mother of pearl when observed using optical microscopy [2]. Carbon solubility in BCC ferrite is much lower than FCC austenite, and the excess carbon is rejected from ferrite and diffuses a short distance to form Fe<sub>3</sub>C. Carbon and substitutional alloying elements redistribute during transformation, and thus it is a reconstructive transformation, or diffusional transformation. The transformation mechanism from austenite to pearlite is schematically shown in Figure 2.4. In hypoeutectoid steels, proeutectoid ferrite is formed on the prior austenite grain boundary. Then, Fe<sub>3</sub>C nucleates at a  $\gamma$ - $\alpha$  grain boundaries with a coherent or semi-coherent interface and an orientation with  $\alpha$ , but an incoherent interface with y. Since carbon concentration in Fe<sub>3</sub>C is higher than that in austenite and ferrite, formation of Fe<sub>3</sub>C requires carbon diffusion from neighbouring austenite grains. When the Fe<sub>3</sub>C is formed, carbon content in the neighbouring austenite grains is decreased, and then the ferrite can nucleate adjacent to the Fe<sub>3</sub>C. The newly formed ferrite also has a coherent interface and an orientation with the proeutectoid ferrite. The nucleation of Fe<sub>3</sub>C and ferrite repeats sideways. The coherence decreases as the pearlite nodules grow, and branching of the lamellae possibly occurs [11].



Figure 2.4: Development of pearlite via the sideways nucleation and cooperative growth of Fe<sub>3</sub>C and ferrite. Here the  $\theta$  phase which is Fe<sub>3</sub>C, is shown to nucleate first, followed by ferrite [10].

The formation of pearlite is dependent on the diffusion of carbon, and the lamellar size is largely determined by the cooling rate. Fast cooling leads to fine pearlite, and slow cooling leads to coarse pearlite [1, 2, 11], as shown in Figure 2.5. Fine pearlite has higher strength than coarse pearlite, according to the Hall-Petch equation [2]:

$$\sigma_{\rm v} = \sigma_0 + k_{\rm v} d^{-1/2} \qquad \qquad Equation \ 2.4$$

where  $\sigma_y$  is the yield strength, *d* is the average grain diameter,  $\sigma_0$  and  $k_y$  are constants for a particular material.

Cementite is much harder and stronger than ferrite. Therefore, increasing the carbon content generally results in a harder and stronger material.



Figure 2.5: Coarse pearlite (the left part) and fine pearlite (the right part) [10].

#### 2.2.4 Martensite and tempered martensite

If the cooling from austenite is fast, e.g. quenching in water, martensite will be formed. Carbon atoms are trapped in the ferrite lattice, because they have little time to diffuse. The carbon atoms are located in the distorted octahedral interstitial sites. This results in a tetragonal distortion of the BCC lattice, and a body centred tetragonal (BCT) structure is formed. The degree of tetragonality is determined by carbon content [1]:

$$c_{a} = 1 + 0.045 \text{ wt.}\%C$$
 Equation 2.5

A very large strain which is called the Bain strain is required during the transformation from the FCC lattice of austenite to the BCT lattice of martensite, as shown in Figure 2.6. An approximately 12% expansion is present in the  $(0 \ 0 \ 1)_{\gamma}$  plane, and an approximately 17% compression is present along the  $[0 \ 0 \ 1]_{\gamma}$  direction.

The shear deformation can cause surface relief on a polished surface, as shown in Figure 2.7. The transformation region remains coherent with the austenite when the surface is tilted, caused by elastic strain. The martensite laths or plates can span the entire austenite grain [11]. There is a Kurdjumov-Sachs orientation relationship between the austenite and the martensite in low carbon steels [1]:

 $\{1 \ 1 \ 1\}_{\gamma} // \{1 \ 1 \ 0\}_{\alpha'}$ <1 -1 0>  $_{\gamma} // <1$  -1 1>  $_{\alpha'}$ 



Figure 2.6: The lattice correspondence for formation of martensite from austenite: (a) tetragonal unit cell outlined in austenite, and (b) lattice deformation (compression in c-axis and expansion in the plane normal to c-axis) to form martensite [1].

The martensitic transformation is athermal, and the amount of martensite only depends on the temperature. The equation used to calculate the amount of martensite is [12]:

$$1 - V'_{\alpha} = e^{\beta(M_s - T_q)} \qquad Equation 2.6$$

where  $V_{\alpha}'$  is the volume fraction of martensite,  $M_s$  is martensite start temperature,  $T_q$  is the lowest temperature reached during quenching, and  $\beta \simeq -0.011$ .

The temperature at which martensite begins to form on cooling,  $M_s$ , is called the Andrews formula and gives the  $M_s$  as a function of alloying additions to the steel [4]:

$$M_{\rm S}(^{\circ}{\rm C}) = 539 - 423{\rm C} - 30.4{\rm Mn} - 17.7{\rm Ni} - 12.1{\rm Cr} - 7.5{\rm Mo}$$
 Equation 2.7

Martensite is a very hard and brittle material but it causes strengthening of steel through the mechanisms of solid solution strengthening and dislocation strengthening [1]. The interstitial solid solution of carbon has a great effect on strengthening. The trapped carbon atoms result in the tetragonality of martensite, and inhibit the movement of dislocations. In addition, the small number of slip systems in the BCT lattice makes dislocation motion much more difficult. If the carbon content is very high, cracks may occur during quenching due to high internal stress [2]. Steels with 100 percent martensite can never be obtained, and there is always some austenite retained, because formation of the last martensite causes very high strains, which strongly suppress growth of existing martensite.



Figure 2.7: Surface relief caused by martensite plates [11].

The brittleness of martensite is usually modified by tempering, which is reheating of steels to a temperature below the eutectoid temperature for a few hours to form finely dispersed carbide, which relieves internal stress [2, 11]. Tempered martensite has a similar strength to martensite, but the ductility and the toughness are largely improved. There are four distinct but overlapping stages during reheating [1]:

- 1) Up to 250°C:  $\varepsilon$ -carbide which is a transition iron carbide with a chemical formula of Fe<sub>2-3</sub>C is precipitated, and tetragonality of martensite is partially lost.
- 2) Between 200°C and 300°C: retained austenite is decomposed.
- Between 200°C and 350°C: ε-iron carbide is replaced by cementite, and tetragonality is completely lost.
- Above 350°C: cementite coarsens and spheroidises, and recrystallisation of ferrite occurs.

If the steel is tempered at a temperature between 500°C and 600°C followed by slow cooling to ambient temperature, or at a temperature between 250°C and 400°C, temper embrittlement is possible in steels containing Mn, Ni, Cr, Sb, P, As and Sn. This can be avoided by carefully controlling the chemical composition of the steel and the tempering temperature to ensure that it is out of the ranges at which temper embrittlement can occur, followed by quenching to room temperature [1, 2]. The microstructure of martensite and tempered martensite are shown in Figure 2.8 and Figure 2.9 respectively.



Figure 2.8: Lath martensite in low-carbon steel (0.03%C, 2% Mn) ×100 [13].



Figure 2.9: TEM image of a typical tempered martensite in a 9% Cr steel [14].

#### 2.2.5 Bainite

If the cooling rate is neither too fast nor too slow, bainite will be formed in a wide temperature range typically from 250-550°C. Bainite can also be formed by isothermal transformation within this temperature range. Bainite is also a mixture of ferrite and cementite, but it has a non-lamellar microstructure distinct from pearlite. The bainitic ferrite is formed by a displacive transformation, whereas the cementite is formed by diffusion of carbon.

Ferrite in bainite nucleates from the austenite as a lens-shaped plate by a displacive transformation similar to that which occurs during the formation of martensite. However, the transformation temperature for bainite is higher than that for martensite, therefore the austenite is not sufficiently strong to accommodate the transformation strain elastically. As a result, plastic deformation of austenite occurs, and a large number of dislocations are generated. The movement of the interface is possibly inhibited by the large density of dislocations and stopped before it spans the entire austenite grain. A single ferrite grain which is called a sub-unit, is very fine, with a typical width of 0.2  $\mu$ m and a length of 10  $\mu$ m. Many sub-units can be grouped together to form sheaves, as shown in Figure 2.10.

Upper bainite is typically formed at 400-550°C. At these temperatures, carbon atoms have sufficient energy to diffuse into surrounding austenite. Upper bainite consists of ferrite with cementite precipitated between ferrite sub-units. Lower bainite is formed at 250-400°C. The lower transformation temperature results in slower diffusion, and thus, it consists of very fine cementite within ferrite sub-units, with some cementite precipitated between ferrite is usually tougher and stronger than upper bainite [1, 2, 11]. Bainite generally exhibits a good combination of strength and toughness [2]. The transformation mechanism is schematically shown in Figure 2.12 and Figure 2.13 respectively.



Figure 2.10: Schematic illustration of sub-units and sheaves [11].



Figure 2.11: Schematic representation of the formation of upper and lower bainite [1].



Figure 2.12: Upper bainite isothermally transformed at 400°C for 800 seconds [15].



Figure 2.13: Lower bainite isothermally transformed at 325°C for 2000 seconds [15].

#### 2.2.6 TTT and CCT diagrams

The resultant microstructural constituents of an isothermal transformation can be indicated by a time-temperature-transformation (TTT) diagram, as shown in Figure 2.14. The C-shaped curve is profoundly dependent on the alloying elements [2]. However, the application of TTT diagrams is limited to isothermal transformation. Therefore, a continuous cooling transformation (CCT) diagram is often used to

predict microstructures obtained at different cooling rates, as shown in Figure 2.15. In a CCT diagram, not only the cooling rate, but the chemical composition, the austenitisation conditions, austenite grain size and the cooling conditions are all factors that can influence the final microstructure. The critical cooling rate which is the minimum quenching rate required to form a fully martensitic microstructure can be studied through the use of a CCT diagram. This cooling rate can be determined by examining the tangent curve to the 'nose' of the C-shape curve (as shown in Figure 2.15). Therefore, the hardenability of steels can be determined from CCT diagrams [16]. Both TTT and CCT diagrams can be used to predict the final microstructures after heat treatment.



Figure 2.14: TTT diagram for an iron carbon steel [2].



Figure 2.15: CCT diagram for an iron carbon steel [2].

#### 2.2.7 Conditioning of austenite

In industry, many steel products are manufactured using hot rolled material. Austenite conditioning is a significantly important process during hot rolling. During austenite conditioning, microstructures and compositions of the terminal hot rolled austenite are optimised to obtain required microstructure and composition for the desired final ferrite microstructure. Heat treatment and deformation are applied to control crystalline defects such as grain boundaries, deformation bands, and incoherent twin boundaries. These defects can act as nucleation sites for ferrite during transformation. The defect structure of the austenite also affects the distribution of low temperature transformation products and work hardening rate. Generally, if the austenite grain is finer, the distribution of low temperature transformation products will be finer and the work hardening rate will be higher [17].

A high ferrite nucleation rate and a low grain growth rate are required in order to obtain fine ferrite grains. These requirements can be achieved during austenite conditioning. A high ferrite nucleation rate can be obtained by a large number of potential nucleation sites and a high nucleation rate per site. Defects e.g. austenite grain boundaries, deformation bands and incoherent twin boundaries can act as ferrite nucleation sites. The density of these sites per unit volume can be expressed as the total interfacial area per unit volume, the parameter  $S_v$ , with the unit mm<sup>-1</sup>. The parameter  $S_v$  is an approximate measure of austenite grain size, and it also indicates the degree of austenite conditioning. Generally, to maximise the parameter  $S_v$  is the principal goal of austenite conditioning [17].

Two approaches can be applied to increase  $S_v$ . The first approach is Recrystallisation Controlled Rolling (RCR) [18]. This is a refinement of austenite grains through repeated recrystallisation during hot deformation which would take place at temperatures above T<sub>95%</sub> which represents the temperature where 95% of grains recrystallise. As a result, the original equiaxed grains are replaced by new finer equiaxed grains. However, these fine grains have a strong tendency to coarsen, thus a pre-existing grain coarsening suppression system should be applied. For this approach, a lower T<sub>95</sub> temperature is required to allow a large temperature range between the reheat temperature and the minimum finishing temperature [17]. The second approach is Conventional Controlled Rolling (CCR). This process involves repeated deformation below T<sub>5%</sub> which represents the temperature where 5% of grains recrystallise. Since little recrystallisation occurs, grain shape changes and transgranular twins and deformation bands occur. For this approach, a higher T<sub>5</sub> is required to allow a greater number of deformations to occur. These two approaches are schematically shown in Figure 2.16, it can be found that both approaches decrease austenite grain size and thus increase  $S_v$ . The increase in  $S_v$  by RCR results from a decrease in average grain size. The increase in  $S_v$  by CCR results

from a change in grain shape and an increase of defects e.g. transgranular twins and deformation bands [17, 19].



Figure 2.16: Grain size evolution through RCR and CCR [17].

#### 2.3 Modelling of transformations from austenite to ferrite

Many models have been developed to predict transformation behaviours in steel processing, in order to control quality of products and reduce cost. Steels may have different transformation products depending on the cooling conditions and their chemical compositions. In all of the phases present within low carbon steel, ferrite is the most common. Transformation from austenite to ferrite is normally via a reconstructive transformation, in which both substitutional elements and interstitial atoms can diffuse between phases, and all the bonds in the austenite are broken and atoms are re-arranged into the new formed structure. Since all the atoms diffuse over distance, a high temperature is required to make atoms sufficiently mobile. For a reconstructive transformation kinetics model, chemical compositions and cooling conditions are normally from the input file. In addition to the kinetics modelling, it is essential to carry out thermodynamic calculations to determine whether there is sufficient driving force for the transformation. After that, nucleation and grain growth, which are the two important stages for a typical reconstructive transformation, need to be calculated separately for each phase at a certain temperature and a certain time. Finally, the overall transformation kinetics can be predicted [4].

#### 2.3.1 Thermodynamics

The driving force for the transformation from austenite to ferrite comes from the free energy difference between FCC austenite and BCC ferrite. From the free energy diagram in Figure 2.17, it can be seen that at a certain temperature T<sub>1</sub>, the original austenite with a bulk carbon content of  $\bar{x}$ , and the overall free energy can be lowered by forming ferrite with a carbon content of  $x^{\alpha\gamma}$  and leaving the rest of austenite with an enriched carbon content of  $x^{\gamma\alpha}$ . This transformation continues with decreasing temperature, until the eutectoid temperature is reached, and then all the remaining austenite transforms to pearlite. The driving force,  $\Delta G^{\gamma \to \gamma' + \alpha}$  can be determined from [4]:

$$\Delta G^{\gamma \to \gamma' + \alpha} = G^{\gamma'} M f_{\gamma} + G^{\alpha} M f_{\alpha} - G^{\gamma} \qquad Equation \ 2.8$$

where  $Mf_{\gamma}$  and  $Mf_{\alpha}$  are mole fractions of the enriched austenite and the product ferrite, and they can be calculated applying the lever rule to Figure 2.17.  $G^{\gamma'}$ ,  $G^{\alpha}$ , and  $G^{\gamma}$  are the free energy of the enriched austenite, the product ferrite, and the original austenite, respectively. They can be expressed by [4]:

$$G^{\gamma'} = x^{\gamma\alpha} \mu_C^{\gamma} \{x^{\gamma\alpha}\} + (1 - x^{\gamma\alpha}) \mu_{Fe}^{\gamma} \{x^{\gamma\alpha}\} \qquad Equation \ 2.9$$

$$G^{\gamma} = \bar{x} \mu_{c}^{\gamma} \{ \bar{x} \} + (1 - \bar{x}) \mu_{Fe}^{\gamma} \{ \bar{x} \}$$
 Equation 2.10

$$G^{\alpha} = x^{\alpha \gamma} \mu_{C}^{\alpha} \{x^{\alpha \gamma}\} + (1 - x^{\alpha \gamma}) \mu_{Fe}^{\alpha} \{x^{\alpha \gamma}\} \qquad Equation \ 2.11$$

where  $\mu_c^{\gamma}{x^{\gamma\alpha}}$  is the chemical potential of carbon in austenite evaluated at the carbon concentration of  $x^{\gamma\alpha}$ , and it is similar for other chemical potentials. From Figure 2.17, the chemical potentials of a component determined by the tangent line are the same in austenite and ferrite in the equilibrium condition. Therefore, Equation 2.8 can be expressed as

$$\Delta G^{\gamma \to \gamma' + \alpha} = \bar{x} \left( \mu_C^{\gamma} \{ x^{\gamma \alpha} \} - \mu_C^{\gamma} \{ \bar{x} \} \right) + (1 - \bar{x}) \left( \mu_{Fe}^{\gamma} \{ x^{\gamma \alpha} \} - \mu_{Fe}^{\gamma} \{ \bar{x} \} \right) \quad Equation \ 2.12$$

Since a chemical potential  $\mu$ , can be expressed as:  $\mu = G + RT lna$ , incorporating it into Equation 2.12 [4]:

$$\Delta G^{\gamma \to \gamma' + \alpha} = \bar{x}RTln \frac{a_C^{\gamma}\{x^{\gamma\alpha}\}}{a_C^{\gamma}\{\bar{x}\}} + (1 - \bar{x})RTln \frac{a_{Fe}^{\gamma}\{x^{\gamma\alpha}\}}{a_{Fe}^{\gamma}\{\bar{x}\}}) \qquad Equation \ 2.13$$

where  $a_C^{\gamma}\{x^{\gamma\alpha}\}$  is the activity of carbon in austenite evaluated at the carbon content of  $x^{\gamma\alpha}$ , and other activity terms have a similar expression.



Figure 2.17: Free energy against carbon content diagram at a temperature T<sub>1</sub>, and the corresponding section of Fe-C phase diagram [4].

The  $\gamma/\gamma+\alpha$ , and  $\alpha/\alpha+\gamma$  phase boundary temperatures can also be determined by some commercial thermodynamic calculation software packages such as MTDATA and ThermoCalc.

#### 2.3.2 Nucleation

From classical theory, nucleation occurs in locations where there are fluctuations in density of chemical concentrations or defects, e.g. interface and inclusions. In a pure system, the overall driving force for nucleation is provided by the free energy differences between the newly formed phase and the initial phase (and sometimes intermediate metastable states should be considered). However, this energy is also used for the creation of the new surface between the phases. If the nucleus is constrained by the surrounding initial phase, additional strain energy should also be

considered. For homogeneous nucleation of  $\alpha$  ferrite in a  $\gamma$  austenite matrix, the overall free energy change can be calculated from [4, 20]:

$$\Delta G = -\frac{4\pi}{3}r^{3}\Delta G_{\nu} + \frac{4\pi}{3}r^{3}\Delta G_{s} + 4\pi r^{2}\sigma_{\gamma\alpha} \qquad Equation \ 2.14$$

where the nucleus is assumed to be a sphere shape with a radius of r,  $\Delta G_v$  is the driving force for the formation of ferrite from austenite,  $\Delta G_s$  is the strain energy per unit volume, and  $\sigma_{\gamma\alpha}$  is the interfacial energy per unit area between ferrite and austenite.

The critical free energy barrier  $G^*$  occurs at a critical radius  $r^*$  when the free energy change  $\Delta G$  is maximum, which is shown in Figure 2.18 and can be calculated by the integral of Equation 2.14:



Figure 2.18: The free energy change during the homogeneous nucleation of a spherical nucleus with a radius of r. G\* and r\* are the critical free energy barrier and the critical radius for the nucleation [4].

Therefore, the critical radius  $r^*$  and the critical free energy barrier  $G^*$  can be calculated, respectively:
$$r^* = \frac{2\sigma_{\gamma\alpha}}{(\Delta G_v - \Delta G_s)} \qquad \qquad Equation \ 2.16$$

$$G^* = \frac{16\pi\sigma_{\gamma\alpha}^3}{3(\Delta G_v - \Delta G_s)^2} \qquad \qquad Equation \ 2.17$$

If a nucleus is smaller than the critical radius, it will be dissolved for the free energy reduction. If a nucleus is larger than the critical radius, the growth will happen to reduce the free energy. Therefore, the number of nuclei which are energetically favoured to grow, can be expressed as a probability multiplied by the total number of atoms in an initial vapour phase [21]:

$$n_c = N * e^{-\frac{G^*}{k_B T}} \qquad Equation 2.18$$

where *N* is the total number of atoms in the initial phase,  $n_c$  is the statistical distribution function for nuclei of critical nuclei, and  $k_B$  is the Boltzmann constant. This equation is based on a vapour phase. After many modifications, the homogeneous nucleation rate in a solid phase can be expressed as [4, 20]:

$$I_{v} = \frac{k_{B}T}{h} n_{v} Zexp\left(-\frac{(G^{*}+Q)}{k_{B}T}\right) \qquad Equation \ 2.19$$

where  $n_v$  is the number of atoms per unit volume, h is the Planck constant,  $\frac{k_BT}{h}$  is the vibration frequency, Q is the activation energy of the transfer of atoms across the nucleus/matrix interface, and Z is the Zeldovich factor, which is [22]:

$$Z = \frac{1}{r^*} \left(\frac{G^*}{3\pi k_B T}\right)^{\frac{1}{2}}$$
 Equation 2.20

However, in reality, heterogeneous nucleation which happens at high energy sites e.g. defects, interface, or impurities, is much more common. In the case of low carbon steels, prior austenite grain boundaries are favoured sites for the heterogeneous nucleation of proeutectoid ferrite. From Figure 2.19, there are three types of austenite grain boundary sites for ferrite nucleation: grain faces, grain edges, and grain corners. Nucleation at each type of site results in a different interfacial energy change, and thus the probability of nucleation is also varied. However, the densities of the grain boundary sites are also different. Therefore, the nucleation rate at each grain boundary site should be calculated separately. The allotriomorphic ferrite grain boundary nucleation rate is [4, 23]:

$$I_b^j = \frac{k_B T}{h} n_s^j exp\left(-\frac{\left(K_2^J G^* + Q\right)}{k_B T}\right) \qquad Equation \ 2.21$$

where *j* denotes grain faces, grain edges or grain corners (*f*, *e*, or *c*),  $n_s^j$  is a site factor about density of nucleation sites per unit area of grain boundary,  $K_2^j$  is a shape factor about austenite/ferrite interfacial energy per unit area, *Q* is the activation energy for self-diffusion of iron, with a typical value of 240 kJ/mol, and *G*<sup>\*</sup> is the critical energy for nucleation. If the strain energy caused by nucleation is ignored, the critical energy for nucleation can be expressed as [22, 23, 24]:

$$G^* = \frac{\sigma_{\gamma\alpha}^3}{\Delta G_V^2} \qquad \qquad Equation \ 2.22$$

where  $\Delta G_V$  is the free energy per unit volume for ferrite nucleation from supersaturated austenite, and  $\sigma_{\gamma\alpha}$  is the austenite/ferrite nucleus interfacial energy per unit area, which is assumed not to vary with interfacial orientation or alloy chemistry.

The total nucleation rate is the summation of the nucleation rates at the three types of sites:

$$I_b = I_b^f + I_b^e + I_b^c \qquad \qquad Equation \ 2.23$$

The number of grain faces nucleation sites per unit area of boundary can be calculated by assuming that each atom can act as a nucleation site, but this number should be halved because there are two sides of a boundary [4, 23]:

$$n_s^f = \frac{K_1}{2\delta^2} \qquad \qquad Equation \ 2.24$$

where  $K_1$  is a factor to describe active fraction of the total number of grain face sites, and  $\delta$  is the atomic spacing, which is typically taken as  $2.5 \times 10^{-10}$  m. The ratio of face to edge sites and the ratio of edge to corner sites are both  $\frac{\delta}{d_r}$  (where  $d_r$  is the average austenite grain size), and thus the number of grain edge sites and the number of grain corners sites can be expressed as [4]:

 $n_s^c = \frac{K_1}{2d_r^2}$ 

$$n_{s}^{e} = \frac{K_{1}}{2\delta d_{r}} \qquad \qquad Equation \ 2.25$$

faces faces edges Equation 2.26

Figure 2.19: Schematic diagram of grain faces, grain edges, and grain corners in a typical austenite grain [25].

From Parker [4], the contribution of the three types of nucleation sites to the overall nucleation rate vary with temperatures and austenite grain size. Generally, at a temperature slightly below  $Ae'_3$ , the small undercooling makes corner nucleation, which requires a low activation energy barrier, to dominate the rate. With decreasing temperatures, edge nucleation becomes more important, and then face nucleation takes over. A large austenite grain size reduces the fraction of grain edges and grain corners, and thus face nucleation becomes more significant with increasing austenite grain size. The nucleation rate calculation is also largely dependent on the chosen values for  $K_1$  and  $K_2^j$ . The values suggested by Reed and Bhadeshia [23] are listed

in Table 2.1. Parker [4] made further development based on the work of Reed and Bhadeshia, and the values of site and shape factors are listed in Table 2.2.

Factor	Value
K <sub>1</sub>	$6.9 \times 10^{-8}$
$K_2^f$	$2.7 \times 10^{-3}$
$K_2^e$	$1.0 \times 10^{-3}$
<i>K</i> <sup><i>c</i></sup> <sub>2</sub>	$3.3 \times 10^{-3}$

Table 2.1: Values of site and shape factors for nucleation rate calculation [23]

Table 2.2: Values of site and shape factors for nucleation rate calculation [4]

Factor	Value
<i>K</i> <sub>1</sub>	$1.0 \times 10^{-9}$
$K_2^f$	0.1
$K_2^e$	0.01
<i>K</i> <sup><i>c</i></sup> <sub>2</sub>	0.001

# 2.3.3 Grain growth

Since carbon is partitioned ahead of the transformation front into the untransformed austenite, ferrite growth rate can be considered to be controlled by the diffusion of carbon. It is well known that allotriomorphic ferrite has a parabolic growth rate, and the growth rate is slowed down with increasing transformation time, because the distance for carbon atoms diffusion becomes longer. As a result, it is easily understood that the growth rate of allotriomorphic ferrite along the austenite grain boundary (also known as lengthening), and the growth rate normal to the austenite grain boundary (also known as thickening) should be different. Generally, the ratio between the lengthening rate and the thickening rate is 3:1 [26, 27].

For a typical transformation from austenite to allotriomorphic ferrite, the carbon diffusion profile across the transformation interface can be schematically illustrated as shown in Figure 2.20. The number of carbon atoms which diffuse across a unit area of the interface in a unit time can be expressed by Fick's first law:

$$J_C = -D_C \frac{dx}{dz} \qquad \qquad Equation \ 2.27$$

where  $J_c$  is the diffusion flux, and  $D_c$  is the diffusion coefficient of carbon. The number of carbon atoms which diffuse across the interface can also be expressed as [4]:

$$J_{C} = (x^{\alpha \gamma} - x^{\gamma \alpha}) \frac{dz}{dt} \qquad \qquad Equation \ 2.28$$

Combining Equations 2.27 and 2.28, the rate of movement of the interface at the point  $z = z^*$  is:

$$\frac{dz}{dt} = \frac{D_C}{(x^{\gamma\alpha} - x^{\alpha\gamma})} \frac{dx_{\gamma}}{dz} \qquad Equation 2.29$$

If the distribution of carbon concentration at the austenite side of the interface is approximately considered as a straight line (as shown in Figure 2.20), then:

$$\frac{dx_{\gamma}}{dz} = \frac{(x^{\gamma \alpha} - \bar{x})}{L}$$
 Equation 2.30

Since the total number of carbon atoms within the system does not change during diffusion, the shaded area A and the shaded area B should be equal, and thus the velocity of the interface can be expressed as [1, 4]:

$$\frac{dz}{dt} = \frac{D_C}{(x^{\gamma\alpha} - x^{\alpha\gamma})} \frac{(x^{\gamma\alpha} - \bar{x})^2}{2z(\bar{x} - x^{\alpha\gamma})} \qquad Equation \ 2.31$$

The parabolic growth of ferrite grains can be mathematically expressed as [1]:

$$z = \alpha_1 t^{\frac{1}{2}} \qquad \qquad Equation \ 2.32$$

where  $\alpha_1$  is the one-dimensional parabolic rate constant, and thus  $\alpha_1$  can be calculated from [4]:

$$\alpha_1 = \left[\frac{D_C (x^{\gamma \alpha} - \bar{x})^2}{2(x^{\gamma \alpha} - x^{\alpha \gamma})(\bar{x} - x^{\alpha \gamma})}\right]^{\frac{1}{2}} \qquad Equation \ 2.33$$



Figure 2.20: Schematic diagram illustrating the carbon diffusion profile across a moving austenite/ferrite interface with a rate of  $\frac{dz}{dt}$ . Carbon atoms partition from the shaded area A to the shaded area B [4].

However, in reality, the gradient of carbon concentration away from the interface is not constant, but can be expressed by an error function solution to the diffusion equation. Therefore, the one-dimensional parabolic rate can be calculated from [4, 28]:

$$W_{\alpha} = \sqrt{\pi} \left( \frac{\alpha_1}{2D_c^{\frac{1}{2}}} \right) \operatorname{erfc} \left[ \frac{z}{2(D_c t)^{\frac{1}{2}}} \right] \exp\left( \frac{\alpha_1^2}{4D_c} \right) \qquad Equation \ 2.34$$

where  $W_{\alpha} = \frac{x^{\gamma \alpha} - \bar{x}}{x^{\gamma \alpha} - x^{\alpha \gamma}}$ , and *erfc* is the error function complement.

Militzer *et. al* [29, 30, 31, 32, 33] proposed a model to predict the transformation start temperature for low carbon steels. The model assumes that nucleation site saturation at austenite grain boundaries is determined by early growth of corner nucleated ferrite. If ferrite grains have spherical growth geometry and a steady state diffusional growth, the corner nucleated ferrite grain growth rate can be calculated from:

$$\frac{dR_f}{dT}\frac{dT}{dt} = D_C \frac{x^{\gamma\alpha} - \bar{x}}{x^{\gamma\alpha} - x^{\alpha\gamma}} \frac{1}{R_f}$$
 Equation 2.35

where  $R_f$  is the radius of the growing ferrite grain. However, it should be noticed that the model only considers ferrite nucleation at austenite grain corners, and thus the application of Equation 2.35 is used to calculate nucleation-site saturation, which is associated with the transformation start temperature calculation. The condition to determine whether the nucleation-site is saturated is given by [29, 33]:

$$R_{f} \geq \frac{x^{\gamma \alpha} - \bar{x}}{x^{\gamma \alpha} - x^{\alpha \gamma}} \frac{d_{\gamma}}{\sqrt{2}} \qquad \qquad Equation \ 2.36$$

where  $d_{\gamma}$  is the austenite grain size.

#### 2.3.4 Overall transformation kinetics

The fundamental theory for overall transformation kinetics calculations was first established by Avrami [34, 35, 36]. For the simplest situation, a new phase  $\alpha$  homogeneously nucleated in matrix  $\gamma$  phase, with a constant nucleation rate per unit volume,  $I_{\alpha}$ , and a constant growth rate,  $G_{\alpha}$ . If the newly formed particles are spherical, the radius of a particle,  $r_{\alpha}$ , at a time t, is given by [4]:

$$r_{\alpha} = G_{\alpha}(t - \tau)$$
 Equation 2.37

where  $\tau$  is the time for nucleation. Thus is volume of the particle at a time  $t > \tau$  is:

$$v_{\alpha} = \frac{4}{3} G_{\alpha}^{3} (t - \tau)^{3} \qquad \qquad Equation \ 2.38$$

Therefore, the volume change in a time interval dt is given by:

$$dV_{\alpha}^{e} = v_{\alpha}N_{\alpha} = \frac{4}{3}G_{\alpha}^{3}(t-\tau)^{3}I_{\alpha}Vdt \qquad Equation \ 2.39$$

At the early stage of phase transformation, all the particles are separated from each other, as shown from Figure 2.21 (a), and Equation 2.39 can be used to describe the transformation kinetics. However, a particle will impinge on its neighbour particles during further growth (Figure 2.21 (b)), and thus the volume change cannot be described using Equation 2.39. Volume change  $dV_{\alpha}^{e}$  from Equation 2.39 is the change in "extended volume" [4, 34]. A probability factor can be induced to calculate the actual volume change,  $dV_{\alpha}$ :

$$dV_{\alpha} = \left(1 - \frac{V_{\alpha}}{V}\right) dV_{\alpha}^{e} = \frac{4}{3} G_{\alpha}^{3} (t - \tau)^{3} I_{\alpha} V \left(1 - \frac{V_{\alpha}}{V}\right) dt \quad Equation \ 2.40$$

Integrating the Equation 2.40:

$$-ln\left(1-\frac{V_{\alpha}}{V}\right) = \frac{4}{3} \int_0^t G_{\alpha}^3 (t-\tau)^3 I_{\alpha} dt \qquad Equation \ 2.41$$

Therefore, the overall transformation kinetics can be calculated from:

$$= 1 - \exp\left[\frac{4}{3}\int_{0}^{t}G_{\alpha}^{3}(t-\tau)^{3}I_{\alpha} dt\right] \qquad Equation 2.42$$

$$\downarrow t_{1} > 0$$
(a)
(b)

 $\varepsilon_{\alpha} = \frac{V_{\alpha}}{V}$ 

Figure 2.21: Schematic images illustrating growing particles of  $\alpha$  from  $\gamma$  matrix: (a) at an early stage when particles are separated from each other, and (b) at a later stage when many particles impinge [4].

For heterogeneous nucleation, which is the more common case in phase transformation from austenite to ferrite, ferrite grains can be considered as growing from austenite grain boundaries. In order to calculate the volume change of ferrite particles, a series of planes parallel to the austenite grain boundary are assumed to interact with the radius of the growing particles [4], as shown in Figure 2.22.



Figure 2.22: Schematic images illustrating the interactions between growing spherical particles from a grain boundary and a parallel plane at a distance y from the boundary [4].

The interaction area of a spherical particle with a parallel plane at a distance y from grain boundary is given by:

$$\pi r^2 = \pi [G_{\alpha}^2 (t - \tau)^2 - y^2]$$
 Equation 2.43

Therefore, the change in extended area of ferrite particles on a plane at an interval time dt can be expressed as [4]:

$$dO^{e}_{\alpha} = \pi O_{b} I_{\alpha,b} [G^{2}_{\alpha}(t-\tau)^{2} - y^{2}] dt \qquad Equation \ 2.44$$

where  $O_b$  is the total area of the plane, and  $I_{\alpha,b}$  is the nucleation rate of ferrite per unit area of boundary. If  $I_{\alpha,b}$  is assumed to be constant, the total extended volume of ferrite growing from austenite boundary can be calculated by integrating the extended area over all the planes [4, 34, 35, 36]:

$$V_{\alpha}^{e} = V S_{\nu} G_{\alpha} t \int_{0}^{1} \left\{ 1 - \exp\left[-\frac{\pi}{3} I_{\alpha,b} G_{\alpha}^{2} t^{3} (1 - 3\phi^{2} - 2\phi^{3})\right] \right\} d\phi \qquad Equation \ 2.45$$

where  $\phi = \frac{y}{G_{\alpha}t}$ , V is the total volume of the sample, and  $S_v$  is the grain boundary surface area per unit volume. The total actual volume of the transformed phase, V<sub> $\alpha$ </sub>, can be calculated by [4]:

$$\frac{V_{\alpha}}{V} = 1 - ex p\left(-\frac{V_{\alpha}^{e}}{V}\right) \qquad Equation 2.46$$

Therefore, the extent of transformation can be calculated by [4]:

$$\varepsilon_{\alpha} = \frac{V_{\alpha}}{V} = 1 - \exp\left\{-S_{\nu}G_{\alpha} \operatorname{t} \int_{0}^{1} \left\{1 - \exp\left[-\frac{\pi}{3}I_{\alpha,b}G_{\alpha}^{2}t^{3}(1 - 3\phi^{2} - 2\phi^{3})\right]\right\}d\phi\right\}$$
  
Equation 2.47

However, Equation 2.47 only works only for spherical particles with constant nucleation rate and linear growth rate. In reality, parabolic growth is the mode for allotriomorphic ferrite grain growth. Particles may have different morphologies, e.g. sphere, plate, disc, ellipsoid, etc. For a parabolic growth of disc-shaped particles with aspect ratio of  $\eta_{\alpha}$ , its thickness  $q_{\alpha}$  is given by [4]:

$$q_{\alpha} = G_{\alpha}(t-\tau)^{\frac{1}{2}} \qquad \qquad Equation \ 2.48$$

Its radius parallel to the boundary is [4]:

$$r_{\alpha} = \eta_{\alpha} G_{\alpha} (t - \tau)^{\frac{1}{2}}$$
 Equation 2.49

The extent of transformation can then be calculated by [4, 23]:

$$\varepsilon_{\alpha} = 1 - \exp\left\{-S_{\nu}G_{\alpha}t^{\frac{1}{2}}\int_{0}^{1}\left\{1 - \exp\left[-\frac{\pi}{2}I_{\alpha,b}\eta_{\alpha}^{2}G_{\alpha}^{2}t^{2}(1-\phi^{4})\right]\right\}d\phi\right\}$$

where  $\phi = \frac{y}{G_{\alpha}t^{\frac{1}{2}}}$ .

Previous research also proposed overall transformation kinetics models based on John-Mehl-Avrami-Kolmogorov (JMAK) theory, but most of them are semi-empirical models. In Militzer's model, the ferrite fraction transformed during continuous cooling is expressed as [33]:

$$\varepsilon_{\alpha} = \frac{x^{\gamma \alpha} - \bar{x}}{x^{\gamma \alpha} - x^{\alpha \gamma}} \left\{ 1 - exp \left\{ \frac{1}{d_{\gamma}} \left\{ \int_{T_{S}}^{T} \frac{1}{\varphi(T)} exp[\frac{b_{1}(T_{Ae3} - T') + b_{2}}{m}] dT \right\}^{n} \right\} \right\}$$

#### Equation 2.51

where  $\varphi(T) = -\frac{dT}{dt}$ , is the instantaneous cooling rate,  $b_1$ ,  $b_2$ , m, and n are fitting factors.

Ohtsuka *et al.* [37] applied a kinetic law of transformation to calculate the transformation kinetics for different steels with the same grain size [38, 39]:

$$\varepsilon_{\alpha} = 1 - e^{-\left(\frac{k(T)t^{n}}{d_{\gamma}^{m}}\right)}$$
 Equation 2.52

where k(T) is the rate constant,  $d_{\gamma}$  is the austenite grain size, n and m are fitting factors. From Equation 2.52:

$$log\left(ln\left(\frac{1}{1-\varepsilon_{\alpha}}\right)\right) = nlogt - mlogd_{\gamma} + logk(T)$$
 Equation 2.53

Therefore, the value of time exponent, *n*, can be calculated from the slope of  $log\left(ln\left(\frac{1}{1-\epsilon_{\alpha}}\right)\right)$  against *logt*. From Equation 2.53

$$nlogt = mlog d_{\gamma} + log \left( ln \left( \frac{1}{1-x} \right) \right) - logk(T)$$
 Equation 2.54

The value of *m* can be calculated from the slope of nlogt against  $logd_{\gamma}$ , when *n* is independent of the austenite grain size.

#### 2.4 Effects of niobium on steels

# 2.4.1 Introduction of niobium

Niobium is a chemical element with the symbol Nb and the atomic number 41. Its standard atomic weight is 92.9 [17]. The density of pure niobium is approximately 8.57 g/cm<sup>-3</sup>. Its melting point is  $2477^{\circ}$ C. The electron configuration is [Kr]  $4d^{4}5s^{1}$ , with

an atomic radius 0.146 nm. Niobium belongs to the family of transition metals which are characterised by the electronic structure of their atoms where the outer shell contains electrons while the inner shell is not completely filled [17]. The principal application of niobium is used as a microalloying element in high strength low alloy (HSLA) steels.

Niobium has a strengthening effect on steels due to grain refinement, precipitation strengthening and phase transformation control. Niobium has a strong effect in HSLA steels because the low carbon content increases the solid solubility of niobium in austenite. Niobium atoms have a large misfit within the iron lattice, austenite grain boundaries are favourable sites for the location of niobium atoms. The atomic radius of Nb is 146 pm, but it is 126 pm for iron. Therefore, the mismatch in atomic radius is:

$$\Delta R = \frac{146 - 126}{126} = 15.9\% \qquad \qquad Equation \ 2.55$$

According to Hume-Rothery theory [1, 2], when  $\Delta R\% > 8\%$ , the solubility is limited, and when  $\Delta R\% > 15\%$ , the solubility is low. Many Nb(C,N) particles can be precipitated during transformation from austenite to ferrite. Niobium is normally known as a ferrite stabiliser, but the A<sub>3</sub> temperature can be reduced in Nb microalloyed steels [17, 40].

Niobium, vanadium, and titanium are three typical microalloying elements. Niobium is a strong carbide forming element, but it shows relatively little tendency to form oxides, sulphides or solid solutions of these compounds. Vanadium has a similar carbide forming tendency to niobium, but it has a higher solubility in austenite at the typical rolling temperature. The lower solubility of niobium results in a greater strengthening effect on mechanical properties due to grain refinement of the final ferrite/pearlite microstructure [41]. Titanium can only show a tendency to form carbides once all oxygen, nitrogen, and sulphur have been consumed, and the precipitation temperature is typically higher than niobium and vanadium.

## 2.4.2 Diffusion of niobium in steels

The diffusion coefficient, D, can be expressed in the form of Arrhenius form [2]:

$$D = D_0 e^{\left(-\frac{Q}{RT}\right)} \qquad Equation 2.56$$

Where  $D_0$  is a constant depending on the nature of the element and the bulk composition, *R* is the perfect gas constant which is approximately 8.314 J/mol·K, *Q* is the activation energy, and *T* is the temperature in K.

According to Kurokawa *et al.* [42], the diffusion of niobium in steels has two important phenomena: first, the inter-diffusion coefficient of niobium in austenite is not strongly influenced by the composition of the solid solution matrix; and second, the coefficient for niobium is somewhat higher than the coefficient for the self-diffusion of iron. The data from other researches for the diffusion of niobium in steels and for self-diffusion of iron are listed in Table 2.3 and Table 2.4 respectively.

Element	Bulk	Q in kJ/mol	D <sub>0</sub> in cm <sup>2</sup> /s
Nb	Fe-γ	266.5 (±1.8)	0.83 (±0.69)
Nb	Fe-γ	264	0.75
Nb	Fe-α	252 (±2.5)	50.2 (±3.0)
Nb	Fe-α	289	100 X D <sub>0</sub> (γ)

Table 2.3: Diffusion coefficients of niobium in iron [17, 43].

Table 2.4: Self-diffusion coefficients for iron [17].

Element	Bulk	Q in kJ/mol	$D_0$ in cm <sup>2</sup> /s
Fe	Fe-γ	284	0.49
Fe	Fe-α	241	2.01

# 2.4.3 Precipitation of Niobium Compounds

In steels, niobium can be present as niobium carbide precipitates or solute niobium atoms. Niobium carbide precipitates and solute niobium atoms have different effects on transformation from austenite to ferrite. Therefore, it is important to study the Nb-NbC phase diagram. Storms and Krikorian [44] studied the Nb-NbC phase diagram, as shown in Figure 2.23.



Figure 2.23: Nb-NbC phase diagram [44]. It should be noted that the x-axis is not the carbon content but the mole ratio of C/Nb.

It can be found that there are three solid-solution single phase regions:  $\alpha$ ,  $\beta$ , and  $\gamma$ . For  $\alpha$  phase, carbon atoms locate in interstitial sites in niobium lattices, therefore the maximum solid solubility is only 0.2 at. % at approximately 2300°C. The  $\alpha$  phase has a BCC crystal structure, and its lattice parameter varies with the carbon content. The  $\beta$  phase, which is Nb<sub>2</sub>C, has a maximum carbon solubility of 33.3 at. %, according to the stoichiometric composition. Nb<sub>2</sub>C has a HCP crystal structure with lattice parameters a = 0.312 nm and c = 0.495 nm [45]. The  $\gamma$  phase is the most interesting phase present in the Nb-C phase diagram. It has a range of carbon content from

NbC<sub>0.72</sub> to NbC, therefore the symbol NbC<sub>x</sub> is used to describe the  $\gamma$  phase. It has a NaCl type FCC crystal structure, which can be represented by two interpenetrating FCC lattices with Nb atoms (or Nb vacancies) locating on one set of FCC lattice points and C atoms (or C vacancies) locating on the other set [17]. The lattice parameter of NbC<sub>x</sub> is affected by the value of x, which indicates the vacancy concentration in the  $\gamma$  phase. Pure NbC has a lattice parameter of 0.445 nm whereas the lattice parameter for NbC<sub>0.7</sub> decreases to 0.443 nm [44]. A lattice of NbC is shown in Figure 2.24.



Figure 2.24: The crystal lattice of NbC [46].

In microalloyed steels, niobium precipitates not only with carbon but also nitrogen. Therefore, niobium carbo-nitride (Nb(C,N)) is typically used to refer to niobium precipitates. NbC and NbN are quite similar compounds and have similar crystallographic features. Therefore, they have complete solid solubility to form a carbo-nitride [17]. The lattice of the precipitate is parallel to the FCC austenite lattice [17]:

However, in ferrite or martensite, there is a Baker-Nutting orientation relationship between the precipitates and the matrix [17]:

 $[1 \ 0 \ 0]_{Nb(CN)} // [1 \ 0 \ 0]_{\alpha}$  $[0 \ 1 \ 1]_{Nb(CN)} // [0 \ 1 \ 0]_{\alpha}$ 

TEM micrographs of niobium carbo-nitride precipitates are shown in Figure 2.25 (a) and Figure 2.26 (a). From Figure 2.25 (b) and Figure 2.26 (b), the EDX spectra have both niobium and nitrogen peaks. Since the samples are carbon extraction replicas, a carbon peak always exists in the EDX spectrum. From Figure 2.25 (c) and Figure 2.26 (c), an FCC cubic lattice with a lattice parameter of 0.437 nm was identified by electron diffraction patterns, thus the precipitates were identified as niobium carbo-nitride [41].



Figure 2.25: (a) Niobium precipitates in a TEM micrograph from a carbon extraction replica; (b) EDX spectrum; and (c) electron diffraction pattern [41].



Figure 2.26: (a) Niobium precipitates in a TEM micrograph from a carbon extraction replica) EDX spectrum; and (c) electron diffraction pattern [41].

The Johnson-Mehl equation can be used to study the kinetics of precipitate formation [47]:

$$X_p = 1 - \exp\left(-\frac{\pi}{3}\dot{N}\dot{G}^3t^4\right) \qquad \qquad Equation \ 2.57$$

where  $X_p$  is fraction of precipitates formed,  $\dot{N}$  is nucleation rate which is usually assumed constant,  $\dot{G}$  is growth rate which is usually assumed constant, and t is reaction time.

From Equation 2.57, it can be found that a precipitation reaction can only achieve a high level of completion when  $\dot{N}$ ,  $\dot{G}$  and t have sufficiently large values. Solute supersaturation has strong effects on both the nucleation rate and the growth rate. In addition, the diffusion coefficient also has a strong effect on the growth rate. The precipitation of Nb(C,N) always occurs in crystalline defects e.g. grain boundaries, incoherent twin boundaries, stacking fault boundaries, subgrain boundaries, or dislocations [17]. The crystalline defects can relieve the elastic strain which is caused by the large mismatch between the matrix and the Nb(C,N) lattice.

The kinetics of precipitation are affected by composition, strain, strain rate, temperature and overall heat treatment [17]. The precipitation rate in recrystallised austenite is quite slow. However, it is remarkably sensitive to the level of strain. The precipitation rates under different levels of strain at 900°C in steels containing 0.04Nb are shown in Figure 2.27. The strain-induced precipitation of Nb(C,N) in austenite follows a C-curve kinetics, with the nose present in the range between 900°C and 950°C [17].



Figure 2.27: Influence of strain level on the kinetics of Nb precipitation at 900°C in a steel containing 0.17C-0.04Nb-0.011N [48].

The distribution of Nb(C,N) precipitates in ferrite is largely affected by the transformation from austenite to ferrite. In polygonal ferrites, the Nb(C,N) precipitates have an interphase distribution, during which the Nb(C,N) precipitates along the advancing austenite-ferrite phase boundary. If the boundary moves forward, the precipitates will be left behind in a sheet-like array. There are many sheets of precipitates in the final microstructure. However, this distribution of precipitates only occurs at high temperatures above 700°C in ferrite. If precipitates occur from a supersaturated low temperature acicular or bainitic ferrite when transformation has finished, they will have a uniform distribution, and these precipitates are responsible for the precipitation hardening effect [17].

Chandra et al. [49], utilised the carbon replica technique to study the particle size of Nb(C,N) after various times of precipitation at 925°C. From their work, dynamic precipitation of Nb(C,N) at 925°C results in fine particles with a mean size of ~ 5 nm, but static precipitation produces larger particles which grow with increasing precipitation time. 3.5 minutes holding samples at 925°C results in particles with a mean size of 25 nm, and the mean size of particles increases to 44 nm after 57 minutes. However, the particle size coarsening trends to slow down after that, with a mean size of 53 nm after 1100 minutes holding at 925°C. Park et. al [50] studied the average particle size of Nb(C,N) particles precipitated at 850°C, 900°C and 950°C, and found that the average particle size increases with the precipitation temperature and time, which is consistent with the results from Akamatsu et. al [51, 52]. Fujita and Bhadeshia [53] propose a precipitation kinetics model for NbC, and it indicates both the volume fraction and the mean particle size increase with holding time. For NbC precipitation in the bainite region (i.e. 580°C-660°C), the precipitation time temperature (PTT) diagram has a C shape curve with the nose temperature at about 615°C [54].

#### 2.4.4 Nb(C,N) precipitation and dissolution temperatures

The Nb(C,N) dissolution temperature and the precipitation temperature are important in heat treatment. The temperatures should be chosen as low as possible, in order to avoid grain coarsening.

According to Palmiere *et al.* [55], there is an equation derived from solubility data to calculate the solubility of NbC:

$$\log_{10}\{[Nb][C]\} = 2.06 - \frac{6700}{T}$$
 Equation 2.58

According to Shams [56], there is another equation to calculate the amount of Nb in solution from the solubility equation of  $Nb_4C_3$ :

$$\log_{10}\{[Nb][C]^{0.87}\} = 3.11 - \frac{7520}{T}$$
 Equation 2.59

According to Rees *et al.* [57], the equilibrium dissolution temperature can be calculated using the ThermoCalc phase diagram modelling package. The effect of manganese on the carbide stability is taken account:

$$\log_{10}\{[Nb][C]\} - 0.248[Mn] = 1.8 - \frac{6770}{T} \qquad Equation \ 2.60$$

Where [Nb], [C] and [Mn] are the concentrations of niobium, carbon and manganese respectively (in weight %), and T is temperature in Kelvin. In the work of Rees [57], the phase boundary temperature for  $(\alpha+\gamma+NbC)/(\gamma+NbC)$  is calculated at 822°C, and the phase boundary temperature for  $(\gamma+NbC)/\gamma$  is calculated at 1195°C with the C content of 0.149 wt. % and the Nb content of 0.026 wt. %.



Figure 2.28: Heat treatment curves used in the work of Rees et al.: (a) curves used to study the effect of solute niobium, and (b) curves used to study the niobium precipitates [57].

The heat treatment curves applied in the work of Rees *et al.* [57] are shown in Figure 2.28 (a) and (b). The heat treatment curves shown in Figure 2.28 (a) were used to study the effect of solute niobium atoms. Two austenite grain sizes were obtained due to the different holding times at 1250°C. After that, samples were quenched to 800°C to avoid the precipitation of NbC. Finally, samples were cooled to room temperature at various cooling rates. The heat treatment curves shown in Figure 2.28 (b) were used to study the effect of niobium precipitates. Precipitates are formed due to a second-stage austenitisation at T<sub>int</sub>. 1250°C is a typical temperature chosen for Nb(C,N) precipitate dissolution [41, 57, 58, 59, 60]. However, Akben *et al.* [61] and Cho *et al.* [62] set the dissolution temperature at 1100°C

The heat treatment curve shown in Figure 2.29 was utilised in the work of Fossaert *et al.* [63]. The austenitisation temperature,  $T_{\gamma}$  was varied from 1100°C to 1250°C. Various cooling rates from 980°C to 750°C were chosen to obtain a range of contents of precipitates. Therefore, the effects of solute niobium atoms and niobium precipitates can be investigated separately. The effect of austenitisation temperatures on austenite grain size is shown in Figure 2.30. It can be found that a higher austenitisation temperature results in a larger austenite grain size.



Time / s Figure 2.29: The heat treatment curve applied in the work of Fossaert *et al.* [63].



Figure 2.30: The relationship between austenite temperatures and austenite grain size [63]. It should be noted that a larger austenite grain size index corresponds to a small austenite grain size.

Fazeli and Militzer [30] measured the amount of dissolved Nb in austenite after various holding times at 900°C, and found that after 20 minutes holding, most dissolved Nb atoms have already been precipitated. They also studied the effect of dissolved Nb content on ferrite transformation start temperature, and applied an equation to express the relationship among Nb(C,N) mass fraction, holding time at 900°C, and ferrite transformation start temperatures:

$$f_{NbCN} = \frac{T_S - T_S^{0min}}{T_S^{20min} - T_S^{0min}} \qquad Equation 2.61$$

They calculated the Nb(C,N) precipitation kinetics from the equation, and concluded that the kinetics is consistent with the typical parabolic growth curve.

# 2.4.5 Effects of niobium in austenite transformation

Niobium microalloyed steels are usually manufactured by hot rolling which is a multipass process at high temperatures. Niobium has two states in hot rolled steels: solute niobium atoms and niobium carbide precipitates. At relatively high temperatures, niobium is in solid solution in austenite. At relatively low temperatures

in the austenite field, niobium carbo-nitride precipitates can be formed. The effects of solute niobium atoms and niobium carbo-nitride precipitates on the transformation from austenite to ferrite might be different and should be studied separately.

# 2.4.5.1 Effects of solute niobium

Solute niobium atoms and the niobium carbo-nitride precipitates have different effects on the transformation from austenite to ferrite. Therefore, it is necessary to eliminate the effects of niobium precipitates in order to study the effects of solute niobium. Two different experimental methods can be employed:

- Quenching from the dissolution temperature to 900°C and then cooling at the required rate [57, 63, 64, 65];
- Reducing carbon and nitrogen contents to a low level [66, 67].

Prior austenite grain size also has a significant effect on transformation. Two methods can be utilised to remove the effect:

- Varying austenitisation temperatures and times to obtain the same austenite grain size in different samples;
- Hot working on the samples to recrystallise the austenite grains to a constant grain size [8].

Solute niobium atoms retard the kinetics of transformation from austenite to ferrite [56, 57, 58, 59, 60, 61, 62, 67, 68, 69]. They can segregate to the austenite grain boundaries and have a solute drag effect on the austenite-ferrite interface [67]. In addition, the solute niobium increases the activation energy required for ferrite nucleation. Therefore, the increasing content of the solute niobium in steels results in a reduction of the  $Ar_3$  up to a niobium content of about 0.05 wt. % [56]. The depression of  $Ar_3$  with increasing solute niobium is also affected by the cooling rate [8, 69]. However, niobium is a ferrite stabiliser, thus further increasing of niobium above 0.05 wt. % may raise  $Ar_3$  [56]. In addition, the actual solute niobium content at the transformation start temperature was not measured in many investigations [56, 57, 58, 59, 60, 61, 62]. Some precipitates could have been formed, especially at

slow cooling rates. Therefore, the effect of solute niobium may be underestimated. Accurate measurement of solute niobium content is necessary in order to study the accurate effects of solute niobium on transformation.

The effects of solute niobium on decreasing  $Ar_3$  at different cooling rates with different initial austenite grain sizes are summarised in Table 2.5. From these data, it can be found that  $Ar_3$  will decrease with increasing solute niobium content. In addition, faster cooling rate and larger austenite grain size also result in a lower  $Ar_3$  temperature. From these three factors, the cooling rate seems the most effective one. However, the retardation effect is also affected by other alloying elements. The start time for isothermal transformation from austenite to ferrite can also be delayed by the presence of solute niobium atoms [70].

When niobium microalloyed steels are heated to a high temperature to dissolve the precipitates, the hardenability can be increased by three factors [63]: first, the increase in austenite grain size; second, the increase in solute niobium content; and third, a decrease in niobium carbide precipitates. Fossaert et al. [63] state that the austenite grain size is not the key factor affecting hardenability of niobium microalloyed steels (as shown in Figure 2.31), because the critical cooling rates remain almost constant even when there is a significant grain growth. The relationship between the solute niobium and the critical cooling rate was shown in Figure 2.32. Even a small amount of solute niobium can strongly retard the decomposition of austenite. Solute niobium can significantly increase the hardenability of steels up to a niobium content of around 0.05 wt. %. A niobium atom has a large misfit with an austenite lattice, which results in a low solubility of niobium in austenite. Therefore, it has one of the strongest interactions with austenite grain boundaries. This results in a decrease in the local driving force for ferrite formation and hindering of carbon diffusion. Therefore, ferrite is difficult to nucleate at austenite grain boundaries [63]. The solute drag effect is another but less satisfactory explanation for the effect of niobium on hardenability. In this mechanism, solute niobium exerts a solute drag effect on the motion of the ferrite/austenite interface. However, the diffusional based solute drag theory is incompatible with the displacive transformation [63].

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# Table 2.5: Continuous cooling data.

	γ grain Nb size (µm) wt.%	Ar <sub>3</sub> (°C) at different Cooling Rates (CR: °C/s)										
		wt.%	CR	Ar <sub>3</sub>								
	184	0	38	430	28	430	19	500	9.8	570	5	609
	391	0	38	430	28	430	19	500	9.8	551	5	563
Austenitisation at 1250°C for 3 or 10 minutes then quench to 900°C [57]	110	0.011	38	430	28	434	19	472	9.8	547	5	590
	143	0.011	38	430	28	438	19	482	9.8	526	5	560
	117	0.026	38	430	28	440	19	485	9.8	537	5	580
	155	0.026	38	430	28	435	19	461	9.8	530	5	563
Austenitisation at 1000°C (0 Nb) or 1100°C (0.022% Nb) for 5 minutes [64]	59	0	10	733	5	733	2	743	1	753	0.5	760
	58	0.022	10	682	5	694	2	719	1	743	0.5	722
Austenitisation at 1260°C and 20% deformed [8]	100 -	0	1.70	670	0.98	700	0.50	725	0.27	745	0.18	760
		0.020	0.66	722	0.47	717	0.32	717	0.25	727	0.18	722
Austenitisation at 1200°C for 3 minutes and hot rolling between 1100°C and 840°C [69]	N/A -	0.031	50	550	10	614	3	622	1	639	0.3	706
		0.052	60	529	10	597	3	606	1	623	0.3	686



Figure 2.31: The relationship between the critical cooling rate to obtain 95% martensite and the austenite grain size. It should be noted that a larger grain size index corresponds to a small austenite grain size [63].



Figure 2.32: The relationship between the solute niobium content and the critical cooling rate [63].

When the transformation temperature from austenite to ferrite decreases with niobium, the shape of grains will become more irregular. In addition, a higher proportion of the grain boundaries will display a lower angle character [17]. After the transformation, a high dislocation density can be found not only in acicular ferrite and bainite, but also in polygonal ferrite. This phenomenon in niobium microalloyed steels lack a full characterisation [17].

Solute atom induced diffusional drag effect on the grain boundary movement has already been demonstrated by many previous researchers. Lücke and Detert [71] found that foreign atoms in solid solution when segregated to grain boundaries can inhibit the grain boundary movement, and foreign atoms should be left behind the moving boundary. The solute-boundary interaction energy, E can be utilised to determine whether the boundary is expected to be dragged or pushed ahead by solute atoms. If E<0, there will be adsorption of solute atoms or impurity at the boundary, and the migration rate will be reduced. If E>0, there will be desorption of solute atoms at the boundary [72]. Segregation of solute atoms to the interface is the basic requirement of solute drag effect. The interfaces, over which the soluteinterface interaction energy is not zero, have a finite width  $\delta$ . The drag on a moving boundary requires the diffusion of solute atoms in the direction of boundary motion. It is easier for solute atoms to diffuse along the grain boundary rather than across it. The drag force, the interaction energy, E, and the diffusion coefficient describing the movement of atoms across the interface D<sub>a</sub>, can be expressed as functions of the distance y [72, 73]. Hillert and Sundman [73] considered transformation from austenite to ferrite with low velocity of the grain boundary and little change in composition. If solute atoms segregate within the moving grain boundary, free energy will be required to drive the solute atom diffusion across the boundary, and to drive the solute atom spike ahead of the boundary. They also pointed out that less free energy is required to drive the spike when the velocity of boundary increases. At a sufficiently high velocity, only the atoms segregated within the boundary contribute to the drag effect [73].

Fu *et al.* [74] studied the effect of increment of solute atoms on the austenite grain growth velocity, which can be expressed as:

$$f_x = \frac{\partial v}{\partial C_S} = \frac{pM_0}{(1 + \lambda M_0 C_S)^2}$$
 Equation 2.62

where  $p = \frac{3\sigma(1+\lambda M_0 C_0)}{2C_P r_p} - \lambda M_0 G_T$ , which is utilised as the criterion factor to assess the competition between solute drag and precipitate pinning in inhibiting the austenite grain growth,  $C_0$  and  $C_p$  are the initial solute content and the solute content in the precipitate,  $C_s = C_0 - f_p C_p$ , it is the solute content in the matrix,  $\sigma$  is grain boundary energy,  $M_0$  is the intrinsic mobility in a pure metal, and  $r_p$  is the precipitate radius. The model in Equation 2.62 is derived from Cahn's theory [75], which is only suitable for single phase system. Therefore, it can be used to predict austenite grain growth, but not transformation from austenite to ferrite.

Hillert and Sundman [73] studied the binary phases system, the drag force P at low interface velocities can be expressed as

$$P = \frac{RTv}{V_m} x_A^0 x_B^0 \int_{-x}^{x} \frac{1}{D} \left[ \exp\left(\frac{\Delta G^0}{2RT}\right) - \exp\left(-\frac{\Delta G^0}{2RT}\right) \right]^2 dy \qquad Equation \ 2.63$$

where  $\Delta G^0 = G_B^0 - G_A^0$ , which is the difference of the free energy between the two phases, V<sub>m</sub> is the molar volume, x is the mole fraction of the solute atoms, and  $x_A^0$  and  $x_B^0$  are the mole fraction of each phase. This model combines the diffusion theory and the energy dissipation theory. It can be utilised both for phase transformations and to the migration of a grain boundary in a single phase system. They also pointed out that a variable diffusivity can have a significant effect, and even an average value of the diffusivity cannot be applied to get an accurate result [73].

Fazeli and Militzer [30] incorporated a solute-interface interaction factor caused by solute Nb atoms to their existed transformation start temperature model as mentioned in Equation 2.35:

$$\frac{dR_f}{dt} = D_C \frac{x^{\gamma \alpha} - \bar{x}}{x^{\gamma \alpha} - x^{\alpha \gamma}} \frac{1}{R_f} \left( 1 + \frac{D_C \alpha C_{Nb}}{R_f} \right)^{-1} \qquad Equation \ 2.64$$

where  $C_{Nb}$  is the dissolved Nb concentration, and  $\alpha$  is a constant related to the intensity of the solute drag effect.

Bhadeshia [72] pointed out that determination of a suitable diffusion coefficient in the process is one of the major difficulties when applying solute drag theory to a real problem. Lee and Lee [64] found that the presence of solute Nb atoms have a strong effect on the  $\gamma/\alpha$  transformation start time rather than the finish time. Since the nucleation and growth are controlled by diffusion of solute elements Nb, Mn and C. They attribute the solute drag effect of Nb to the increment of activation energy by a new term,  $Q_{sd}$ , which was experimentally determined by multiplying by a factor f=5000 [64, 76]:

$$D = D_C \exp\left(-\frac{Q_{sd}}{RT}\right) = D_C \exp\left(-5000C_{Nb}\left(\frac{2750}{T} - 1.85\right)\right) \qquad Equation \ 2.65$$

The diffusion controlled growth rate for a flat interface can be expressed as

$$\frac{(C_* - C_0)}{(C_P - C_*)} = \lambda \exp(\lambda^2) \operatorname{erfc}(\lambda) \pi^{0.5} \qquad Equation 2.66$$

And the diffusion controlled growth rate for a curved interface can be expressed as

$$\frac{(C_* - C_0)}{(C_P - C_*)} = 2\lambda^2 [1 - \lambda \exp(\lambda^2) \operatorname{erfc}(\lambda)\pi^{0.5}] \qquad Equation 2.67$$

where  $C_0$ ,  $C_*$  and  $C_P$  are the initial solute element concentration in the matrix, solute element concentration in the matrix phase at the interface, and the solute element concentration in the transformed phase at the interface, respectively, and  $\lambda = \alpha/(2D^{0.5})$  and  $\alpha$  is the parabolic rate constant.

Purdy and Brechet [77] considered the solute drag effect caused by Mn in a Fe-C-Mn system. They assumed that the paraequilibrium transformation rate is controlled by the fast diffusing interstitial elements e.g. carbon, but the substitutional elements cannot have a long range redistribution across the interface between the austenite and the ferrite. Therefore, many substitutional atoms segregate at the interface between the austenite and ferrite. From their theory, the substitutional element concentration profile across the interface can be illustrated in Figure 2.33 (a), and the chemical potential profile across the interface can be illustrated in Figure 2.33 (b).



Figure 2.33: (a) The equilibrium substitutional element profile across an interface with a thickness of 2Λ; (b) The interaction potential of the substitutional element with the interface, where the effective depth of the potential well is E'<sub>0</sub>. The solid line represents a deeply quenched interface, and the broken line represents a slowly moving interface [77].

From Figure 2.33 (b), the interaction energy between the substitutional element and the interface can be expressed as [77]:

when	$x < -\Lambda$	$E(x) = \mu_{\alpha}^{0}$	
when	$-\Lambda < x < 0$	$E(x) = \mu_{\alpha}^{0} + \Delta E - E_{0} + \frac{\Delta E - E_{0}}{\Lambda}x$	
when	$0 < x < \Lambda$	$E(x) = \mu_{\alpha}^{0} + \Delta E - E_{0} + \frac{\Delta E + E_{0}}{\Lambda}x$	
when	$\Lambda < x$	$E(x) = \mu_{\gamma}^0$	Equation 2.68

Therefore, the solute drag force can be calculated based on Cahn's theory [75]:

$$P = -N_{\nu} \int_{-\Lambda}^{\Lambda} (c - c_{20}) \frac{\partial E}{\partial x} dx \qquad Equation 2.69$$

where  $N_v$  is the number of solute atoms per unit volume.

Enomoto [78] studied the diffusion-controlled growth of ferrite from austenite in a Fe-C-Mn alloy based on the researches of Purdy and Brechet [77], and incorporated the solute drag effect of an alloying element into the model. The chemical potential of solute atoms in the grain boundary is given by

$$\mu_i = RT\{lnc_i(x) + \varepsilon_{ij}c_j(x)\} + E_i(x) \qquad Equation 2.70$$

where  $c_i(x)$  is the concentration of the *i*th solute,  $\varepsilon_{ij}$  is the Wagner's interaction parameter between the *i*th and *j*th solutes, and  $E_i(x)$  is the binding energy of solute to the austenite and ferrite boundary at a distance x. Enomoto [78] also produced a model to describe the solute concentration profile:

$$\frac{\partial c_2}{\partial x} + \frac{c_2}{RT}\frac{\partial E_2}{\partial x} + c_2\varepsilon_{12}\frac{\partial c_1}{\partial x} + \frac{v}{D^b}(c_2 - c_2^0) = 0 \qquad \qquad Equation \ 2.71$$

where  $c_1$  is the carbon concentration in the boundary region,  $c_2$  is the solute element (which is Mn in his research) concentration in the boundary,  $c_2^0$  is the bulk concentration of the solute atoms, v is the boundary velocity,  $D^b$  is the diffusivity of the solute element,  $\varepsilon_{ij}$  is the Wagner's interaction parameter between the C and Mn, and  $E_2$  is the binding energy of solute to the austenite and ferrite boundary. The free energy dissipated by the solute drag effect is given by

$$\Delta G_{drag} = P_2 V_m \qquad \qquad Equation \ 2.72$$

where  $P_2$  is the solute drag force, and  $V_m$  is the molar volume. From the calculation, he concluded that the drag effect caused by intrinsic mobility is so low that can be neglected.

Takahama and Sietsma [79] expressed the grain boundary mobility as:

$$\mu = \mu_0 exp\left(-\frac{Q}{RT}\right) \qquad \qquad Equation \ 2.73$$

where  $\mu$  describes the mobility of austenite/ferrite boundaries during transformation,

 $\mu_0$  is a fitting parameter, and *Q* is the activation energy. The retardation effect on boundary mobility caused by solute drag and pinning can be revealed by the factor  $\mu_0$ . The boundary velocity v is given by

$$v = \mu \frac{\Delta G}{V_m} = \mu_0 exp\left(-\frac{Q}{RT}\right) \frac{\Delta G}{V_m}$$
 Equation 2.74

where  $\Delta G$  is Gibbs free energy difference, which is also the driving force for the transformation, and  $V_m$  is the molar volume. In the model,  $\Delta G$  includes the energy dissipation caused by solute drag effect ( $\Delta G_{sd}$ ) and pinning effect ( $\Delta G_{pin}$ ). Therefore, the effective mobility factor is [79]:

$$\mu_0 = \mu_{org} - \mu_{sd} - \mu_{pin} \qquad \qquad Equation \ 2.75$$

where  $\mu_{org}$  is the original mobility factor,  $\mu_{sd}$  and  $\mu_{pin}$  are the reduction of the mobility factors caused by solute drag effect and pinning effect, respectively. They also considered dissolved atoms at grain boundaries or inside grains, and proposed another model [79]:

$$\mu_{sd} = \sum_{i} \left( a_i^b f_i^b + a_i^m f_i^m \right) [i]_s \qquad \qquad Equation \ 2.76$$

where  $a_i^b$  is the proportionality factor for the solute drag effect of solute atoms in the  $\gamma/\gamma$  boundary before transformation,  $a_i^m$  is the proportionality factor for solute atoms inside austenite grains, and  $f_i^b$  and  $f_i^m$  are the fraction of atoms in the grain boundary or inside austenite grains, respectively.

## 2.4.5.2 Effects of niobium carbonitride

During the transformation from austenite to ferrite, the formation of Nb(C,N)precipitates accelerates the nucleation of ferrite, because the amount of niobium atoms in solution is decreased and the precipitates at the austenite interface can act as preferential nucleation sites. Therefore, the Ar<sub>3</sub> temperature can be increased. According to Jung et al. [66], ferrite nucleation at the austenite/precipitate interface requires low activation energy because ferrite/precipitate boundaries and ferrite/austenite boundaries are low energy interfaces. This explanation can be supported by the orientation relationships between the Nb(C,N) particles and the ferrite nucleated on it and between the Nb(C,N) particles and the austenite matrix [66]. However, Kop et al. [80] did not find ferrite nucleated on coarse Nb(C,N) particles. In addition, they calculated that the pinning force caused by the Nb(C,N) precipitates can be negligible compared to the driving force for transformation, and they found that the mobility of the transformation front is not changed by the ratio of the number of niobium precipitates and of the solute niobium atoms. Therefore, there is a debate on the effects of niobium precipitates and further research with accurate measurement is required.

During reheating, Nb(C,N) precipitates can retard austenite grain growth and recrystallisation through a pinning effect [81, 82, 83, 84, 85]. Both solute and precipitated niobium particles can retard recrystallisation and transformation kinetics during steel processing. According to DeArdo [17], the pinning force caused by the strain induced precipitation must be higher than 20 MPa, which is the driving force available for recrystallisation, before it can be retarded. The pinning force can be calculated by [17, 86, 87]:

$$F_{PIN} = 4r\sigma N_s$$
 Equation 2.77

where *r* is the particle radius,  $\sigma$  is the interfacial energy of the austenite grain boundary, and *N<sub>s</sub>* is the number of particles per unit area.

Hansen *et al.* [86] proposed a subgrain boundary model for  $N_s$  for calculating the pinning force, which assumes particles are present at austenite grain boundaries and subgrain boundaries prior to recrystallisation. It is probably the most realistic model for the calculation of the pinning force [17, 87]:

$$F_{PIN}^{S} = 3\sigma f_{V} l (2\pi r^{2})^{-1} \qquad Equation 2.78$$

where  $\sigma$  is the austenite grain boundary energy,  $f_V$  is the volume fraction particles,

*l* is the subgrain size, and *r* is the particle radius. Equation 2.77 indicates that high values of  $f_V$  and small particle sizes can result in a high pinning force. If particles are not uniformly distributed, localised pinning forces at the preferential precipitation sites are much higher than the expected value from a uniform distribution of particles [87].

Fu *et al.* [74] studied the effect of second phase particles on austenite grain growth. They expressed the grain growth velocity as:

$$v = \frac{M_{eff}G_{int}}{V_m} \qquad \qquad Equation \ 2.79$$

where  $M_{eff}$  is the effective interface mobility,  $V_m$  is the molar volume and  $G_{int}$  is the driving force for interface movement, which can be expressed as [74]:

$$G_{int} = \frac{\rho \mu b^2}{2} - \frac{3\sigma f_p}{2r_p} \qquad \qquad Equation \ 2.80$$

where  $\rho$ ,  $\mu$ , b,  $\sigma$ ,  $r_p$ , and  $f_p$  are the residual dislocation density, shear modulus, Bugers vector, grain boundary energy, the precipitate radius and the volume fraction, respectively. Takahama and Sietsma [79] combined the dissolved Nb atoms solute drag effect and the NbC particles pinning effect together, and proposed a new model for the grain boundary mobility during transformation:

$$\mu_{0} = \mu' - \mu_{sd-Nb} - \mu_{pin-NbC}$$
$$= \mu' - (a_{sd}T_{A} + b)[Nb]_{S} - a_{p}[Nb]^{2/3} \qquad Equation \ 2.81$$

where  $\mu_0$  is the effective mobility factor,  $\mu'$  is the consistent mobility factor which is affected by neither the Nb solute drag effect nor the NbC pinning effect,  $\mu_{sd-Nb}$  is the average mobility factor for the solute drag effect of Nb,  $\mu_{pin-NbC}$  is the average mobility factor for the pinning effect of NbC,  $a_p$  is the proportionality factor for the pinning effect,  $a_{sd}$  is the proportionality factor for the solute drag effect of Nb, *b* is a constant factor, and  $T_A$  is the austenitisation temperature. In this model, the influence of austenitisation temperature on the solute drag effect is considered, and the pinning effect is assumed to be proportional to [NbC]<sup>2/3</sup>.

Banerjee *et al.* [88] applied a Zener pinning approach and proposed a model for austenite grain growth affected by Nb and Ti precipitates:

$$\frac{d}{dt}d_m = M(P_D - P_P) \qquad \qquad Equation \ 2.82$$

where  $P_D$  is the driving pressure for grain growth,  $P_P$  is the pinning pressure induced by precipitates, and *M* is the mobility of the grain boundary, which is given by [88]:

$$M = M_0 exp\left(-\frac{Q}{RT}\right) \qquad \qquad Equation \ 2.83$$

where  $M_0$  is a pre-exponential factor, Q is an activation energy, R is the gas constant, and T is the absolute temperature. The driving pressure  $P_D$  is given by [88]:

$$P_D = \frac{4}{d_m} \gamma \qquad \qquad Equation \ 2.84$$

where  $\gamma$  is the grain boundary energy. The Zener pinning pressure can be expressed by [88]:

$$P_Z = \frac{3f}{2r}\gamma \qquad \qquad Equation \ 2.85$$

where *f* is the volume fraction of the precipitate, and *r* is the average particle radius. Combing  $P_D$  and  $P_Z$ , the critical grain size diameter,  $d_C$ , can be expressed by:

$$d_C = \frac{8r}{3f} \qquad \qquad Equation \ 2.86$$

From Rios's theory [89], the critical grain size has been proven to be 8 times smaller than the classical expression. Therefore, the pinning pressure is given by:

$$P_P = 8P_Z = \frac{12f}{r}\gamma$$
 Equation 2.87

From the Section 2.2.7, an increase in the number of nucleation sites can increase the parameter  $S_v$ . In addition, the pinning effect can inhibit grain coarsening. Therefore, the presence of niobium precipitates can refine austenite grain size [90, 91]. A niobium containing steel probably has a finer grain size than an identical C-Mn steel after the same hot rolling process. According to the Hall-Petch equation (shown in Equation 2.4), niobium steels can be strengthened by grain refinement. NbC precipitates have a large lattice misfit with both austenite and ferrite, therefore it is semi-coherent or incoherent with the iron matrix [92]. Precipitation hardening can also contribute a maximum of 80-100 MPa to the total yield strength with normal compositions and processing [17].

#### 2.5 Summary

In this literature review, previous research into the metallurgy of low alloy steels, austenite transformation, and the effects of solute niobium and niobium precipitates has been discussed. Steels with various properties can be obtained from austenite transformation. A typical reconstructive transformation from austenite to ferrite includes two key stages: nucleation and grain growth. The overall transformation kinetics can be calculated using JMAK equation. Niobium is a typical microalloying element, and it has a strong tendency to form carbides. Niobium atoms in austenite
as a solid solution and niobium precipitates have different effects on the austenite transformation. Solute niobium atoms retard the transformation from austenite to ferrite, and many previous researchers attribute this to the solute drag effect. However, niobium precipitates accelerate the transformation. The precipitates can retard the austenite grain growth and recrystallisation, and they have a grain refinement effect. However, accurate amounts of solute niobium atoms and niobium precipitates are difficult to measure, thus it is difficult to quantitatively define the effects of niobium. Further research is required to study the details of these effects, and an accurate phase transformation model which includes the effects of Nb can be developed.

## **3 Experimental Procedure**

### **3.1 Introduction**

This chapter includes a description of the materials, the experimentation and the techniques utilised in the project. The investigation has been concerned with the effects of niobium on austenite grain size and transformation from austenite to ferrite applied to low alloy steels. Figure 3.1 is a flow chart of the experimental programme of the project.



Figure 3.1: Flow chart illustrating the experimental program of the research.

#### 3.2 Materials

Six steel plates with different compositions were provided by Tata Steel RD&T. They were hot rolled commercial low alloy steels, and their compositions are listed in Table 3.1. Steel 1 is niobium free, Steel 2 has 0.009 wt. % niobium, Steel 3 has 0.028 wt. % niobium, Steel 4 has 0.029 wt. % niobium, but its carbon content is 0.205 wt. %, which is almost twice of the first three, Steel 5 has 0.045 wt. % niobium, and Steel 6 has 0.067 wt. % niobium. Steels 5 and 6 are from a different batch to Steels 1-4, and their carbon contents are a similar level to Steels 1-3. Other elements e.g. Si, Mn, Al, Ti, and N have similar contents in all of these steels, and the content is the major difference in Steels 1, 2, 3, 5, and 6, and the carbon content is the major difference between Steel 3 and Steel 4. Steel 3 has a niobium content which is typical of commercial low alloy steels.

Compositions (wt. %)	Steel 1	Steel 2	Steel 3	Steel 4	Steel 5	Steel 6
С	0.11	0.105	0.105	0.205	0.088	0.096
Nb	<0.001	0.009	0.028	0.028	0.045	0.067
Si	0.23	0.23	0.23	0.23	0.23	0.23
Mn	0.99	1.00	0.99	1.02	1.01	1.01
Р	0.002	0.002	0.002	0.002	0.018	0.018
S	0.0010	0.0009	0.0009	0.0010	0.0011	0.0011
AI	0.034	0.031	0.030	0.032	0.032	0.029
Ν	0.0060	0.0060	0.0060	0.0049	0.0050	0.0050
Ti	0.001	0.001	0.001	0.001	0.0005	0.0006
Cr	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Мо	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Ni	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cu	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
V	<0.001	<0.001	<0.001	<0.001	<0.001	>0.001

Table 3.1: Chemical compositions of steels investigated (balance Fe)

#### 3.3 Thermodynamic Calculations

In order to determine the temperatures for austenitisation, precipitation for niobium carbonitride, isothermal transformation and continuous cooling, thermodynamic calculations were performed by MTDATA using the TCFE v1.22 database with elements Fe, C, Si, Mn, Al, Nb, Ti, and N selected. The MTDATA software package was developed by the National Physical Laboratory, and it allows thermodynamic predictions based on Gibbs free energy minimisation. During thermodynamic calculations, phases e.g. austenite, ferrite, cementite, AIN, NbC, and TiN were allowed, and other possible phases were excluded because they would not exist in the applied heat treatment. The temperature range used was from 600°C to 1300°C, and the temperature step was initially set as 10°C, and then set as 1°C for more accurate calculation over a specific range. With the help of MTDATA, multicomponent phase diagrams of steels were plotted, and an isopleth phase diagram which isolated the effect of niobium on phase diagram was calculated. The phase boundary temperatures of each steel were calculated. The amount of each phase and the elemental distribution in these phases at a particular temperature were also calculated. Another software package named ThermoCalc with the TCFE v6 database was also utilised to calculate phase boundary temperatures, and the predictions were compared with MTDATA results. An existing Tata Steel model which is called CamModel developed by S. V. Parker [4], the EWI model which was developed by S. S. Babu [93,94], and the MTTTDATA model which was developed by T. Okumura and T. Sourmail [95] were all utilised and compared to predict the TTT diagram of the steels used in the research. From the predicted TTT diagrams and thermodynamic calculation results, austenitisation temperatures, precipitation treatment temperatures, and transformation temperatures and holding times were determined.

#### 3.4 Sample Preparation

The steel plates provided by Tata Steel were machined to solid cylindrical bars with 5 mm in diameter and 10 mm in length for dilatometric analysis. A schematic diagram of a sample is shown in Figure 3.2. After heat treatments in the dilatometer, samples were first cut into two halves using a Struers Accutom-5 circular saw

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equipped with an alumina cutting wheel. After cutting, one section was stored as a backup, and the other one was metallographically prepared for optical microscopy and scanning electron microscopy (SEM). A PolyFast phenolic hot mounting resin with carbon filler was used for mounting samples. Then, the mounted samples were ground on SiC paper with 220 grit, 600 grit, and 1200 grit, followed by fine grinding with a 9  $\mu$ m water based diamond suspension. Each step took 3 minutes. After that, the samples were polished with a 3  $\mu$ m diamond suspension for 8 minutes and with a 1  $\mu$ m diamond suspension for 10 minutes. All grinding and polishing work was automatically operated using a Struers Tegrapol-25. Then, some polished samples were etched with 2% nital, which is 2% nitric acid in methanol, for 10 to 20 seconds. Some other samples were further polished using 0.02  $\mu$ m Buehler colloidal silica suspensions in order to make a distortion free surface for niobium carbonitride observation under an InLens mode or a backscatter mode of SEM.



Figure 3.2: Schematic illustration of a sample for dilatometry and cutting.

In order to prepare carbon extraction replicas for transmission electron microscopy (TEM), some polished samples were lightly etched with 2% nital, and then coated with a carbon film using a Q150T ES Carbon Evaporator. A carbon rod with a sharp tip and another carbon rod with a dull tip were closely touched with each other, which

are used as the carbon source. The operation parameters for carbon coating are listed in Table 3.2. After coating, a few lines were carved across the carbon film using a clean razor blade, in order to make the carbon films easily drop off during the subsequent electro-etching. The electro-etching was operated within 10% hydrochloric acid in methanol under a voltage of 10 V, and then the sample was cleaned by immersing into methanol and de-ionised water, respectively. A lot of small carbon extraction replicas which were floating on de-ionised water, were collected using copper grids, and then cleaned on filter paper.

Parameter	Value		
Material	Carbon		
Pulse Current (A)	70		
Pulse Length (seconds)	0.80		
Number of Pulses	1		
Pulse Interval (seconds)	10		
Out Gas Time (seconds)	30		
Out Gas Current (A)	45		
Out Gas Source	Yes		
Pump Hold	Yes		
Tooling Factor	2.0		

# Table 3.2: Operation parameters for carbon coating on steel samples in a Q150T ESCarbon Evaporator.

#### 3.5 Dilatometry

A Bähr Dilatometer DIL 805D was utilised for all heat treatments in this research. Dilatometry is a powerful technique to investigate solid-solid phase transformation behaviour. Since phases have different lattice parameters, the specific volume of a sample changes during phase transformation. A dilatometer is able to heat or cool a sample and record dimensional changes during heat treatment, and thus transformation behaviours can be studied.

A cylindrical sample with 10 mm in length and 5 mm in diameter was lightly ground to get a flat surface, and then an S type thermocouple was spot welded to the middle of the sample using the spot welding apparatus attached to the dilatometer. There are two types of rods to fix samples in place; alumina rods and silica rods. The maximum temperature for alumina rods is 1500°C, and the maximum temperature for silica rods is 1100°C. However, alumina rods have a significant dilatation at high temperatures, and thus the change in length is not accurate. Although silica rods have a lower temperature limit, they were utilised in the research due to the more accurate results, and a few minutes heating over the temperature limit did not damage the rods. A set of heat treatments which included austenitisation, precipitation for niobium carbonitride, interrupted isothermal transformation, and continuous cooling were applied to samples, as schematically illustrated in Figures 3.3 and 3.4. Some samples were directly quenched from the austenitisation temperature to study the prior austenite grain size. Many samples had an austenitisation for a few minutes, and then were quenched to the isothermal transformation temperature and held for a long time to ensure samples fully transformed, followed by guenching to room temperature. The isothermal transformation was sometimes interrupted after a short time, in order to study nucleation and grain growth rates. For some other samples, a precipitation heat treatment was applied before isothermal transformation. The heating, the austenitisation, and the precipitation treatment were all under vacuum. The vacuum was turned off during isothermal transformation to avoid influence caused by pumping on the change in length. Helium gas was used as cooling medium, but it can be changed to other gases if necessary. The flow rate of the cooling gas can be adjusted for different cooling rates, and there are two gas valves for different ranges of flow rates. Gas valve 1 with a small amount of gas flow is suitable for relatively slow cooling with accurate temperature control, and it was applied for all the cooling faster than 1°Cs<sup>-1</sup> in this research. Gas valve 2 with a large amount of gas flow is suitable for an extremely fast cooling, but its accuracy is not as good as gas valve 1.

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Furnace cooling with no gas valve open was applied when the cooling rate was slower than 1°Cs<sup>-1</sup>.



Figure 3.3: Temperature profile for interrupted isothermal transformations.



Figure 3.4: Temperature profile for continuous cooling.

During heat treatments, the time, temperature, change in length, and vacuum condition were all recorded by the DIL805D software associated with the dilatometer. The transformation kinetics were analysed by a curve of change in length against time, or another curve of change in length against temperature. The transformation start point and the transformation finish point were determined by drawing tangent lines on curve of the change in length, as shown in Figure 3.5. Then, the curve of

transformation progress as a function of time can be plotted by setting the transformation start point as 0 and the transformation finish point as 100% transformation progress, as shown in Figure 3.6. With the ferrite fraction measured from optical microscopy images, the curve of the phase transformed fraction of a function of time can also be plotted by setting the transformation finish point as the value of the measured ferrite fraction, as shown in Figure 3.7.



Figure 3.5: An example of how to determine the transformation start point and transformation finish point.



Figure 3.6: The transformation progress curve derived from the original change in length curve in Figure 3.5.



Figure 3.7: The transformed fraction curve derived from the original change in length curve in Figure 3.5

#### 3.6 Optical Microscopy

After heat treatments, samples were metallographically prepared and etched in 2% nital. Then, the samples were observed in a Reichert-Jung MEF3 optical microscope with a MicroPublisher 5.0 RTV digital camera attached. The main aim of using optical microscopy was to get an indication of the bulk microstructure at 100X, 200X and 500X magnifications (with a horizontal field width of 1140 µm, 570 µm and 228 µm, respectively) under bright field mode. From optical microscopy images, transformation products e.g. ferrite, pearlite, bainite, and martensite, can be easily observed. Grain size measurement and phase quantification are both based on optical microscopy images, because the low magnification images involve more areas, and thus the measurement is more accurate.

#### 3.7 Field Emission Gun Scanning Electron Microscopy (FEG-SEM)

Scanning electron microscopy (SEM) is a technique which can observe the microstructure at a high magnification. In this research, a LEO 1530VP field emission gun scanning electron microscope (FEG-SEM) was utilised. In SEM, a primary electron beam interacts with a specimen, and various signals generated from the interaction can be detected, as illustrated in Figure 3.8. Secondary electrons and

backscattered electrons can be detected, then information on microstructure can be analysed.

Secondary electrons typically have low energy, and are sensitive to topography. The InLens image also derives from secondary electrons, but with a much shorter working distance, and thus it provides a better observation of the surface features. Backscatter electrons typically have a higher energy than the secondary electrons, and thus they can be emitted from a deeper region. The strength of backscatter signals depends on the atomic number of the sample. Therefore, differences in atomic number make a strong contrast in the backscatter mode.



Figure 3.8: Schematic illustration for various electron-specimen interactions.

In this research, the InLens mode with an accelerating voltage of 5 kV was applied to obtain micrographs with a working distance at 5 mm, and a 30  $\mu$ m aperture was chosen. Images at magnifications from 1,000X to 20,000X (with horizontal field width of 350  $\mu$ m and 17.5  $\mu$ m, respectively) were taken to study the microstructure after different heat treatments. Since Nb has an atomic weight of 92.9, which is much higher than iron, the backscatter mode with an accelerating voltage of 20 kV with a working distance at 6 mm, and a 60  $\mu$ m aperture were applied to study NbC particles. Since the NbC particle size varies with heat treatment, the magnifications were chosen from 10,000X to 50,000X. Energy dispersive X-ray (EDX) analysis was also associated with backscatter imaging to identify chemical compositions.

#### 3.8 Electron Backscatter Diffraction (EBSD)

Electron backscatter diffraction (EBSD) is an advanced technique to study microstructural and crystallographic information. In this research, EBSD was carried out using the Carl Zeiss 1530 VP FEG-SEM equipped with an electron backscatter diffraction camera. In this research, EBSD was mainly used for ferrite grain size measurement. Samples were glued on a holder with a 70° tilting to the horizontal. The scanning area was chosen as 200  $\mu$ m \* 200  $\mu$ m, and the step size was set as 0.2  $\mu$ m. During scanning, the FEGSEM was operating under an accelerating voltage of 20 kV, with an aperture size of 60 mm, and the working distance was normally chosen as 15 mm. The TSL OIM Data Collection software was utilised for automatic indexing during scanning, and the results were analysed using the TSL OIM Analysis software. In a scanned image, ferrite grains were all selected with all other phases partitioned, and thus the ferrite grain size was accurately measured.

#### 3.9 Dual Beam

An FEI Nova 600 NanoLab dual beam system which consists of a FEGSEM and a gallium source focused ion beam (FIB) was used in the research. The main use of the Dual Beam system in this project was to lift out a small TEM sample from a bulk FEGSEM sample. The lift out can be applied in a chosen area, and thus some interesting features e.g. an interface of ferrite/martensite, and segregation of NbC particles, can be accurately chosen and lifted out as a TEM sample for further characterisation. The flowchart of a typical lift out process is illustrated in Figure 3.9. An interesting feature was firstly found from a FEGSEM image. Then, the FEGSEM sample was tilted to 52°, and Pt was deposited on the surface across the feature to protect it from cutting. After that, both the upper and lower regions of the Pt deposition were removed using the gallium ion source, and the Pt deposited cross section was also cleaned using ion source. That was followed by tilting the sample to 7°, and cutting most of the cross section off from the matrix with only a small area attached. In the next step, the cross section was welded to the needle, and then it was entirely cut off from the matrix. After that, the needle was moved close to a Cu

grid of a TEM sample holder, and the cross section was welded to the Cu grid using Pt deposition, followed by cutting it off from the needle. The last step was the final thinning, and the cross section was thinned from both sides until its thickness was less than 200  $\mu$ m. The image of each step in a lift out process is illustrated in Figure 3.10 (a) to (f), respectively, and the related operation conditions are listed in Table 3.3.



Figure 3.9: Flowchart of a typical lift out process.



Steps	Procedures	Dimension of cutting area (µm)	Current (nA)	Voltage (kV)	Tilt angle	Pt GIS
1	Pt deposition on a feature	X=15; Y=2; Z=2	0.3	30	52°	Yes
2-1	Removal matrix from both sides of the feature	X=22; Y=12; Z=10	20	30	52°	No
2-2	Cleaning the cross section	X=22; Y=12; Z=10	7	30	52°	No
3	Cutting the section from the bulk sample	N/A	0.1	30	7°	No
4	Welding the lift out section to the needle	N/A	0.03	30	0°	Yes
5-1	Welding the lift out section to Cu grid	N/A	0.5	30	0°	Yes
5-2	Cutting the lift out section off from the needle	N/A	0.1	30	0°	No
6	Final thinning	N/A	0.1	30	52° <u>+</u> 1.5°	No

## Table 3.3: Operation parameters of each step in lift out procedure

#### 3.10 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a technique which can observe the microstructure at a higher magnification than SEM. Since TEM samples should be electron transparent, the thickness of samples must be less than 200 nm, and thus the sample preparation quality is very important. In this research, TEM samples were prepared in two ways: carbon extraction replica or FIB lift out. Electro-polishing was also tried, but the magnetism of a 3 mm steel disc always causes some problems in the TEM. However, FIB lift out samples are quite small and are only a few microns in length, and thus its magnetism is negligible in the TEM. For carbon extraction replica samples, the steel matrix has been dissolved with only precipitates embedded in the carbon films, and thus it also has no magnetic problem. Carbon extraction replica samples were used to identify NbC particles, and to study the particle size after different heat treatments. Since the steel matrix had been fully dissolved, NbC particle distribution was also studied. However, the real microstructure cannot be observed from carbon extraction replicas, and thus FIB lift out samples were used to study NbC particle distribution at grain boundaries and dislocations around them.

A JEOL 2000FX transmission electron microscope (TEM) equipped with an Oxford Instruments Inca EDX detector, was used to study the niobium carbonitride distribution after heat treatment. Images at a magnification from 25,000X to 400,000X (with horizontal field width of 5.3 µm and 330 nm, respectively) using an accelerating voltage of 200 kV were taken to study the niobium carbonitride particle distribution. EDX analyses and diffraction patterns were also associated with the phase characterisation. An FEI Tecnai F20 field emission gun transmission electron microscope (FEGTEM) fitted with high angle annular dark field (HAADF) detector and an X-Max 80 mm SDD detector was also utilised in the research. It was mainly used for bright field imaging, HAADF imaging and EDX mapping, using an acceleration voltage of 200 kV. During the EDX spectrum mapping, Fe, C, Mn, and Nb were normally the selected elements, but AI, Ti, Si, and N were also selected sometimes for the analysis of certain types of particles.

#### 3.11 Grain Size Measurement and phase quantification

The influences of Nb on both austenite grain growth and ferrite grain size are quite important for the study of the effects of Nb on phase transformation behaviour. The austenite grain growth as a function of temperature or time in steels with different Nb contents was studied, and the ferrite grain size after transformations was also studied. There are currently many grain size measurement techniques, e.g. linear intercept method, ASTM grain size chart comparison method, and EBSD. The linear intercept method is commonly used and easily operated, but it is not accurate enough, and it is inappropriate for multiphase samples. The ASTM chart comparison is also a commonly used method, but it is not accurate enough, and cannot show the actual grain size distribution. EBSD is accurate and works well for multiphase samples, however, each EBSD scanning can take quite a long time, and the scanning area is typically smaller than optical microscopy images.

In order to accurately study grain size, especially in a multiphase sample, a new method using a 'grain boundary tracing technique' has been developed in this research. It can be used to measure phase fraction, average grain size of a particular phase, and the grain size distribution from optical microscopy images. In this method, the scale bar from an optical microscopy image was firstly input in the Image Tool software (step 1). Then, phase boundaries of martensite or pearlite were drawn by black lines in Adobe Photoshop software, using a pen tablet called "Wacom Bamboo Pen & Touch" (step 2), and all the martensite and pearlite regions were painted to black (step 3). After that, ferrite was selected using a function called "threshold" in the Image Tool software (step 4), and the ferrite area fraction was measured using a function called "counting black/white pixels" (step 5). For grain size measurement, ferrite grain boundaries were drawn by black lines (step 6), and all ferrite grains except those which were at image edges and not fully displayed, were painted in white (step 7). Then, the white grains were highlighted using "threshold" (step 8) and automatically selected in the Image Tool software (step 9). The average grain size was then calculated by analysing all the selected objects (step 10). The ferrite grain size distribution was obtained by classification of all of the selected objects with different ranges of feret diameters (step 11). After that, grains

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within different size ranges were automatically painted with different colours, and the number of grains within each size range was automatically counted (step 12). The flowchart of the procedure used is illustrated in Figure 3.11. Images illustrating the phase fraction measurement procedures, which were steps 1-5, are shown in Figure 3.12. Images illustrating the average grain size measurement, which were steps 6-10, are shown in Figure 3.13. Images illustrating the ferrite grain size distribution measurement, which were steps 11-12, are shown in Figure 3.14. From the Image Tool software, the feret diameter of a grain is calculated by:

$$d = \left(\frac{4A}{\pi}\right)^{\frac{1}{2}}$$
 Equation 3.1

where A is the area of a grain measured from the image analysis software.

In this method, all ferrite grains in an image are involved in measurement, and other phases e.g. pearlite and martensite would not affect the ferrite grain size measurement. However, grains at the edge of an image were not counted, because their grain sizes are not fully measured. If these grains are involved in the grain size measurement, the resulted average grain size will be smaller than the true value. This is an image analysis method based on typical optical microscopy images, and thus the sample preparation is quite easy and fast. Since the grain size of every ferrite grain can be obtained, the ferrite grain size distribution of a sample can also be plotted. Grains with different ranges of size are displayed by different colours, and thus the grain size distribution can be clearly observed. Since different phases in an image can be easily selected, the phase fractions of ferrite, pearlite, and martensite can also be measured simultaneously. Using the phase fraction measurement, the transformation progress can be accurately studied after interrupted isothermal transformations.

It is very difficult to measure the prior austenite grain size, because austenite does not exist at room temperature in these steels. If the steels are quenched to room temperature just after austenitisation treatment, austenite will transform to martensite, and the boundaries of martensitic regions will indicate the prior austenite grain

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boundaries. However, it is very difficult to observe martensite grain boundaries of the steels after chemical etching. Neither 2% nital nor picral can clearly highlight martensite grain boundaries. In order to clearly observe prior austenite grain boundaries, thermal etching was utilised instead of chemical etching. Samples were firstly polished to get a flat surface. Then the samples were welded to a thermocouple and heated to the austenitisation temperature in the dilatometer. It is important that the polished surface is not touched. After a few minutes austenitisation, the samples were directly quenched to room temperature. Using the thermal etching, the prior austenite grain boundaries could be clearly observed on the polished surface, as shown in Figure 3.15.



Figure 3.11: Flowchart of the grain boundary tracing method to quantify phase fraction and grain size



Figure 3.12: Images illustrating the procedures to measure the phase fraction: (a) inputting the scale bar of an image into the software, which is step 1; (b) using the pen tablet to draw grain boundaries, which is step 2; (c) and (d) painting of a particular phase, which is step 3; (e) using the "threshold" function to select the painted phase, which is step 4; and (f) calculating the phase fraction, which is step 5.



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Figure 3.13: Images illustrating the procedures to measure the average ferrite grain size: (a) drawing black lines on ferrite grain boundaries, which is step 6; (b) painting of ferrite grains using a different colour, which is step 7; (c) highlighting of all ferrite grains except those at the edge of the image, which is step 8; (d) Selection of all the highlighted ferrite grains, which is step 9; and (e) results of ferrite grain size measurements using the Image Tool software, which is step 10.







Figure 3.14: Images illustrating the procedures to measure the ferrite grain size distribution: (a) classification of grains by the range of feret diameter, which is step 11; and (b) coloured grain image and the number of grains in each range, which is step 12.



Figure 3.15: A typical optical microscopy image for a thermally etched sample. The polished sample was austenitised at 1250°C for 30 seconds, and then quenched to room temperature. The prior austenite grain boundaries can be clearly observed.

## 4 Thermodynamic calculations

#### **4.1 Introduction**

Before doing heat treatments, the temperatures, times and cooling rates should be determined in order to determine the influence of the Nb on the transformation kinetics. In this research, thermodynamic calculations were utilised to determine phase boundary temperatures, and then heat treatment temperatures were determined. Both MTDATA and ThermoCalc are powerful tools for thermodynamic calculations. They are based on Gibbs free energy minimisation, thus they are typically used for calculation of the equilibrium state. However, with some additional codes, metastable equilibrium phases can also be analysed, and then CCT and TTT diagrams can be studied. CamModel which was developed by H.K.D.H. Bhadeshia, S.V. Parker *et. al* from Cambridge University around 15 years ago and has been modified many times during the last 10 years, was also utilised to predict the CCT and TTT diagrams of steels.

#### 4.2 Phase boundary calculations

In order to determine temperatures for heat treatments such as austenitisation, precipitation of niobium carbonitride, isothermal transformation, and also to study phases present at various temperatures, thermodynamic calculations were carried out using MTDATA in conjunction with the TCFE v1.22 database and also with ThermoCalc using the TCFE v6 database.

An isopleth phase diagram, which is a section of multi-phase diagram, can be plotted using MTDATA, and then the effects of each element on the phase diagram can be isolated. Figure 4.1 is an isopleth phase diagram in a Nb-microalloyed low alloy steel with a niobium content from 0 to 0.01 wt. %, while the carbon content was fixed at 0.105 wt. % and the iron content was varied to balance. It was found that the niobium carbide dissolution temperature, which is the phase boundary between  $\gamma$ -Fe and  $\gamma$ -Fe+NbC on the diagram, increases from ~700°C to ~1000°C as the niobium

content increases from 0 to 0.01 wt.%, however, the niobium content has little effect on other phase boundaries, including  $\gamma$ -Fe,  $\alpha$ -Fe or Fe<sub>3</sub>C.



Figure 4.1: An isopleth phase diagram for Nb content from 0 to 0.01 wt. %, while the C content was fixed to 0.105 wt. %, the Si content was fixed to 0.23 wt. %, the Mn content was fixed to 0.99 wt. %, and the Fe content was varied to balance.

The phase boundaries for steels 1 to 6 were calculated, and are listed in Table 4.1. The results further prove that the niobium content has little effect on the Ae<sub>3</sub> and Ae<sub>1</sub> temperatures. Table 4.1 also indicates that both carbon and niobium can increase the niobium carbide dissolution temperature. The austenitisation temperature should be above the niobium carbide dissolved. Therefore, the austenitisation temperature can be chosen at 1250°C, which is a typical austenitisation temperature for Nb-containing steels [41, 57, 58, 59, 60, 63]. For steels 1 to 3, the Ae<sub>3</sub> temperature is around 845°C. The Ae<sub>3</sub> temperature for steel 4 is 818°C because of the higher carbon content. The Ae<sub>3</sub> temperatures for steels 5 and 6 are 859°C and 857°C, respectively. The isothermal transformation temperature should be below the Ae<sub>3</sub> temperature, in order for austenite to commence transformation, and 750°C, 700°C, 650°C, 600°C and 550°C are all suitable temperatures for isothermal transformation.

isothermal transformation at a temperature between  $Ae_3$  and  $Ae_1$ , transformation from austenite to ferrite cannot be completed, and there will always be some retained austenite left, which will be transformed to martensite during the subsequent quenching after the isothermal transformation.

Multiphase diagrams of steels 1-6 were calculated using ThermoCalc and are plotted in Figures 4.2 to 4.7, respectively. From the multiphase diagrams, it can be found that Fe<sub>3</sub>C, AIN, Nb(C,N) and Ti(C,N) are the possibly secondary phases. In order to make solute Nb atoms precipitate as Nb(C,N) particles before isothermal transformations, a precipitation heat treatment can be applied at 900°C, at which Nb(C,N) virtually reaches the maximum amount and it is still above Ae<sub>3</sub>. Multiphase diagrams also indicated that Nb(C,N) is likely to be fully dissolved at 1250°C in all the steels. Figure 4.8 indicates the solubility of Nb in steels at 1250°C. It can be seen that Nb can be fully dissolved at 1250°C when the Nb content is less than 0.1 wt. %.

Steels	C content (wt. %)	Nb content (wt. %)	Nb(C,N) dissolution (ºC)	Ae <sub>3</sub> (ºC)	Ae₁ (ºC)
1	0.11	0	N/A	844	697
2	0.105	0.009	1020	846	697
3	0.105	0.028	1141	846	695
4	0.205	0.028	1175	818	700
5	0.088	0.045	1174	859	696
6	0.096	0.067	1220	857	696

Table 4.1: Phase boundary calculation using MTDATA, which allows for elements Fe, C, Si, Mn, Al, N, Nb, Ti (TCFE v1.22).



Figure 4.2: Multi-phase diagram of steel 1 calculated by ThermoCalc with the TCFE v6 database.



Figure 4.3: Multi-phase diagram of steel 2 calculated by ThermoCalc with the TCFE v6 database.



Figure 4.4: Multi-phase diagram of steel 3 calculated by ThermoCalc with the TCFE v6 database.



Figure 4.5: Multi-phase diagram of steel 4 calculated by ThermoCalc with the TCFE v6 database.



Figure 4.6: Multi-phase diagram of steel 5 calculated by ThermoCalc with the TCFE v6 database.



Figure 4.7: Multi-phase diagram of steel 6 calculated by ThermoCalc with the TCFE v6 database.



Figure 4.8: The solubility of Nb at 1250°C, calculated by ThermoCalc with the TCFE v6 database.

#### 4.3 TTT and CCT predictions

Time Temperature Transformation (TTT) diagrams and Continuous Cooling Transformation (CCT) diagrams are important tools to study transformation behaviour. From TTT and CCT diagrams, the transformation kinetics can be studied, and the microstructural constituents present at different temperatures with different cooling rates can also be studied.

An EWI model which has been developed by S. S. Babu from Edison Welding Institute (EWI) [93, 94] was used in this research to predict TTT and CCT diagrams (as shown in Figure 4.9). Since niobium is not accounted for in the EWI model, it was only used to make predictions for steel 1 which is niobium free. From the EWI model, the transformation from austenite to pearlite and bainite starts in a few seconds.

An MTTTDATA model which has been developed by T. Okumura and T. Sourmail [95] allows for elements Fe, C, Cr, Ni, Co, Mo, Mn, Si, Al, Cu, V, and Nb, therefore it was used in this research to predict TTT diagrams. It is a FORTRAN code based on the MTDATA thermodynamics software package. The predicted TTT diagrams are

shown in Figure 4.10. It can be found that steel 1, steel 2 and steel 3 with different niobium contents all have the same TTT curve, however, the transformation in steel 4 with a higher C content is slightly delayed. The results from the MTTTDATA model initially indicate that Nb has little effect on transformation kinetics. A possible reason is that the effects of Nb on transformation have not been included in the modelling approach. However, the MTTTDATA calculation indicates that carbon has a retardation effect on the isothermal transformation start time.



Figure 4.9: TTT and CCT diagrams predicted by the EWI model for Steel 1.



Figure 4.10: TTT diagrams for steels 1 to 4 predicted by the MTTTDATA model. The TTT curves for steels 1-3 are overlapped.



Figure 4.11: TTT diagrams for steels 1 to 4 predicted by the existing CamModel.

An existing 'CamModel' which has been developed by H.K.D.H. Bhadeshia, S. V. Parker *et. al* [4] is a powerful tool to predict the thermodynamics and kinetics of phase transformation in steels. It also involves the effects of niobium on the phase transformation to some extent, and TTT diagrams for steels 1 to 4 were predicted using this model, as shown in Figure 4.11. From the TTT diagrams, it can be found that the transformation from austenite to ferrite in steel 1, which is niobium free, starts in less than 1 second. The transformation start time in steel 2 with 0.009 wt. %

niobium is slightly delayed by a few seconds, and the transformation start time in steel 3 with 0.028 wt. % niobium is even delayed by approximately 10 seconds. The transformation start time in steel 4 with 0.029 wt. % niobium and 0.205 wt. % carbon is further delayed. The results indicate that the transformation start time from austenite to ferrite is delayed with either increasing niobium content or carbon content.

The CamModel can also be utilised to predict continuous cooling transformation behaviour. The predicted CCT diagrams of steels 1-4 are shown in Figures 4.12 -4.15, respectively. The weight percentage of each phase for steels 1-4 after continuous cooling with different cooling rates are shown in Figures 4.16 – 4.19. From the diagrams, it can be found that the ferrite start temperature decreases with increasing Nb. The critical cooling rate to obtain martensite was around 10°Cs<sup>-1</sup> in steels 1 and 2, but it was increased to around 40°C/s in steel 3. Allotriomorphic ferrite is the dominant phase in steel 1 after a slow cooling rate, but there was more Widmanstätten ferrite than allotriomorphic ferrite in steels 2 and 3. In addition, a large amount of bainite can be formed in steel 3 with an intermediate cooling rate. According to staff from Tata Steel, the CamModel works satisfactorily for certain steels, but for many different kinds of steels, and especially for Nb-microalloyed steels, it still requires further development to accurately predict the transformation behaviour. Even though, the current predictions for TTT and CCT diagrams have qualitative indications to determine temperatures and times for experimental heat treatments. From the CamModel predictions, Nb possibly has a retardation effect on the isothermal transformation start time. It also decreases the ferrite formation temperature and pearlite formation temperature during continuous cooling, but has limited effect on the bainite formation temperature. It seems that Nb only has a strong effect on the diffusional transformation, and therefore Nb containing steels may have more displacive transformation products than Nb free steel after continuous cooling. However, all of these predictions need to be validated with experimental work, which has not previously been done in a thorough and systematic manner.



Figure 4.12: CCT diagrams for steel 1 predicted by the existing CamModel.



Figure 4.13: CCT diagrams for steel 2 predicted by the existing CamModel.



Figure 4.14: CCT diagrams for steel 3 predicted by the existing CamModel.



Figure 4.15: CCT diagrams for steel 4 predicted by the existing CamModel.


Figure 4.16: Weight percentage of each microstructural constituent after various cooling rates for steel 1 predicted by the existing CamModel.



Figure 4.17: Weight percentage of each microstructural constituent after various cooling rates for steel 2 predicted by the existing CamModel.



Figure 4.18: Weight percentage of each microstructural constituent after various cooling rates for steel 3 predicted by the existing CamModel.



Figure 4.19: Weight percentage of each microstructural constituent after various cooling rates for steel 4 predicted by the existing CamModel.

#### 4.4 Discussion

From the thermodynamic calculations for the six steels, it appears that Nb has little effect on the Ae<sub>3</sub> and Ae<sub>1</sub> temperatures, but the Nb(C,N) dissolution temperature increases with increasing either Nb content or C content. Therefore, the appropriate temperatures for the austenitisation heat treatment can be determined. The austenitisation temperature can be chosen at 1250°C, at which most Nb(C,N) is likely to be dissolved, and the existing transformation products e.g. ferrite, bainite, martensite, and cementite can be fully transformed to austenite. The temperature for Nb(C,N) precipitation heat treatment can be chosen to be 900°C, which allows Nb(C,N) to reach its maximum amount under equilibrium state, but austenite decomposition has not yet occurred. In addition, the starting point for continuous cooling transformations can also be chosen at 900°C, in order to avoid the precipitation of Nb(C,N). The subsequent isothermal transformation temperatures should be chosen below the Ae<sub>3</sub> temperature.

The EWI model, the MTTTDATA model, and the CamModel have all been utilised to predict the transformation behaviours of some specific steels. The EWI model does not account for the Nb, and thus it can only work for the Nb-free steel. The MTTTDATA model claims to allow for Nb, however, from the predictions, steels 1-3 with different Nb contents had exactly the same TTT curves, possibly because the MTTTDATA does not consider the effect of Nb on transformation start time. From the CamModel predictions, the TTT curves of steels 1-4 can be distinguished, and it was found that Nb has a retardation effect on transformation start point for both TTT and CCT curves. By comparing the three models, it seems that the CamModel is currently the best one to make accurate predictions for Nb-microalloying steels. However, its developers are aware that the CamModel predictions are not accurate for some steels, and it still requires further development for Nb-microalloying steels. Even for the Nb-free Steel 1, both the EWI model and the MTTTDATA model predict that the transformation start time should be a few seconds, but the CamModel indicates that it should be less than 1 second. In addition, both the EWI model and the MTTTDATA model predictions indicate that the TTT curves have a 'double C shape', but from the CamModel predictions, the 'double C shape' is not as clear.

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Therefore, all of these predictions need to be validated with experimental work for a thorough and systematic study. Indeed, not only the transformation start point, but also the overall transformation curve should be studied, in order to have a deep understanding of the effects of Nb on transformation behaviour.

# 4.5 Summary

In this chapter, the results of thermodynamic and kinetic calculations have been presented and discussed. MTDATA and ThermoCalc have been utilised for thermodynamic calculations. From the results, the phase boundary temperatures have been obtained, and therefore temperatures for heat treatments can be determined. CCT and TTT diagrams for steels used in the research have been predicted by some previous models. The MTTTDATA results apparently show that niobium has little effect on transformation kinetics, but the existing CamModel indicates that niobium can delay the transformation start time. Both the models indicate that carbon has a retardation effect on isothermal transformation start time. There are many differences in the prediction results between different models, and the effect of Nb on transformation behaviours has not yet been accurately characterised and quantified. A model with a full understanding of these effects is therefore required. In the following chapter, heat treatments will be applied to steels to study the effect of Nb on the prior austenite grain growth and the transformation kinetics from austenite to ferrite.

# 5 Effects of Nb on grain size

# **5.1 Introduction**

It has been widely agreed in the literature that Nb has a refinement effect on ferrite grain size, and thus can result in an improvement in mechanical properties. However, the mechanism of the refinement effect caused by Nb has not yet been fully understood. The transformation kinetics from austenite to ferrite are significantly affected by the prior austenite grain size. Therefore, in order to study the effect of Nb on transformation kinetics, the prior austenite grain size should be consistent, so that its effect on the subsequent transformation kinetics can be eliminated. In addition, the effect of Nb on the prior austenite grain growth can also be an indication of the effect of Nb on recrystallisation during hot rolling. Therefore, the effect of Nb on the prior austenite grain size also needs to be carefully studied.

## 5.2 As received materials

The steels provided by Tata Steel R&D were all hot rolled. Steels 1-4 were from the same batch, with the same initial conditions, whereas steels 5 and 6 were from a different batch, and the rolling conditions were different from steels 1-4. The asreceived micrographs of the 6 steels are shown in Figure 5.1 (a)-(f) respectively. It is obvious that steels 1 to 4 have the typical banded microstructure of pearlite layers, however, steels 5 and 6 do not. The banded microstructure in steel 4 is much more apparent than those in steels 1 to 3, because steel 4 has the double carbon content of steels 1 to 3. Steels 2 to 6 are all niobium containing steels, and therefore there should be some NbC particles forming during hot rolling. However, these NbC particles are typically quite small, and the Nb contents are less than 0.1 wt. % in all these steels, therefore, it is difficult to observe these NbC particles under FEGSEM. However, some NbC particles were observed in the steel 6 as-received samples, which had the highest Nb content, as shown in Figure 5.2.



(a) steel 1

(b) steel 2



(c) steel 3

(d) steel 4



(e) steel 5

(f) steel 6

Figure 5.1: Optical micrograph of steels 1-6 as received samples.



Figure 5.2: FEGSEM images and EDX spectra of NbC in steel 6 as-received samples.

It is recognised that samples with a banded microstructure are typical commercial steel products, however, it was necessary to do a homogenisation heat treatment by holding at 1250°C for 2 hours and furnace cooling to room temperature, in order to study the effect of the banded microstructure on the subsequent heat treatments. The microstructural differences before and after the homogenisation heat treatment for steel 1 and steel 6 are shown in Figures 5.3 and 5.4. It can be seen that the banded microstructure of pearlite layers has been removed, but also that the ferrite grain size has increased significantly. The difference in the NbC distribution in steel 6 between the as-received samples and the homogenised samples has been compared using FEGSEM, as shown in Figure 5.5. It can be found that after the homogenisation heat treatment, the NbC particles have a more homogeneous distribution than that in the as-received sample. In order to study the effect of the homogenisation heat treatment on the prior austenite grain size, both the

homogenised sample and the as-received sample were thermal etched at 1250°C for various times, and then they were quenched to room temperature using a dilatometer. Their prior austenite grain sizes were measured using the "Grain boundary tracing technique". Their average prior austenite grain sizes as a function of holding time at 1250°C were compared in Figure 5.6, and it can be seen that the homogenisation heat treatment has little influence on the austenite grain growth of steel 6 at 1250°C. The Nb contents in steels 1-4 are not quite high, and the low amount of Nb can be fully dissolved and redistributed during austenitisation at 1250°C. In addition, the homogenisation heat treatment has little and redistributed during austenitisation at subsequent transformation behaviours. Therefore, most of the samples used in the work are as-received samples.



Figure 5.3: optical micrographs of steel 1: (a) an as-received sample; (b) a homogenised sample by holding at 1250°C for 2 hours and furnace cooling to room temperature.



Figure 5.4: Optical micrographs of steel 6: (a) an as-received sample; (b) a homogenised sample by holding at 1250°C for 2 hours and furnace cooling to room temperature.



Figure 5.5: Comparison of NbC particles distribution in steel 6 between the asreceived sample and the homogenised sample. The NbC particles were counted in 25 FEGSEM images for each sample.



Figure 5.6: Comparison of austenite grain growth at 1250°C between as-received samples and homogenised samples of steel 6. In order to measure the austenite grain size, the samples were thermal etched at 1250°C for various times, and then they were quenched to room temperature using a dilatometer.

#### 5.3 Effect of solute Nb atoms on austenitisation grain growth

From thermodynamic calculations, all niobium precipitates should have been dissolved at 1250°C. The accurate study of the effect of solute Nb atoms on austenite grain growth is quite important for both scientific and industrial purposes. However, it is difficult to characterise the austenite grain size at 1250°C. Therefore, samples were quenched to room temperature at 100°Cs<sup>-1</sup> after an austenitisation heat treatment, and the samples directly transformed from austenite to martensite, and thus the prior austenite grain boundary can be seen at room temperature. Even so, the prior austenite grain boundaries are difficult to reveal using chemical etching, therefore, thermal etching was utilised in this research.

There are a lot of methods for grain size measurement, e.g. the linear intercept method and ASTM grain size number comparison. However, these methods encounter several difficulties when there is more than one phase presented (e.g. ferrite and pearlite), and none of these methods can accurately describe the grain size distribution. A new method named the 'Grain boundary tracing technique' has been developed and applied for grain size measurement in this project. With this method, grains with different size are labelled with different colours, and the grain size distribution can be easily characterised. For each sample, at least 300 grains are involved in the measurement to get an accurate result. Coloured grain size images of steel 1 after 5 seconds, 30 seconds and 300 seconds holding at 1250°C were obtained to get a clear overview of the grain size distribution, and a typical image for each sample is shown in Figure 5.7. The grain size distribution of steel 1 after different austenitisation times at 1250°C is plotted in Figure 5.8. From Figures 5.7 and 5.8, it can be found that the prior austenite grain size distribution becomes wider with increasing austenitisation time. After 300 seconds austenitisation, the grain size distribution becomes much wider than that with 5 seconds austenitisation, and the average grain size is significantly larger. Typical coloured grain size images of steels 2-4 with various austenitisation times at 1250°C are shown in Figure 5.9, Figure 5.11 and Figure 5.13, respectively. Grain size distribution curves of steels 2-4 with various austenitisation times are plotted in Figure 5.10, Figure 5.12 and Figure 5.14, respectively. The average prior austenite grain sizes for steels 1-4 as a function of austenitisation time at 1250°C are plotted in Figure 5.15 and listed in Table 5.1.

From Figures 5.7 to 5.14, it can be found that the austenite grains become larger with increasing holding time at 1250°C for all these steels. For each steel, the sample with the longest austenitisation time has the widest grain size distribution. From Figure 5.15, it can be seen that steel 3 has the smallest average grain size when the austenitisation time is longer than 1 minute. In addition, steel 3 also has the slowest prior austenite grain growth rate in steels 1-4. Steels 1-3 have similar initial conditions, and the Nb content is the only difference, therefore it can be concluded that Nb has a retardation effect on the prior austenite grain growth at 1250°C. From thermodynamic calculations, all niobium-rich precipitates are expected to be dissolved above 1150°C. This has been investigated by TEM observation using carbon extraction replicas, which showed that there were no Nb(C,N) precipitates in the samples quenched from 1250°C. Therefore, it is proposed that the observed difference in prior austenite grain size is caused by solute niobium atoms. From Figure 5.15, steel 4 has a faster prior austenite grain growth than steel 3, and thus it can be found that carbon has an accelerated effect on prior austenite grain growth. From Figure 5.15, it can also be found that 5 seconds austenitisation at 1250°C for steel 1, 60 seconds austenitisation for steel 2, 300 seconds austenitisation for steel 3, and 150 seconds austenitisation for steel 4 all result in an average prior austenite grain size of ~80µm. Therefore, the prior austenite grain size can be adjusted to the same value by careful choice of the initial heat treatment to avoid its effect on the subsequent transformation kinetics.



Figure 5.7: Grain size characterisation for steel 1 after 5 seconds, 30 seconds, and 300 seconds holding at 1250°C. Different colours of grains indicate the grain size ranges (unit: μm).



Figure 5.8: Prior austenite grain size distribution of steel 1 with different austenitisation times at 1250°C and subsequent quenching to room temperature, with prior austenite grain boundaries revealed by thermal etching.



Figure 5.9: Grain size characterisation for steel 2 after 30 seconds, 60 seconds, and 300 seconds holding at 1250°C. Different colours of grains indicate the grain size ranges (unit: μm).



Figure 5.10: Prior austenite grain size distribution of steel 2 with different austenitisation times at 1250°C and subsequent quenching to room temperature, with prior austenite grain boundaries revealed by thermal etching.



Figure 5.11: Grain size characterisation for steel 3 after 30 seconds, 60 seconds, and 300 seconds holding at 1250°C. Different colours of grains indicate the grain size ranges (unit: μm).



Figure 5.12: Prior austenite grain size distribution of steel 3 with different austenitisation times at 1250°C and subsequent quenching to room temperature, with prior austenite grain boundaries revealed by thermal etching.



Figure 5.13: Grain size characterisation for steel 4 after 60 seconds, 150 seconds, and 300 seconds holding at 1250°C. Different colours of grains indicate the grain size ranges (unit: μm).



Figure 5.14: Prior austenite grain size distribution of steel 4 with different austenitisation times at 1250°C and subsequent quenching to room temperature, with prior austenite grain boundaries revealed by thermal etching.



Figure 5.15: Average prior austenite grain size for steels 1-4 as a function of austenitisation time at 1250°C. The error bar indicates the standard deviation of all the measured grains in the sample.

Table 5.1: Average prior austenite grain size after various austenitisation times a	t
1250°C for steels 1-4 ( $\mu$ m). The error bar indicates the standard deviation of all th	е
measured grains in the sample.	

Holding times at 1250°C (s)	Steel 1	Steel 2	Steel 3	Steel 4
30	102.6 <u>+</u> 41.4	60.9 <u>+</u> 22.3	54.6 <u>+</u> 21.6	47.8 <u>+</u> 21.2
60	110.2 <u>+</u> 48.6	76.7 <u>+</u> 30.4	61.9 <u>+</u> 23.9	65.1 <u>+</u> 26.1
300	137.6 <u>+</u> 60.3	100.8 <u>+</u> 38.7	80.5 <u>+</u> 33.8	91.4 <u>+</u> 33.3

## 5.4 Effect of Nb(C,N) particles on austenite grain growth

Nb has two typical forms in steels, i.e. solute Nb atoms and Nb(C,N) precipitates. The effect of solute Nb atoms on austenite grain growth at 1250°C has been studied and discussion in the previous section. However, Nb normally precipitates as Nb(C,N) particles during hot rolling, and thus its effect on austenite grain growth needs to be studied. In order to study the effect of Nb(C,N), samples of steels with different Nb contents were austenitised at 1000°C for various times, and then quenched to room temperature.

According to the thermodynamic calculations in Chapter 4, Nb(C,N) dissolution temperatures for steels 3 and 6 are 1091°C and 1120°C, respectively. At 1000°C the pre-existing Nb(C,N) particles in steels 3 and 6 have not been dissolved, which has been proved by the FEGSEM images with the related EDX spectra in Figure 5.16, where white spots are pre-existing NbC particles.



Figure 5.16: FEGSEM images of steels 3 and 6 with 10 minutes holding at 1000°C under backscatter mode, with the related EDX spectra. White particles in the images are pre-existing NbC particles.

From the coloured grain images of steel 1 shown in Figure 5.17, it can be observed that the sample with 10 minutes holding at 1000°C has a larger average grain size than the 5 minutes holding sample, and there is little coarsening from 10 minutes to 1 hour holding at 1000°C, as shown by the grain size distribution plots shown in Figure 5.18. For steel 3, the grains are much finer after 5 minutes or 10 minutes holding at 1000°C, but there is a significant coarsening after 30 minutes holding, as shown in Figure 5.19. From the grain size distribution plots shown in Figure 5.20, it

can be seen that the number fraction of grains has increased after a size of 40  $\mu$ m for the samples with 30 minutes holding and 1 hour holding. From Figure 5.21, steel 6 has a significant grain coarsening after 10 minutes holding at 1000°C, and the sample with 1 hour holding at 1000°C has a similar grain size distribution to the 10 minutes holding sample as shown in Figure 5.22. The austenite grain growth against holding time at 1000°C for steels 1, 3 and 6 are plotted in Figure 5.23, and the average prior austenite grain sizes are listed in Table 5.2. Steel 1 always has a much larger average grain size than steels 3 and 6. The difference in the austenite grain growth rate at 1000°C between a Nb-free steel (steel 1) and Nb containing steels (steels 3 and 6) are likely to be caused by the presence of NbC particles.



Figure 5.17: Grain size characterisation for steel 1 after 300 seconds, 600 seconds, 1800 seconds, and 3600 seconds holding at 1000°C. Different colours of grains indicate the grain size ranges (unit: μm).



Figure 5.18: Prior austenite grain size distribution of steel 1 with different austenitisation times at 1000°C.



Figure 5.19: Grain size characterisation for steel 3 after 300 seconds, 600 seconds, 1800 seconds, and 3600 seconds holding at 1000°C. Different colours of grains indicate the grain size ranges (unit: μm).



Figure 5.20: Prior austenite grain size distribution of steel 3 with different austenitisation times at 1000°C.







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Figure 5.21: Grain size characterisation for steel 6 after 300 seconds, 600 seconds, and 3600 seconds holding at 1000°C. Different colours of grains indicate the grain size ranges (unit: μm).



Figure 5.22: Prior austenite grain size distribution of steel 6 with different austenitisation times at 1000°C.



Figure 5.23: Prior austenite grain growth against austenitisation times at 1000°C for steels with different Nb contents. The error bar indicates the standard deviation of all the measured grains in the sample.

Table 5.2: Average prior austenite grain size for steels 1, 3, and 6 after various times austenitisation at 1000°C (unit:  $\mu$ m). The error bar indicates the standard deviation of all the measured grains in the sample.

	0	•	
Austenitisation times at 1000°C (s)	Steel 1	Steel 3	Steel 6
300	33.2 <u>+</u> 16.8	13.4 <u>+</u> 5.7	11.0 <u>+</u> 4.5
600	45.5 <u>+</u> 24.9	13.1 <u>+</u> 6.2	18.7 <u>+</u> 9.7
1800	48.6 <u>+</u> 26.1	17.7 <u>+</u> 10.6	19.9 <u>+</u> 13.5
3600	53.7 <u>+</u> 33.8	23.5 <u>+</u> 13.1	20.8 <u>+</u> 11.7

With increasing the austenitisation temperatures from 1000°C to 1250°C, the preexisting Nb(C,N) particles will be more and more dissolved, and thus the austenite grain coarsening behaviour will be affected due to the different forms of Nb. Coloured grain images of steels 1, 2, 3 and 6 with 5 minutes holding at 1100°C are shown in Figure 5.24, and their grain size distribution plots are shown in Figure 5.25. It can be clearly observed that steel 6 with the 0.067 wt. % Nb has the smallest average grain size after 300 seconds holding at 1100°C from all of these samples, and steel 3 with 0.028 wt. % Nb has a similar level of grain size, but steel 1 which is Nb free has the largest average grain size. After 5 minutes holding at 1200°C, steels 1, 2 and 6 all seem to have a similar grain size distribution, however, steel 3 has an even smaller average grain size than steel 6, as shown in Figures 5.26 and 5.27. At 1250°C, steel 3 still has the smallest average grain size, but steel 1 has the largest average grain size, as shown in Figures 5.28 and 5.29. The overall average prior austenite grain growth against temperature from 1000°C to 1250°C for steels 1, 2, 3 and 6 are shown in Figure 5.30, and their values are listed in Table 5.3. It can be found that steel 3 always has a low level of average grain size, and steel 1 always has the largest average grain size, with steel 2 always having a value in between them. The average grain size for steel 6 is as small as that of steel 3 at 1000°C and 1100°C, but it increases to the same level as steel 2 after 1200°C. From Figure 5.31, this indicates that 5 minutes is not long enough to allow all of the NbC particles to dissolve at 1200°C. However, no NbC particles can be observed after 5 minutes holding at 1250°C of steel 3. These results indicate that the fine grain size in steel 3 at all these temperatures is caused by NbC particles and solute Nb atoms. Although steel 6 has a much higher Nb content than steel 3, its average grain size is much larger than that of steel 3 at 1200°C and 1250°C. A possible reason is that NbC particles have not been fully dissolved in steel 6 even at 1250°C, and the undissolved NbC particles have a reduced retardation effect on austenite grain coarsening than solute Nb atoms. From the FEGSEM images, there are a lot of NbC particles left un-dissolved in steel 6 after 5 minutes holding at 1250°C, as shown in Figure 5.32. Although thermodynamic calculation results indicate that the Nb(C,N) dissolution temperature of steel 6 should be 1220°C, the 5 minutes holding may not be long enough to dissolve all the NbC particles. It also indicates that the retardation effect on austenite grain growth caused by the solute Nb atoms is stronger than that caused by the NbC particles. In addition, from the FEGSEM images shown in Figure

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5.16, it seems that the NbC particles are quite large, so that it may only affect a few grains.



Figure 5.24: Grain size characterisation for steels 1, 2, 3 and 6 after 300 seconds holding at 1100°C. Different colours of grains indicate the grain size ranges (unit: µm).



Figure 5.25: Prior austenite grain size distribution of steels 1, 2, 3 and 6 with 300 seconds austenitisation at 1100°C.



Figure 5.26: Grain size characterisation for steels 1, 2, 3 and 6 after 300 seconds holding at 1200<sup>o</sup>C. Different colours of grains indicate the grain size ranges (unit: μm).



Figure 5.27: Prior austenite grain size distribution of steels 1, 2, 3 and 6 with 300 seconds austenitisation at 1200°C.



Figure 5.28: Grain size characterisation for steels 1, 2, 3 and 6 after 300 seconds holding at 1250°C. Different colours of grains indicate the grain size ranges (unit: μm).







Figure 5.30: Prior austenite grain growth against temperature for steels 1, 2, 3 and 6.

Table 5.3: Average prior austenite grain size of steels 1, 2, 3 and 6 after 5 minutes
austenitisation at different temperatures (unit: μm).

Austenitisation temperature	Steel 1	Steel 2	Steel 3	Steel 6
1000°C	33.2	21.1	13.4	11.0
1100°C	47.4	38.7	31.5	31.3
1200°C	67.5	65.2	49.5	63.5
1250°C	109.8	108.6	80.5	109.4



Figure 5.31: FEGSEM image of steel 3 with 5 minutes holding at 1200°C under backscatter mode, with the related EDX spectrum. White particles in the images are NbC particles.



Figure 5.32: FEGSEM images of steel 6 with 5 minutes holding at 1250°C under backscatter mode, with the related EDX spectra. White particles in the images are NbC particles.

## 5.5 Effect of Nb on ferrite grain size

Ferrite grain size is a very important factor in influencing the mechanical properties of steel products. In industry, Nb is known to have a refinement effect on ferrite grain size. However, the mechanism of the refinement effect has not yet been fully characterised. The ferrite grain size is largely affected by the prior austenite grain size, and therefore the effect of prior austenite grain size should be isolated in order to accurately study the effect of Nb on ferrite grain size. Solute Nb atoms and NbC particles are expected to have different levels of retardation effects on austenite grain growth, therefore their effects on ferrite grain size should also be studied separately.

Steel 1 which is Nb free and steel 3 with 0.028 wt. % Nb have been used to study the effect of Nb on ferrite grain size. From the austenite grain size study shown in

Figure 5.30, steel 1 with 5 minutes holding at 1000°C has an average austenite grain size of approximately 33 µm, and steel 3 with 5 minutes holding at 1100°C has an average austenite grain size of approximately 32 µm. Therefore, the average prior austenite grain sizes of steels 1 and 3 can be controlled to similar values after 5 minutes austenitisation at 1000°C for steel 1 and 5 minutes austenitisation at 1100°C for steel 3, and then the effect of prior austenite grain size can be isolated. Both the samples subsequently underwent an isothermal transformation at 750°C, and the optical micrographs and the coloured grain images are shown in Figure 5.33. The ferrite grain size distribution plots are shown in Figure 5.34. It is calculated that the sample of steel 1 has an average ferrite grain size of 17.5 µm, which is slightly larger than the sample of steel 3 with an average ferrite grain size of 14.6 µm. The ferrite grain sizes of the two samples have also been compared after a continuous cooling at 0.5°Cs<sup>-1</sup>. The optical micrographs and the coloured grain images are shown in Figure 5.35, and the ferrite grain size distribution plots are shown in Figure 5.36. It is calculated that the sample of steel 1 has an average ferrite grain size of 14.2 µm, which is slightly smaller than the sample of steel 3 with an average ferrite grain size of 15.1 µm. From both the isothermal transformation and continuous cooling results, there is not much difference in the resulting ferrite grain size between the Nb free steel and the Nb containing steel. During austenitisation at 1100°C, Nb in steel 3 is mostly in NbC form, which is illustrated by Figure 5.31, where NbC particles have not yet been fully dissolved after 5 minutes holding at 1200°C. Therefore, it can be concluded that NbC has little refinement effect on the ferrite grain size during transformation from austenite to ferrite.

The refinement effect of solute Nb atoms on ferrite grain size during transformation from austenite to ferrite can be studied using steel 1 and steel 3 with austenitisation at 1250°C. From the austenite grain size study shown in Figure 5.15, 5 seconds holding at 1250°C for steel 1 results in an average austenite grain size of ~83  $\mu$ m, which is quite similar to the value of steel 3 with 300 seconds holding at 1250°C. Both the samples also underwent an isothermal transformation at 750°C and a continuous cooling at 0.5°Cs<sup>-1</sup>. The optical micrographs and the coloured grain images are shown in Figures 5.37 and 5.39, respectively. The ferrite grain size distribution plots are shown in Figures 5.38 and 5.40, respectively. For the

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isothermally transformed samples, it is calculated that the sample of steel 1 has an average ferrite grain size of 21.2 µm, and the sample of steel 3 has an average ferrite grain size of 20.8 µm. For the continuous cooled samples, their average ferrite grain sizes are 20.8 µm and 19.5 µm. All of these ferrite grain size results are listed in Table 5.4. It can therefore be concluded that both NbC particles and solute Nb atoms have little refinement effect on ferrite during transformation from austenite to ferrite. However, Nb can still have an indirect refinement effect on the ferrite grain size by delaying the prior austenite grain growth. This conclusion can also be supported by the ferrite grain size measurement for Nb containing steels with different holding times at 900°C before isothermal transformations. According to the thermodynamic calculation results, holding at 900°C can make solute Nb atoms precipitate as NbC particles. The amount of remaining solute Nb atoms is varied with different holding times at 900°C. Coloured grain images of samples of steel 3, which were austenitised at 1250°C for 300 seconds, then held at 900°C for 0 seconds, 1200 seconds, 2400 seconds, or 3600 seconds before isothermal transformation at 750°C, are shown in Figure 5.41. Ferrite grain size distribution plots are shown in Figure 5.42. These results show that samples with no holding at 900°C or 1 hour holding at 900°C exhibit little difference in the ferrite grain size distribution. Nb atoms in the sample without holding at 900°C are all solute Nb atoms at the beginning of the isothermal transformation at 750°C, but Nb atoms are mostly precipitated as NbC particles after 1 hour holding at 900°C [30]. Therefore, it would appear that the form of Nb in samples before transformation has little influence on the transformed ferrite grain size.



Figure 5.33: Optical micrographs and the related coloured grain images of steel 1 with 5 minutes austenitisation at 1000°C and then isothermally transformed at 750°C for 15 minutes, and steel 3 with 5 minutes austenitisation at 1100°C and then isothermally transformed at 750°C (unit: µm).



Figure 5.34: Ferrite grain size distribution of steel 1 with 5 minutes austenitisation at 1000°C and then isothermally transformed at 750°C for 15 minutes, and steel 3 with 5 minutes austenitisation at 1100°C and then isothermally transformed at 750°C.



Figure 5.35: Optical micrographs and coloured grain images of steel 1 with 5 minutes austenitisation at 1000°C and then followed by continuous cooling at 0.5°Cs<sup>-1</sup>, and steel 3 with 5 minutes austenitisation at 1100°C and then followed by continuous cooling at 0.5°Cs<sup>-1</sup> (unit: μm).



Figure 5.36: Ferrite grain size distribution of steel 1 with 5 minutes holding at 1000°C and then followed by continuous cooling at 0.5°Cs<sup>-1</sup>, and steel 3 with 5 minutes austenitisation at 1100°C and then followed by continuous cooling at 0.5°C s<sup>-1</sup>.





3-1250°C300s-750°C900s

Figure 5.37: Optical micrographs and coloured grain images of steel 1 with 5 seconds holding at 1250°C and then isothermally transformed at 750°C, and steel 3 with 5 minutes holding at 1250°C and then isothermally transformed at 750°C (unit: μm).



Figure 5.38: Ferrite grain size distribution of steel 1 with 5 seconds austenitisation at 1250°C and then isothermally transformed at 750°C, and steel 3 with 5 minutes austenitisation at 1250°C and then isothermally transformed at 750°C.



1-1250°C5s-0.5ºCs<sup>-1</sup>



Figure 5.39: Optical micrographs and coloured grain images of steel 1 with 5 seconds austenitisation at 1250°C and then followed by continuous cooling at 0.5°Cs<sup>-1</sup>, and steel 3 with 5 minutes austenitisation at 1250°C and then followed by continuous cooling at 0.5°Cs<sup>-1</sup> (unit: µm).



Figure 5.40: Ferrite grain size distribution of steel 1 with 5 seconds austenitisation at 1250°C and then followed by continuous cooling at 0.5°Cs<sup>-1</sup>, and steel 3 with 5 minutes austenitisation at 1250°C and then followed by continuous cooling at 0.5°Cs<sup>-1</sup>.

Sample	Average ferrite grain size	Sample	Average ferrite grain size
1-1000°C300s- 750°C900s	17.5	3-1100°C300s- 750°C900s	14.6
1-1000°C300s- 0.5°Cs⁻¹	14.2	3-1100°C300s- 0.5°Cs⁻¹	15.1
1-1250°C5s- 750°C900s	21.2	3-1250°C300s- 750°C900s	20.8
1-1250°C5s- 0.5°Cs⁻¹	20.8	3-1250°C300s- 0.5°Cs⁻¹	19.5

Table 5.4: Ferrite grain size of steels 1 and 3 after different heat treatment (unit: µm)



Figure 5.41: Coloured grain images of steel 3 with no holding, 20 minutes holding, 40 minutes holding or 1 hour holding at 900°C, and then isothermally transformed at 750°C (unit: μm).



Figure 5.42: Ferrite grain size distribution of steel 3 with no holding, 20 minutes holding, 40 minutes holding or 1 hour holding at 900°C, and then isothermally transformed at 750°C.

## 5.6 Discussion

Nb is widely added to steel for its grain size refinement effect. From the current work, it has been shown that Nb has a retardation effect on austenite grain growth above 1000°C, irrespective of whether the Nb is in the form of solute atoms or NbC precipitates. From literature, it is believed that NbC particles can delay austenite grain growth via a particle pining effect [81, 82, 83, 84], and solute Nb atoms can delay austenite grain growth via a solute drag effect [74]. However, the Nb contents in the steels used in this research are relatively low (all less than 0.07 wt. %), and therefore the amount of NbC particles present may not be sufficient to apply a strong particle pinning effect. This is supported by the long distances observed between each NbC particle, as shown in the FEGSEM images in Figures 5.2, and 5.31.

The retardation effect caused by Nb should generally increase with Nb content, as is the case between steels 1-3 which have progressively increasing Nb contents. However, steel 6 has the smallest austenite grain size at 1000°C, but its austenite grain size is much larger than steel 3 at 1250°C. This is possibly because steel 6 has a much higher Nb content than the steels 1-4, and thus its Nb(C,N) dissolution temperature is much higher. At both 1000°C and 1100°C, few NbC precipitates have been dissolved in both steel 3 and steel 6. However, steel 6, which has a higher Nb content, therefore has more NbC particles, and thus the average prior austenite grain size of steel 6 is slightly smaller than that of steel 3. At 1200°C, many NbC particles in steel 3 are dissolved with only a few of them left, but it is still below the Nb(C,N) dissolution temperature of steel 6, and there are still a lot of Nb(C,N) particles in steel 6. As a result, the larger amount of solute Nb atoms in steel 3 makes its average prior austenite grain size smaller than steel 6. The same thing also happens at 1250°C. At 1250°C, NbC particles are fully dissolved in steel 3, but only a few of them are dissolved in 5 minutes in steel 6. These results indicate that the solute Nb atoms have a stronger retardation effect than the Nb(C,N) particles in these steels.

From the austenite grain size measurements, the prior austenite grain size before transformation from austenite to ferrite is largely dependent on the austenitisation temperature, holding time at the temperature, and the alloying elements. In order to eliminate the effect of prior austenite grain size on the subsequent transformation to ferrite, the austenitisation time can be adjusted to make the prior austenite grain size of all samples a similar value before the transformation. After continuous cooling at a slow cooling rate, or a sufficient time in the case of isothermal transformation, samples with different Nb contents but the same prior austenite grain size have a similar ferrite grain size. Although Nb has little refinement effect on the ferrite grain size still has an indirect refinement effect on ferrite grain size. The effects of Nb on transformation kinetics and its effect on different transformation products will be discussed in more detail in the next chapter.

In this research, the newly developed 'Grain boundary tracing technique' has been applied for the grain size measurement, and is capable of producing coloured images which are able to provide both a visual representation and quantification of the grain size distribution. The linear intercept method is typically used for grain size measurement. Although it is simple and fast, it cannot describe the grain size distribution but can only give an average grain size. The accuracy of the linear intercept is largely dependent on how many lines are drawn in each micrograph. In addition, the linear intercept method becomes very difficult and complex if there is more than one phase in a micrograph. The grain boundary tracing technique can not only measure the grain size of each phase, but also measure the phase fraction of samples.

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Electron back scatter diffraction (EBSD) is another technique which can be used for grain size measurement. EBSD can also describe the grain size distribution plot of each phase. However, the contrast in EBSD is obtained from misorientation angles, and thus it is very difficult to recognise prior austenite grain boundaries from quenched samples. In EBSD, the misorientation angles at grain boundaries are easily confused with the large number of misorientation angles between martensitic laths. Therefore, EBSD can only be used to study the ferrite grain size, an example of which is shown in Figure 5.43. From Figure 5.43, the major differences between the EBSD grains maps and the coloured grain images derived from grain boundary tracing technique are that the diameter of each grain is not shown with colours in the unique grains map, and the grains at edge of the image which are not fully displayed in the image are still involved in the calculation. The ferrite grain size distribution plots from the grain boundary tracing technique and from EBSD are compared in Figures 5.44 and 5.45. It can be found that the ferrite grain size distribution plots are generally consistent, but the distribution curves from EBSD are slightly wider than those from the tracing technique. However, an EBSD sample takes much longer time to prepare and scan, and its scanning area is normally smaller than the optical micrograph using in the tracing technique.



Figure 5.43: EBSD results for the sample 3-1250°C300s-900°C1200s-750°C900: (a) unique grain map, colours do not indicate grain size; and (b) Grain boundary map.



Figure 5.44: Comparison of ferrite grain size distribution plots from the grain boundary tracing technique and from EBSD for the sample 3-1250°C300s-900°C1200s-750°C900s.



Figure 5.45: Comparison of ferrite grains size distribution plots from grain boundary tracing technique and from EBSD for the sample 3-1250°C300s-900°C2400s-750°C900s.

## 5.7 Summary

In this chapter, the influence of grain size on phase transformations has been discussed. A newly developed technique, the 'Grain boundary tracing technique', has been proven to be a good method to accurately measure both prior austenite grain size and ferrite grain size. From the results, both solute Nb atoms and NbC

particles can apply a retardation effect on austenite grain growth. In these steels, solute Nb atoms appear to have a stronger retardation effect on austenite grain growth than NbC particles. The prior austenite grain sizes for steels with different niobium contents have been adjusted to a consistent value by changing the austenitisation time, which has allowed the effect of the austenite grain size on the subsequent transformation to be eliminated. For samples with different Nb contents but the same prior austenite grain size, their ferrite grain sizes after the same transformation have been found to be quite similar. Therefore, it appears that the Nb can only indirectly refine the ferrite grain size by delaying prior austenite grain growth. In the following chapter, steels with the same austenite grain size but with different niobium contents will be subjected to various heat treatments to study the effects of niobium on phase transformation kinetics in detail.

# 6 Effect of Nb on transformation kinetics from austenite to ferrite

## 6.1 Introduction

It is widely believed that Nb plays an important role in the phase transformation kinetics in steels. However, the effects of solute Nb atoms and Nb(C,N) precipitates on transformation kinetics have not yet been fully characterised. This chapter presents and discusses the results concerning both isothermal transformations and continuous cooling of steels with systematically different Nb contents. The phase transformation kinetics have been investigated by dilatometry, and the microstructure has been studied by optical microscopy, FEG-SEM, and TEM. Isothermal transformations were also interrupted at various times to study the transformation rate in detail. Steels with the same average prior austenite grain size but different Nb contents were subjected to isothermal transformations, and continuous cooling to analyse the effects of solute niobium atoms. In addition, steels were also subjected to another holding at 900°C for precipitates. The results are then analysed and discussed with a view to highlighting the influence of both solute Nb atoms and Nb(C,N) precipitates on phase transformations in these steels

## 6.2 Effect of prior austenite grain size on transformation behaviours

The transformation kinetics from austenite to ferrite are affected by both alloying elements and prior austenite grain size. From the previous chapter, the prior austenite grain size is affected by the austenitisation time and temperature. In order to study the effect of prior austenite grain size on the subsequent isothermal transformation, samples of steel 1 with different austenitisation times at 1250°C were then isothermally transformed at 750°C and 700°C, which are typical isothermal transformations temperature to obtain polygonal ferrite. The transformation kinetic curves are plotted in Figures 6.1 and 6.2. The kinetic data including t0.1%, t5%, and t50% during the isothermal transformations for samples are listed in Tables 6.1 and 6.2. From the transformation kinetics curves, it can be found that the isothermal transformation becomes slower with increasing austenitisation times at 1250°C. From the tables, there is little difference in the transformation start time (t0.1%)

between samples, but the time for 50% transformation of the samples generally increases with the austenitisation time. Steel 1 is Nb free, and thus the only factor which affects the transformation kinetics is the prior austenite grain size. From austenite grain growth study in Chapter 5, it indicates that the prior austenite grain size increases with increasing austenitisation times at 1250°C. Therefore, the isothermal transformation becomes slower if the prior austenite grain size is larger. Optical micrographs of steel 1 isothermally transformed at 700°C or 750°C are shown in Figure 6.3. From the micrographs, it can be observed that samples with lower austenitisation times have much smaller ferrite grain size and pearlite grain size, but the total amount of transformed ferrite is quite similar. However, after a long enough transformation time, all the samples achieve a similar level of final ferrite fraction. Since the prior austenite grain size has important influences on the subsequent transformation kinetics and the final ferrite grain size, it should be controlled to a consistent value to eliminate the effect, and then effects of Nb on transformation behaviours can be isolated and studied.



Figure 6.1: Isothermal transformation kinetics at 700°C of steel 1 with different austenitisation times at 1250°C.



Figure 6.2: Isothermal transformation kinetics at 750°C of steel 1 with different austenitisation times at 1250°C.

Table 6.1: Kinetics of isothermal transformation at 700°C for steel 1 with different	
austenitisation times at 1250°C (unit: seconds)	
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Austenitisation times at 1250°C	Time for 0.1% transformed (t0.1%)	Time for 5% transformed (t5%)	Time for 50% transformed (50%)
5	2.6	5.8	33.6
30	1.7	4.4	33.7
60	3.5	7.7	37.3
120	5.8	11.5	42.7
180	4.6	8.7	49
300	6.7	14.6	101

Austenitisation times at 1250°C	Time for 0.1% transformed (t0.1%)	Time for 5% transformed (t5%)	Time for 50% transformed (50%)
5	3.5	10.6	104
30	4.0	10.3	115
60	4.0	8.5	163
120	2.6	12.7	192
180	2.2	6.7	180

Table 6.2: Kinetics of isothermal transformation at 750°C for steel 1 with different austenitisation times at 1250°C (unit: seconds)





1-1250°C180s-750°C900s



## 6.3 Effects of solute niobium atoms on isothermal transformation

In order to study the effect of solute Nb atoms on transformation kinetics, steels 1-3 with similar chemical compositions except for the Nb content were heated to 1250°C to ensure all pre-existing Nb(C,N) precipitates were fully dissolved. The austenitisation times were carefully chosen according to the prior austenite grain growth study from Chapter 5. After 5 seconds austenitisation at 1250°C for steel 1, 1 minute austenitisation at 1250°C for steel 2, or 5 minutes austenitisation at 1250°C for steel 3, all of these samples have an average prior austenite grain size of ~80  $\mu$ m. Therefore, the subsequent isothermal transformation is only affected by solute Nb atoms.

The transformation kinetics curves of steels 1-3 during isothermal transformation at 750°C are plotted in Figure 6.4. It can be clearly observed that steel 3 with 0.028 wt. % Nb has the slowest transformation kinetics, and steel 1 with no Nb has the fastest transformation kinetics in the steels. Steel 4 is not included, because according to the dilatometry results, few ferrite has been formed during 15 minutes holding at 750°C for steel 4. Optical micrographs of steels 1-4 with the same prior austenite grain size and then isothermally transformed at 750°C are shown in Figure 6.5. It can be seen that steels 1-3 have a similar microstructure of ferrite and martensite. After isothermal transformation at 750°C, most of austenite was transformed to ferrite. However, since 750°C is above the A<sub>1</sub> temperature, some untransformed austenite remained during holding, and was subsequently transformed to martensite during quenching from 750°C to room temperature. From the optical micrograph of steel 4, it can be seen that it is mostly martensite, and therefore underwent little transformation from austenite to ferrite during holding at 750°C. This phenomenon conflicts with the thermodynamic calculation results from MTDATA and ThermoCalc, which indicate that the A<sub>e3</sub> temperature of steel 4 is 818°C. However, from CamModel calculation, the paraequilibrium A<sub>3</sub> temperature of steel 4 is only 788°C, which is slightly higher than the isothermally holding temperature, and thus it indicates that only a few of austenite can transform to ferrite during the isothermal transformation. Steel 4 has a high Nb content and a high C content, both of which may delay the transformation kinetics, and thus few ferrite can be observed after 15 minutes holding at 750°C.

The transformation kinetics curves of steels 1-4 during isothermal transformation at 725°C are plotted in Figure 6.6. It can be clearly observed that steel 1 with no Nb has the fastest transformation kinetics in the steels, and steel 3 has much slower transformation kinetics than steels 1 and 2. However, steel 4 with a similar Nb content but double the carbon content of steel 3, has much slower transformation kinetics and a much lower ferrite fraction. Optical micrographs of these samples are shown in Figure 6.7. It can be seen that the ferrite fraction in steel 3 is slightly less than those in steels 1 and 2, but steel 4 has the least ferrite fraction due to its high carbon content.

The transformation kinetics curves of steels 1-4 during isothermal transformation at 700°C are plotted in Figure 6.8. It has a similar trend to the transformation at 725°C, in which steel 1 has the fastest transformation and steel 4 has a much lower transformed fraction to ferrite than other steels. From the optical micrographs shown in Figure 6.9, it can be seen that the pearlite has been formed during isothermal transformation at 700°C in all the steels.

Isothermal transformation at 675°C also results in similar kinetics curves to those at 700°C, as shown in Figure 6.10. The isothermal transformation kinetics becomes slower with increasing Nb content. However, the kinetic curve of steel 1 is not a typical parabolic curve this time, but becomes a straight line at the first tens of seconds and then keeps stable. From the optical micrographs shown in Figure 6.11, displacive transformation products are dominating in steel 1, but there are mainly ferrite and martensite with a few of pearlite in steels 2-4. The displacive transformation is generally much faster than the reconstructive transformation, which is a probable reason to explain the shape of the kinetic curve of steel 1.

When the isothermal transformation temperature reduces to 650°C, the kinetic curve of steel 2 also becomes a straight line as steel 1, as shown in Figure 6.12. It can also be found that steel 1 has a 'stasis' after 90% transformation, and the transformation restarts after tens of seconds. This phenomenon has also been found by Furuhara *et. al* [96] in upper bainite transformation at 580°C and 600°C. From their optical micrographs shown in Figure 6.13, steel 1 and steel 2 have more displacive

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transformation products, but steel 3 and steel 4 are mainly ferrite, pearlite and martensite.



Figure 6.4: Isothermal transformation kinetics at 750°C for steels 1-3 with the same prior austenite grain size. Steel 1 was austenitised at 1250°C for 5 seconds, steel 2 was austenitised at 1250°C for 1 minute, and steel 3 was austenitised at 1250°C for 5 minutes before the isothermal transformation at 750°C.



Steel 3

Steel 4

Figure 6.5: Optical micrographs of steels 1-4 after 15 minutes isothermal transformation at 750°C. Steels 1-4 were austenitised at 1250°C for 5 seconds, 60 seconds, 300 seconds, and 150 seconds, respectively.



Figure 6.6: Isothermal transformation kinetics at 725°C for steels 1-4 with the same prior austenite grain size. Steels 1-4 were austenitised at 1250°C for 5 seconds, 60 seconds, 300 seconds, and 150 seconds, respectively.



Figure 6.7: Optical micrographs of steels 1-4 after 15 minutes isothermal transformation at 725°C. Steels 1-4 were austenitised at 1250°C for 5 seconds, 60 seconds, 300 seconds, and 150 seconds, respectively.



Figure 6.8: Isothermal transformation kinetics at 700°C for steels 1-4 with the same prior austenite grain size. Steels 1-4 were austenitised at 1250°C for 5 seconds, 60 seconds, 300 seconds, and 150 seconds, respectively.



Steel 3

Steel 4

Figure 6.9: Optical micrographs of steels 1-4 after 15 minutes isothermal transformation at 700°C. Steels 1-4 were austenitised at 1250°C for 5 seconds, 60 seconds, 300 seconds, and 150 seconds, respectively.



Figure 6.10: Isothermal transformation kinetics at 675°C for steels 1-4 with the same prior austenite grain size. Steels 1-4 were austenitised at 1250°C for 5 seconds, 60 seconds, 300 seconds, and 150 seconds, respectively.



Figure 6.11: Optical micrographs of steels 1-4 after 15 minutes isothermal transformation at 675°C. Steels 1-4 were austenitised at 1250°C for 5 seconds, 60 seconds, 300 seconds, and 150 seconds, respectively.



Figure 6.12: Isothermal transformation kinetics at 650°C for steels 1-4 with the same prior austenite grain size. Steels 1-4 were austenitised at 1250°C for 5 seconds, 60 seconds, 300 seconds, and 150 seconds, respectively.



Figure 6.13: Optical micrographs of steels 1-4 after 15 minutes isothermal transformation at 650°C. Steels 1-4 were austenitised at 1250°C for 5 seconds, 60 seconds, 300 seconds, and 150 seconds, respectively.

From all of these isothermal transformation results, a steel with a higher Nb content always has slower isothermal transformation kinetics. The steels were all austenitised at 1250°C which is much higher than the Nb(C,N) dissolution temperatures. Therefore the Nb should be in solid solution form at the beginning of the isothermal transformation, and this has been investigated by the TEM carbon extraction replica study on samples guenched directly from 1250°C, in which no Nb(C,N) particles have been observed. However, from a TEM carbon extraction replica study on the isothermally transformed samples from steel 3, there are a lot of Nb(C,N) particles segregated near grain boundaries, as shown in Figure 6.14. These Nb(C,N) particles are quite small, with a typical diameter about 20 nm, which is much smaller than the pre-existing Nb(C,N) particles shown in Chapter 5. It is reasonable to suggest that during the isothermal transformation, solute Nb atoms were initially segregated at grain boundaries where they acted to delay the transformation kinetics, and then precipitated as Nb(C,N) particles which were left near grain boundary during the isothermal transformation. FIB lift out is an advanced technology to prepare a TEM sample of a chosen small area. The Nb contents in steels 1-4 are all less than 0.03 wt. %, and the low amount of Nb makes it difficult to characterise Nb(C,N) particles in a lift out sample. Therefore, steel 5 with a higher Nb content was utilised for Nb(C,N) particle characterisation. Figure 6.15 is the TEM high angle annular dark field (HAADF) image and the related Nb-Ka1 map of a sample from steel 5 with 5 minutes austenitisation at 1250°C to fully dissolve pre-existed Nb(C,N) particles, and then isothermal transformation at 750°C for 15 minutes followed by quenching to room temperature. From Figure 6.15, it can be seen that there are many small Nb-rich particles which are bright spots, and the particles appear to be associated with a high density of dislocations.





Figure 6.14: TEM images and the related EDX spectra of carbon extraction replica samples from steel 3 with 5 minutes austenitisation at 1250°C and then isothermally transformed at 650°C or 700°C for 15 minutes.



HAADF image

· · · ·

Nb map

Figure 6.15: TEM HAADF image and EDX map for Nb Kα1 peak of a FIB lift out sample of steel 5 with 5 minutes austenitisation at 1250°C and then isothermally transformed at 750°C for 15 minutes.

#### 6.4 Interrupted isothermal transformations

A typical isothermal transformation from austenite to ferrite has a sigmoidal transformation kinetic curve. The ferrite nucleation rate and ferrite grain growth rate are the two key factors for the transformation kinetics. In order to accurately study the effect of solute Nb atoms on each rate, the isothermal transformations were interrupted after a certain time and then the samples quenched to room temperature. For each interrupted sample, the ferrite fraction was measured using the grain boundary tracing technique, and the change in length was compared with the final change in length to estimate the transformation progress.

For steel 1, the isothermal transformation at 750°C was interrupted after 10 seconds, 60 seconds, and 120 seconds. The measured ferrite fraction and the transformation progress estimated from the change in length are compared with the dilatometer curve of a fully transformed sample, as shown in Figure 6.16. The transformation kinetics are generally consistent from the different methods. The equilibrium ferrite fraction from the thermodynamic calculation is also plotted in Figure 6.16. The final ferrite fraction is only slightly less than the equilibrium state, which indicates that the transformation is nearly finished. Optical micrographs of the interrupted samples and the fully transformed sample are shown in Figure 6.17. The sample with 10 seconds transformation at 750°C has mostly martensite from quenching, with only a few ferrite grains formed at prior austenite grain boundaries. After 60 seconds transformation at 750°C, more ferrite has been formed at prior austenite grain boundaries, but the centre of prior austenite grains remain untransformed in the short time, and it is transformed to martensite during the subsequent quenching. The ferrite becomes thicker and longer with increasing transformation time. After 120 seconds transformation, there are more ferrite grains formed, and after 900 seconds holding at 750°C, only a small amount of austenite remains untransformed and is quenched to martensite. The ferrite grain size and numbers of grains have also been measured and are listed in Table 6.3. From the table, it can be found the ferrite grain number increases quickly in the first tens of seconds, and the ferrite grain size also grows quickly simultaneously. After that, the ferrite grain size becomes stable, but there is still a slow increase in ferrite grain number. These measured data are consistent with the kinetics curve in Figure 6.16.



Figure 6.16: Interrupted isothermal transformation kinetics for steel 1 with 10 seconds, 60 seconds, 120 seconds, or 900 seconds holding at 750°C. The samples were all austenitised at 1250°C for 5 seconds.



Figure 6.17: Optical micrographs of samples from steel 1 after 10 seconds, 60 seconds, 120 seconds, or 900 seconds interrupted isothermal transformations at 750°C. The samples were all austenitised at 1250°C for 5 seconds.

Holding time (seconds)	Number of grains in one micrograph	Average grain size (μm)	Ferrite fraction
10	178	11.2	0.04
60	206	19.4	0.34
120	226	19.9	0.44
900	257	20.9	0.73

Table 6.3: Ferrite grain growth during isothermal transformations at 750°C for steel 1 with 5 seconds austenitisation at 1250°C.

For steel 2 with 0.009 wt. % Nb and 60 seconds austenitisation at 1250°C, the isothermal transformation at 750°C was also interrupted after 10 seconds, 60 seconds and 120 seconds. The measured transformed fraction and the transformation progress estimated from change in length are compared with the dilatometer curve of a fully transformed sample, as shown in Figure 6.18. The data are generally consistent in these samples. Optical micrographs of the samples are shown in Figure 6.19, and the number of ferrite grains and ferrite grain size data are listed in Table 6.4. There is little ferrite formed in 10 seconds. After 60 seconds, a few ferrite grains have been formed at prior austenite grain boundaries. After 120 seconds, both the number of grains and the ferrite grain size continue to increase. The ferrite grain size has reached a similar level of the final ferrite grain size, but much more ferrite grains will be nucleated later. Comparing with the interrupted samples of steel 1 with the same average prior austenite grain size, it is clear that the interrupted transformed samples of steel 2 always have less ferrite fraction than samples of steel 1 after the same transformation time, and samples from steel 2 have less ferrite grains and a smaller average ferrite grain size than samples from steel 1 after 10 seconds, 60 seconds and 120 seconds holding at 750°C. Since the only difference between steel 1 and steel 2 is the Nb content, it can be concluded that solute Nb atoms have a retardation effect on both the ferrite nucleation rate and the ferrite grain growth rate.



Figure 6.18: Interrupted isothermal transformation kinetics for steel 2 with 10 seconds, 60 seconds, 120 seconds, or 900 seconds holding at 750°C. The samples were all austenitised at 1250°C for 60 seconds.



120 seconds

900 seconds



Holding time (seconds)	Number of grains in one micrograph	Average grain size (μm)	Ferrite fraction
10	77	8.3	0.012
60	125	15.3	0.147
120	164	19.4	0.323
900	280	20.7	0.721

Table 6.4: Ferrite grain growth during isothermal transformations at 750°C for steel 2 with 60 seconds austenitisation at 1250°C.

For steel 3 with 0.028 wt. % Nb, the isothermal transformation at 750°C was interrupted after 10 seconds, 60 seconds, 120 seconds and 180 seconds, as shown in Figure 6.20, and the optical micrographs are shown in Figure 6.21. It was noticed that the isothermal transformation was quite slow in the first 60 seconds. There is little ferrite presented in the 10 seconds sample and the 60 seconds sample. The FEGSEM images in Figures 6.22 and 6.23 clearly show that ferrite grains are firstly nucleated at prior austenite grain boundaries, and become longer and thicker simultaneously. In addition, more ferrite grains are nucleated with increasing holding time. The ferrite grains measurement data are listed in Table 6.5. It can be seen that both the number of ferrite grains and ferrite grain size are smaller than those of steel 2 after the same holding time. The ferrite grain growth in steel 2 has nearly finished after about 120 seconds transformation, but it takes steel 3 about 180 seconds to finish the ferrite grain growth. When the ferrite grain size achieves a similar level of the final ferrite grain growth, the transformation is still in progress, and more ferrite grains will be formed to increase the total ferrite fraction, but the average ferrite grain size remains constant.

The ferrite grain growth against isothermal transformation time at 750°C for the steels are plotted in Figure 6.24, and the number of ferrite grains against the transformation time for the steels are plotted in Figure 6.25. Steel 1 which is Nb free,

has the fastest ferrite grain growth rate and the ferrite nucleation rate. Steel 3 with 0.029 wt. % Nb has the slowest ferrite grain growth rate and the nucleation rate.

In order to study the mechanism of the retardation effect caused by solute Nb atoms, the interrupted transformed samples of steel 3 were characterised using TEM. Figures 6.26 and 6.27 are TEM images and related EDX spectra for carbon extraction replica samples of steel 3 with 60 seconds isothermal transformation at 750°C. From the TEM images in Figure 6.26, there are many Nb(C,N) particles segregated at grain boundaries. For some grain boundaries, Nb(C,N) particles distribute at both sides, but for some other grain boundaries, they only distribute at one side. However, most other grain boundaries have no Nb(C,N) particles presented, as shown in Figure 6.27. These TEM images indicate that solute Nb atoms prefer to segregate at grain boundaries during the isothermal transformation. This phenomenon is consistent with the solute drag theory [32, 73, 77]. The segregated Nb atoms have a low diffusion coefficient, and thus the mobility of the interface is decreased. In the carbon extraction replica technique, the matrix has been etched, with only precipitates left on the carbon film, therefore the amount of the precipitates is possibly more than its real value. In order to do a more accurate characterisation, a small area across a ferrite/martensite grain boundary was lifted out using FIB, and the microstructure was analysed using TEM under HAADF mode, as shown in Figure 6.28. From Figure 6.28, no obvious Nb(C,N) particles can be seen in the grain boundary. EDX maps of grain boundaries are shown in Figures 6.29 and 6.30, and there is no obvious signal of Nb in the maps. The Nb content is only 0.028 wt. % in the steel 3, and thus it is extremely difficult to distinguish the signal of solute Nb atoms from background on an EDX spectrum. Under current TEM technique, Nb can only be observed when it is precipitated as Nb(C,N) particles. The TEM images indicate that only a few of solute Nb atoms have been precipitated after 60 seconds holding at 750°C, and thus the solute drag effect continues to work on the transformation kinetics in the next few minutes.



Figure 6.20: Interrupted isothermal transformation kinetics for steel 3 with 10 seconds, 60 seconds, 120 seconds, or 900 seconds holding at 750°C. The samples were all austenitised at 1250°C for 300 seconds.



Figure 6.21: Optical micrographs of samples after interrupted isothermal transformation for steel 3 after 10 seconds, 60 seconds, 120 seconds, or 900 seconds holding at 750°C. The samples were all austenitised at 1250°C for 300 seconds.



Figure 6.22: FEGSEM images using the InLens mode for steel 3 with 10 seconds interrupted isothermal transformation at 750°C.



Figure 6.23: FEGSEM images using the InLens mode for steel 3 with 60 seconds interrupted isothermal transformation at 750°C.

Holding time (seconds)	Number of grains in one micrograph	Average grain size (µm)	Ferrite fraction
10	26	7.9	0.01
60	128	10.5	0.05
120	143	14.8	0.15
180	195	20.4	0.42
900	280	20.7	0.72

Table 6.5: Ferrite grain growth during isothermal transformation at 750°C for steel 3 with 300 seconds austenitisation at 1250°C.



Figure 6.24: Ferrite grain growth during isothermal transformation at 750°C for steels 1-3. Steel 1 was austenitised at 1250°C for 5 seconds, steel 2 was austenitised at 1250°C for 60 seconds, and steel 3 was austenitised at 1250°C for 300 seconds.



Figure 6.25: Increase of ferrite grains number during isothermal transformation at 750°C for steels 1-3. Steel 1 was austenitised at 1250°C for 5 seconds, steel 2 was austenitised at 1250°C for 60 seconds, and steel 3 was austenitised at 1250°C for 300 seconds.



Figure 6.26: TEM images and the related EDX spectrum for carbon extraction replica samples of steel 3 with 300 seconds austenitisation at 1250°C and then isothermally transformed at 750°C for 60 seconds. Many tiny NbC particles are found in some grain boundaries.



Figure 6.27: TEM images for carbon extraction replica samples of steel 3 with 300 seconds austenitisation at 1250°C and then isothermally transformed at 750°C for 60 seconds. Many grain boundaries have few Nb precipitates.



Figure 6.28: HAADF TEM images for the lift out sample of steel 3 with 300 seconds austenitisation at 1250°C and then isothermally transformed at 750°C for 60 seconds, no obvious NbC particles can be found at the grain boundaries.







Mn Ka1



Figure 6.29: TEM EDX Map for a FIB lift out ferrite/martensite interface of steel 3 with 300 seconds austenitisation at 1250°C and then isothermally transformed at 750°C for 60 seconds.





Figure 6.30: TEM EDX Map for a FIB lift out ferrite/martensite interface of steel 3 with 300 seconds austenitisation at 1250°C and then isothermally transformed at 750°C for 60 seconds.

The sample of steel 3 with 180 seconds isothermal transformation at 750°C was also characterised using TEM to study the Nb(C,N) particles distribution. From the TEM carbon extraction replica images shown in Figure 6.31, it is clear that many small Nb(C,N) precipitates which are only a few nanometres in diameter, segregate around grain boundaries. The particle size and the segregation can be more clearly observed in high magnification TEM images and the related EDX spectra are shown in Figure 6.32. After 180 seconds isothermal transformation, many grain boundaries are associated with Nb(C,N) particles. FIB lift out was also applied to a small area of the grain boundary in the sample, in order to study the relationship between particles and dislocations near grain boundaries. TEM images using the HAADF mode for the lift out sample are shown in Figure 6.33; many Nb(C,N) particles can be found, with a high density of dislocations around them. From the TEM images under bright field mode and the related EDX spectrum in Figure 6.34, the particles have a low Nb peak, because a Nb(C,N) particle is typically quite small, and thus most of the EDX signals come from iron matrix. TEM EDX maps for the FIB lift out sample are shown in Figures 6.35 and 6.36, and many small Nb-rich particles can be found in the maps.

It is reasonable to conclude that solute Nb atoms will form first at prior austenite grain boundaries, and then exert a solute drag effect on the interface mobility. After 60 seconds holding at 750°C, some solute Nb atoms precipitate as Nb(C,N) particles, but many others are still in solid solution, and thus the solute drag effect continues to work on grain boundaries. After 180 seconds, Nb(C,N) particles can be found on much more grain boundaries. From Figure 6.24, the ferrite grain growth rate in steel 3 is much slower than those of steels 1 and 2 between 60 seconds and 180 seconds isothermal transformation at 750°C. From Figure 6.4, steels 1 and 2 have much more fraction transformed than steel 3 after 180 seconds; this can be attributed to influence of solute Nb atoms.

In addition, it is reasonable to suggest that the Nb(C,N) particles also exert a particle pinning effect on the interface mobility, which can also reduce the ferrite grain growth rate and thus the transformation kinetics. The large amount of dislocations around

the Nb(C,N) particles indicated in the thin foil TEM may be an evidence for the particle pinning effect.



Figure 6.31: TEM images for carbon extraction replica samples of steel 3 with 300 seconds austenitisation at 1250°C and then isothermally transformed at 750°C for 180 seconds. Many NbC particles are segregated at grain boundaries.



Figure 6.32: TEM images and the related EDX spectra for carbon extraction replica samples of steel 3 with 300 seconds austenitisation at 1250°C and then isothermally transformed at 750°C for 180 seconds. Many tiny NbC particles are found in some grain boundaries.



Figure 6.33: HAADF TEM images for the lift out sample of steel 3 with 300 seconds austenitisation at 1250°C and then isothermally transformed at 750°C for 180 seconds. Many tiny particles which are possibly Nb(C,N) particles can be observed.



Figure 6.34: TEM image and the related spot EDX spectra for a lift out sample of steel 3 with 300 seconds austenitisation at 1250°C and then isothermally transformed at 750°C for 180 seconds. The Nb peak indicates that they are possibly Nb(C,N) particles.





Figure 6.35: TEM EDX Map for a FIB lift out ferrite/martensite interface of steel 3 with 180 seconds interrupted isothermal transformation at 750°C.




Figure 6.36: TEM EDX Map for a FIB lift out ferrite/martensite interface of steel 3 with 180 seconds interrupted isothermal transformation at 750°C.

The isothermal transformation at 700°C for steel 1 was also interrupted after 10 seconds, 30 seconds and 60 seconds, and the transformation progress is plotted in Figure 6.37. The optical micrographs are shown in Figure 6.38, and the ferrite nucleation and grain growth data are listed in Table 6.6. The isothermal transformation at 700°C is very fast, with most transformation occurring in the first 60 seconds. From the optical microscopy image, it can be found that there are some displacive transformation products, but ferrite is still the dominant phase.

The isothermal transformation at 700°C for steel 3 was interrupted after 10 seconds, 60 seconds and 120 seconds, and the transformation progress is plotted in Figure 6.39. The optical microscopy images are shown in Figure 6.40, and the ferrite grain size measurement data are listed in Table 6.7. There is little ferrite formed after 10 seconds. After 60 seconds holding at 700°C, ferrite begins to nucleate at prior austenite grain boundaries, and then becomes thicker and longer. After 900 seconds, most austenite is transformed to ferrite and pearlite, with some transformation of the remaining austenite to martensite during the subsequent quenching.

The ferrite grain growth rates for steels 1 and 3 during isothermal transformation at 700°C are plotted in Figure 6.41, and the ferrite nucleation rates during isothermal transformation are plotted in Figure 6.42. From the plots, steel 3 with a higher Nb content has slower grain growth rate and nucleation rate than steel 1. The interrupted isothermal transformation results at 700°C are consistent with those at 750°C. It is reasonable to say that the differences in the transformation effect not only on the ferrite grain growth, but also on the ferrite nucleation rate. In addition, from all of the interrupted isothermal transformation samples, their measured ferrite fraction and the change in length are consistent with the fully transformed dilatometer curves, which prove the reproducibility of the dilatometer results.



Figure 6.37: Interrupted isothermal transformation kinetics for steel 1 with 10 seconds, 30 seconds, 60 seconds, or 900 seconds holding at 700°C. The samples were all austenitised at 1250°C for 5 seconds.



Figure 6.38: Optical micrographs of samples of steel 1 with 5 seconds austenitisation at 1250°C, and followed by 10 seconds, 30 seconds, 60 seconds, or 900 seconds isothermal transformation at 700°C.

Table 6.6: Ferrite grain growth during isothermal transformation at 700°C for steel 1 with 5 seconds austenitisation at 1250°C.

Holding time (seconds)	Number of grains in one micrograph	Average grain size (µm)
10	76	16.0
30	317	18.5
60	443	18.2
900	494	19.7



Figure 6.39: Interrupted isothermal transformation kinetics for steel 3 with 10 seconds, 60 seconds, 120 seconds, or 900 seconds holding at 700°C. The samples were all austenitised at 1250°C for 300 seconds.



120 seconds

900 seconds

Figure 6.40: Optical micrographs of samples of steel 3 with 300 seconds austenitisation at 1250°C, and followed by 10 seconds, 60 seconds, 120 seconds, or 900 seconds isothermal transformation at 700°C.

Table 6.7: Ferrite grain growth during isothermal transformation at 700°C for ste	el 3
with 300 seconds austenitisation at 1250°C.	

Holding time (seconds)	Number of grains in one micrograph	Average grain size (µm)
10	6	5.7
60	76	16.7
120	227	19.1
900	507	19.3



Figure 6.41: Ferrite grain growth for steels 1 and 3 during isothermal transformation at 700°C. Steel 1 was austenitised at 1250°C for 5 seconds, and steel 3 was austenitised at 1250°C for 300 seconds.



Figure 6.42: Increase of ferrite grains number for steels 1 and 3 during isothermal transformation at 700°C. Steel 1 was austenitised at 1250°C for 5 seconds, and steel 3 was austenitised at 1250°C for 300 seconds.

## 6.5 Effects of niobium precipitates on isothermal transformation

Nb typically has two forms in steels: solute Nb atoms or Nb(C,N) precipitates. The effect of solute Nb atoms on the isothermal transformation from austenite to ferrite has been studied by quenching samples from 1250°C to the isothermal transformation temperatures. In order to study the effects of Nb(C,N) precipitates on

the transformation behaviour, samples were cooled to 900°C after austenitisation at 1250°C, and held for a certain time to allow solute Nb atoms to precipitate as Nb(C,N) particles before the subsequent isothermal transformations. The isothermal transformation kinetics at 750°C of steel 1 with 5 seconds austenitisation at 1250°C, and then 1200 seconds holding at 900°C or no holding at 900°C are plotted in Figure 6.43, and their optical microscopy images are shown in Figure 6.44. There is little difference in the transformation kinetics of the samples, and their microstructures are also quite similar. This is because steel 1 is Nb free, and 1200 seconds holding at 900°C results in little prior austenite grain growth.

The isothermal transformation kinetics at 750°C of steel 2 with 60 seconds austenitisation at 1250°C, and then 1200 seconds holding at 900°C or no holding at 900°C are plotted in Figure 6.45, and their optical microscopy images are shown in Figure 6.46. The sample with 1200 seconds holding at 900°C has slightly faster isothermal transformation kinetics than the sample without holding at 900°C, possibly because the solute Nb atoms which can delay the transformation kinetics have been precipitated. However, their microstructures are quite similar.

Steel 3 has 0.028 wt. % Nb, and samples from steel 3 were austenitised at 1250°C for 300 seconds, and then held at 900°C for 300 seconds, 1200 seconds and 3600 seconds followed by isothermal transformation at 750°C, as plotted in Figure 6.47. It can be seen that the transformation kinetics become faster with increasing holding time at 900°C. However, there is little increase in transformation kinetics between the sample with 1200 seconds holding and the sample with 3600 seconds, possibly because most solute Nb atoms have already been precipitated during 1200 seconds holding. The microstructures of the samples with different holding times are very similar, as shown from the optical microscopy images in Figure 6.48.

The Nb content in Steel 5 is 0.045 wt. %, which is even higher than steel 3. A sample from steel 5 was austenitised at 1250°C for 300 seconds, and then held at 900°C for 1 hour and followed by isothermal transformation at 750°C, and its transformation

kinetic curve was compared to a sample of steel 5 isothermal transformed at 750°C with 300 seconds austenitisation at 1250°C but no holding at 900°C, as shown in Figure 6.49. From the optical microscopy images in Figure 6.50, it can be found that the 1 hour holding at 900°C significantly accelerates the transformation kinetics, and the transformed ferrite fraction is also significantly increased by holding at 900°C. This is possibly because the precipitation of Nb(C,N) also reduces the amount of solute carbon atoms, and thus the ferrite fraction in the equilibrium state is increased. The presence of Nb(C,N) particles in the sample with 1 hour holding at 900°C and then isothermal transformation at 750°C was studied using TEM, as shown in Figure 6.51. From a FIB lift out area across ferrite/martensite interface, many Nb(C,N) particles have been observed, with a high density of dislocations around them. Some Nb(C,N) particles are found near the interface, but there are also many particles away from the interface. TEM EDX maps of the FIB lift out sample are shown in Figures 6.52-6.54. Many more Nb-rich particles can be found in the sample compared to the previous EDX maps of steel 3. There are two possible reasons: one is that steel 5 has a higher Nb content than steel 3; and another reason is that the 1 hour holding at 900°C results in larger Nb(C,N) particles which can be easily observed. From Figure 6.53, it can be seen that some Nb-rich particles are also associated with AI, they are NbAI(C,N) particles. From the thermodynamic calculation results in Chapter 4, NbC and AIN are both precipitated during holding at 900°C, and sometimes particles are precipitated on the same site and mixed as a larger complex NbAI(C,N) particle during holding at 900°C.

From the study on the samples with holding at 900°C, it can be concluded that holding at 900°C accelerates the subsequent isothermal transformation kinetics. Solute Nb atoms precipitate as Nb(C,N) particles, and thus the solute drag effect is reduced. Nb(C,N) particles can exert a particle pinning effect on the transformation kinetics, but their effect appears to be weaker than the solute drag effect from the dilatometer results.



Figure 6.43: Isothermal transformation kinetics at 750°C of steel 1. One sample was austenitised at 1250°C for 5 seconds, and then held at 900° for 1200 seconds before the subsequent isothermal transformation. The other sample was also austenitised at 1250°C for 5 seconds, but with no holding at 900°C and directly isothermally transformed at 750°C.



Figure 6.44: Optical micrographs of steel 1: (a) the sample was austenitised at 1250°C for 5 seconds, and then held at 900° for 1200 seconds before the subsequent isothermal transformation; and (b) the other sample was also austenitised at 1250°C for 5 seconds, but with no holding at 900°C and directly isothermally transformed at 750°C.



Figure 6.45: Isothermal transformation kinetics at 750°C of steel 2. One sample was austenitised at 1250°C for 60 seconds, and then held at 900° for 1200 seconds before the subsequent isothermal transformation. The other sample was also austenitised at 1250°C for 60 seconds, but with no holding at 900°C and directly isothermally transformed at 750°C.



No holding at 900°C

1200 seconds holding at 900°C

Figure 6.46: Optical micrographs of steel 2: (a) the sample was austenitised at 1250°C for 60 seconds, and then held at 900° for 1200 seconds before the subsequent isothermal transformation; and (b) the other sample was also austenitised at 1250°C for 60 seconds, but with no holding at 900°C and directly isothermally transformed at 750°C.



Figure 6.47: Isothermal transformation kinetics of steel 3 at 750°C with 300 seconds austenitisation at 1250°C and various holding times at 900°.



Figure 6.48: Optical micrographs of steel 3 with 300 seconds austenitisation at 1250°C, followed by different holding times at 900°C before the subsequent isothermal transformation at 750°C.



Figure 6.49: Isothermal transformation kinetics at 750°C of steel 5. One sample was austenitised at 1250°C for 300 seconds, and then held at 900° for 3600 seconds before the subsequent isothermal transformation. The other sample was also austenitised at 1250°C for 300 seconds, but with no holding at 900°C and directly isothermally transformed at 750°C.



5-1250°C300s-750°C900s

5-1250°C300s-900°C3600s-750°C900s

Figure 6.50: Optical micrographs for samples from steel 5 with 5 minutes austenitisation at 1250°C, followed by no holding at 900°C or 1 hour holding at 900°C and then isothermally transformed at 750°C.



Figure 6.51: Bright field TEM images of FIB lift out samples of steel 5 with 5 minutes austenitisation at 1250°C and 1 hour holding at 900°C and then isothermally transformed at 750°C.



Figure 6.52: TEM EDX map of a FIB lift out sample from steel 5 with 5 minutes austenitisation at 1250°C followed by 1 hour holding at 900°C and then isothermally transformed at 750°C for 15 minutes.



Figure 6.53: TEM EDX map of a FIB lift out sample from steel 5 with 5 minutes austenitisation at 1250°C followed by 1 hour holding at 900°C and then isothermally transformed at 750°C for 15 minutes.



Figure 6.54: TEM EDX map of a FIB lift out sample from steel 5 with 5 minutes austenitisation at 1250°C followed by 1 hour holding at 900°C and then isothermally transformed at 750°C.

Holding at 900°C allows solute Nb atoms to precipitate as Nb(C,N) particles before isothermal transformation. Nb(C,N) particles can also be present at a low austenitisation temperature, when pre-existing Nb(C,N) particles have not been fully dissolved. From the prior austenite grain size study in Chapter 5, steel 1 with 5 minutes austenitisation at 1000°C, and steels 3 and 6 with 5 minutes austenitisation at 1100°C all result in an average prior austenite grain size of ~30 µm. The samples were then isothermally transformed at 750°C, and the transformation kinetics curves are shown in Figure 6.55. The Nb free steel 1 has obviously the fastest transformation kinetics, and the final ferrite fraction in steel 1 is much higher than those in steels 3 and 6, which can be seen from their optical microscopy images shown in Figure 6.56. It can also be found that steel 6 with 0.067 wt. % Nb has slightly slower transformation than steel 3 with 0.028 wt. % Nb. According to the thermodynamic calculation results and microstructure images, many pre-existed Nb(C,N) cannot be dissolved after 5 minutes austenitisation at 1100°C for steels 3 and 6, and there are only a few solute Nb atoms in austenite matrix. Steel 6 has a higher Nb(C,N) dissolution temperature and a higher Nb content than steel 3, and thus there should be more Nb(C,N) particles in steel 6 than those in steel 3. From FEGSEM images of steels 3 and 6 shown in Figures 6.57 and 6.58 respectively, more Nb(C,N) particles can be found in steel 6 than that in steel 3. FIB lift out samples of steel 6 were characterised using TEM to study Nb(C,N) particles, as shown in Figure 6.59. A large pre-existing Nb(C,N) particle (>100 nm) can be found away from grain boundary, and thus it has little contribution to delay transformation kinetics. The slower transformation rate of steel 6 is likely to be caused by a net effect of the solute drag effect and Nb(C,N) particles pinning effect.



Figure 6.55: Isothermal transformation kinetics at 750°C for samples from steels 1, 3, and 6. Steel 1 was austenitised at 1000°C for 5 minutes, and steels 3 and 6 were austenitised at 1100°C for 5 minutes. The austenitisation temperatures are below the calculated Nb(C,N) dissolution temperatures.



1-1000°C300s-750°C900s

3-1100°C300s-750°C900s

Figure 6.56: Optical micrographs of a sample from steel 1 with 5 minutes austenitisation at 1000°C and isothermal transformation at 750°C, and a sample from steel 3 with 5 minutes austenitisation at 1100°C and isothermal transformation at 750°C.



Figure 6.57: FEGSEM images using backscatter mode to show Nb(C,N) particles in the sample of steel 3 with 5 minutes austenitisation at 1100°C and then isothermal transformation at 750°C.



Figure 6.58: FEGSEM images using backscatter mode to show Nb(C,N) particles in the sample of steel 6 with 5 minutes austenitisation at 1100°C and then isothermal transformation at 750°C.





Figure 6.59: TEM images (a) HAADF image and (b) bright field image, and the related EDX spectra, for FIB lift out samples of steel 6 with 5 minutes austenitisation at 1100°C and then isothermal transformation at 750°C

## 6.6 Nb(C,N) particle size distribution

From the TEM study by carbon extraction replica or FIB lift out, many Nb(C,N) particles have been found in samples with various kinds of heat treatments. The Nb(C,N) particles can be smaller than 5 nm, or sometimes over 100 nm. It seems that Nb(C,N) particles formed at different stages of heat treatment may have different particle sizes. Therefore, it is necessary to study the Nb(C,N) particle size in samples with different heat treatments. In this work, steel 5 was used as the example for the particle size study, because its Nb content is relatively high, and it is not difficult to ensure that any pre-existing Nb(C,N) is fully dissolved.

For a sample of steel 5 with 5 minutes austenitisation at 1250°C and then 15 minutes isothermal transformation at 750°C, the TEM images are shown in Figure 6.60. It can be seen that there are a lot of particles which were confirmed to be Nb(C,N) particles from both the EDX spectra and the diffraction patterns. These particles are quite small, typically with a diameter of ~10 nm. Most particles in the sample are elliptical or spherical. In Figures 6.60 (a) and (b), the small particles are likely to have precipitated during isothermal transformation at 750°C. The related diffraction patterns in Figures 6.61 and 6.62 are continuous or discontinuous rings. The lattice parameter calculated from the rings is consistent with the NbC face centred cubic structure. The ring shape of diffraction patterns also indicate that there are many small NbC particles with different orientations clustered together.



Figure 6.60: TEM carbon extraction replica images for a sample from steel 5 with 5 minutes austenitisation at 1250°C and isothermal transformation at 750°C for 15 minutes.



Figure 6.61: The diffraction rings for particles in Figure 6.60 (a).







Figure 6.63: TEM carbon extraction replica images for a sample from steel 5 with 5 minutes austenitisation at 1250°C followed by 1 hour holding at 900°C and then isothermal transformation at 750°C.

For a sample of steel 5 with 5 minutes austenitisation at 1250°C, followed by 1 hour precipitation heat treatment at 900°C, and then isothermal transformation at 750°C, the TEM carbon extraction replica images are shown in Figures 6.63. In the sample,

there are many small Nb(C,N) particles with a diameter less than 10 nm, and also some large particles with a diameter larger than 50 nm. Many particles have a spherical morphology (Figures 6.63 (b), (c) and (d)), however, some particles are cuboidal (Figures 6.63 (e) and (f)), and some particles are even elongated (Figures 6.63 (a) and (f)). From these TEM images, it can be seen that many particles are clustered together, but there are also some separate particles as shown in Figures 6.63 (a) and (b).

The above two samples have undergone typical heat treatments in the study. It is clear that the Nb(C,N) particle size distribution in the sample with austenitisation at 1250°C followed by 1 hour precipitation heat treatment at 900°C and then isothermal transformation at 750°C is different from that in the sample without the precipitation heat treatment at 900°C. In order to accurately study the effect of the 1 hour precipitation heat treatment for Nb(C,N) particles, a sample was austenitised at 1250°C for 5 minutes, followed by 1 hour precipitation heat treatment at 900°C, and then directly guenched to room temperature without any isothermal transformation. Its TEM carbon extraction replica images are shown in Figures 6.64. The EDX spectra indicate that particles are mostly Nb(C,N). Comparing between Figure 6.60, Figure 6.63 and Figure 6.64, it can be seen that particles in Figure 6.64 are generally larger than particles in Figures 6.60 and 6.63, and the particles in Figure 6.64 are more separately distributed. Most particles in the sample have a cuboidal morphology. Figure 6.65 is the diffraction pattern for the particle shown in Figure 6.64 (a): it is the NbC face centred cubic structure tilted to  $[\overline{1} \ 1 \ 2]$  zone axis. Figure 6.66 is the diffraction pattern for a particle shown in Figure 6.64 (b): it is the NbC face centred cubic structure tilted to  $[\bar{1} 0 1]$  zone axis. The clear spots of the diffraction patterns indicate that these are single large NbC particles rather than many small particles clustered together. Figure 6.67 is a high resolution TEM image of a single large Nb(C,N) particle in the sample with 1 hour holding at 900°C and then isothermal transformation at 750°C. It has also been shown that the large particle is not an agglomeration segregation of many small particles.



Figure 6.64: TEM carbon extraction replica images for a sample from steel 5 with 5 minutes austenitisation at 1250°C followed by 1 hour holding at 900°C and then quenched to room temperature.



Figure 6.65: The diffraction pattern for the particle in Figure 6.64 (a).



Figure 6.66: The diffraction pattern for the particle in Figure 6.64 (b).



Figure 6.67: High resolution TEM image of a Nb(C,N) particle from the sample with 5 minutes austenitisation at 1250°C, followed by 1 hour holding at 900°C and then isothermal transformation at 750°C.

Another sample of steel 5 was austenitised at 1250°C for only 13 seconds, followed by isothermal transformation at 750°C without the precipitation heat treatment at 900°C, the TEM carbon extraction replica images are shown in Figure 6.68. From the images, it can be seen that there are many small Nb(C,N) particles clustered around one large particle. In Figure 6.68 (f), there is an extremely large Nb(C,N) particles. From the FEGSEM images in Figure 6.69, some quite large Nb(C,N) particles can also be found. The 13 seconds austenitisation at 1250°C cannot fully dissolve all pre-existed Nb(C,N) particles, and thus the large particles are probably pre-existing.



Figure 6.68: TEM carbon extraction replica images for a sample from steel 5 with 13 seconds austenitisation at 1250°C and isothermal transformation at 750°C.





Figure 6.69: FEGSEM image and the EDX spectrum for the sample with 13 seconds austenitisation at 1250°C and isothermal transformation at 750°C

For all the samples mentioned above, the particle size was measured using the "Grain boundary tracing technique", however, many high magnification TEM images were analysed in order to recognise the boundary for many clustered particles, and totally more than 2300 particles were measured. Then, Nb(C,N) particle size distribution was analysed and compared in Figure 6.70. It can be seen that the

number fraction of particles larger than 20 nm is significantly increased in the samples with the 1 hour precipitation heat treatment. It can also be found that there are fewer particles smaller than 20 nm in the samples without the isothermal transformation at 750°C.



Figure 6.70: The plot of particle size distribution in samples from steel 5 with different heat treatments.

Comparing the TEM carbon extraction replica images and the particle size distribution plots, it can be seen that particles in the sample 1250°C300s-750°C900s are all smaller than 20 nm, and many small particles are clustered together. Since there are no Nb(C,N) particles in the sample directly quenched from 1250°C, the small particles must be precipitated from the dissolved niobium atoms during the isothermal transformation at 750°C. From Figure 6.70, all of the samples which had isothermal transformation at 750°C have a peak at about 10 nm, but the peak in the sample 1250°C300s-900°C3600s-750°C900s is much lower than the samples without holding at 900°C, because many solute Nb atoms have been precipitated during the 1 hour holding at 900°C. For the sample 1250°C300s-900°C3600s-750°C900s, there are many particles larger than 20 nm. Comparing to the particle size distribution of the sample 1250°C300s-900°C3600s, and become coarser during the 1 hour holding. It appears that the particle size distribution curve of the sample

1250°C300s-900°C3600s-750°C900s is the summation of the curves 1250°C300s-750°C900s and 1250°C300s-900°C3600s and exhibits a bimodal particle size distribution.

## 6.7 Effects of Nb on continuous cooling kinetics

The above work has studied the effect of Nb on isothermal transformation behaviour. In industry, continuous cooling is a more common type of transformation for steels. Therefore, it is necessary to study the effect of Nb in continuous cooling transformations. It is well known that a slow cooling rate normally results in ferrite and pearlite, a fast cooling rate may result in martensite, and an intermediate cooling rate sometimes produces bainite. In order to focus on the transformation from austenite to ferrite, the continuous cooling work starts from a slow cooling rate at 0.1°Cs<sup>-1</sup>. In order to ensure steels 1-4 have the same average prior austenite grain size at the beginning of the continuous cooling, steel 1 was austenitised at 1250°C for 5 seconds, steel 2 was austenitised at 1250°C for 60 seconds, steel 3 was austenitised at 1250°C for 300 seconds, and steel 4 was austenitised at 1250°C for 150 seconds. After the austenitisation at 1250°C, samples were first quenched to 900°C to ensure solute Nb atoms have not been precipitated at the beginning of the continuous cooling, and then slowly cooled to room temperature at 0.1°Cs<sup>-1</sup>. The transformation kinetics with a cooling rate of 0.1°Cs<sup>-1</sup> for steels 1-4 are shown in Figure 6.71, and the optical microscopy images are shown in Figure 6.72. It can be seen that transformation start temperatures are decreased with increasing Nb content in steels, and steel 4 with a higher carbon content has a much lower transformation start temperature. Steel 2 has a quite similar but only slightly lower transformation start temperature than steel 1. Steel 2 has only 0.009 wt. % Nb, and the 0.1°Cs<sup>-1</sup> cooling rate gives sufficient time to allow the solute Nb atoms mostly precipitated during the cooling from 900°C to the transformation start temperature. From their optical micrographs, ferrite and pearlite are present, without any martensite. Steel 4 has much more pearlite because of its higher carbon content.



Figure 6.71: Transformation kinetics of continuous cooling at 0.1°Cs<sup>-1</sup> for steels 1-4 with 5 seconds, 60 seconds, 300 seconds, and 150 seconds austenitisation at 1250°C, respectively. Samples were quenched to 900°C after the austenitisation at 1250°C and then continuously cooled at 0.1°Cs<sup>-1</sup>.



Figure 6.72: Optical micrographs of steels 1-4 with 5 seconds, 60 seconds, 300 seconds, and 150 seconds austenitisation at 1250°C, respectively. Samples were quenched to 900°C after the austenitisation at 1250°C and then continuously cooled at 0.1°Cs<sup>-1</sup>.

The transformation kinetics of steels 1-4 with a cooling rate at 0.5°Cs<sup>-1</sup> are plotted in Figure 6.73, and their optical microscopy images are shown in Figure 6.74. The transformation start temperatures are also decreased with increasing Nb content, but this time steel 2 clearly has a lower transformation start temperature than steel 1. From the optical micrographs, steel 1 still consists of ferrite and pearlite, but there are a few of the displacive transformation products present in steels 2 and 3. In steel 4, the displacive transformation products have almost the same area fraction as ferrite. From the continuous cooling transformation kinetics curve of steel 4, there is a clear kink on the curve which occurred at about 620°C when the sample was half transformed.



Figure 6.73: Transformation kinetics of continuous cooling at 0.5°Cs<sup>-1</sup> for steels 1-4 with 5 seconds, 60 seconds, 300 seconds, and 150 seconds austenitisation at 1250°C, respectively. Samples were quenched to 900°C after the austenitisation at 1250°C and then continuously cooled at 0.5°Cs<sup>-1</sup>.



Figure 6.74: Optical micrographs of steels 1-4 with 5 seconds, 60 seconds, 300 seconds, and 150 seconds austenitisation at 1250°C, respectively. Samples were quenched to 900°C after the austenitisation at 1250°C and then continuously cooled at  $0.5^{\circ}$ Cs<sup>-1</sup>.

Displacive transformation happens during the 0.5°Cs<sup>-1</sup> continuous cooling, and thus there should be more displacive transformation products in samples with faster cooling rates. To study the effect of Nb on transformation kinetics, steels 1 and 3 were only utilised for continuous cooling faster than 1°Cs<sup>-1</sup>. From Figure 6.75, steel 3 has much lower transformation start and finish temperatures than steel 1. From the optical micrographs shown in Figure 6.76, there are still ferrite and pearlite in steel 1, but the displacive transformation products becomes the major microstructural constituent in steel 3, with only a small amount of ferrite remaining. It is not surprising that there is a large amount of displacive transformation products present in steel 3, because of the lower transformation start and finish temperatures.


Figure 6.75: Transformation kinetics of continuous cooling at 1°Cs<sup>-1</sup> for steels 1 and 3 with austenitisation at 1250°C for 5 seconds and 300 seconds respectively. Samples were quenched to 900°C after the austenitisation at 1250°C and then continuously cooled at 1°Cs<sup>-1</sup>.



Figure 6.76: Optical micrographs of steels 1 and 3 with 5 seconds and 300 seconds austenitisation at 1250°C, respectively. Samples were quenched to 900°C after the austenitisation at 1250°C and then continuously cooled at 1°Cs<sup>-1</sup>.

The transformation kinetic curves for steels 1 and 3 with 2°Cs<sup>-1</sup> cooling are plotted in Figure 6.77. The 2°Cs<sup>-1</sup> cooling decreases the transformation start temperature of steel 1 from about 780°C to about 740°C, which is only slightly higher than that of steel 3. However, the whole transformation rate curve of steel 3 is much lower than that of steel 1. From the optical micrographs shown in Figure 6.78, it can be seen that the low transformation start temperature of steel 1 results a large amount of

bainite being formed. For steel 3, its microstructure looks quite similar to the sample with 1°Cs<sup>-1</sup> cooling, which contains mostly bainite with a small amount of ferrite.



Figure 6.77: Transformation kinetics of continuous cooling at 2°Cs<sup>-1</sup> for steels 1 and 3 with austenitisation at 1250°C for 5 seconds and 300 seconds respectively. Samples were quenched to 900°C after the austenitisation at 1250°C and then continuously cooled at 2°Cs<sup>-1</sup>.



Steel 1

Steel 3

Figure 6.78: Optical micrographs of steels 1 and 3 with 5 seconds and 300 seconds austenitisation at 1250°C, respectively. Samples were quenched to 900°C after the austenitisation at 1250°C and then continuously cooled at 2°Cs<sup>-1</sup>.

The transformation kinetics curves for steels 1 and 3 with 5°Cs<sup>-1</sup> cooling are plotted in Figure 6.79. At this cooling rate, the transformation start temperature of steel 3 is much lower than that of steel 1, and it is about 100°C lower than that of steel 3 with a

cooling rate at 2°Cs<sup>-1</sup>. From the optical microscopy images shown in Figure 6.80, both steels 1 and 3 consist of bainite and ferrite, but the amount of ferrite is much less in steel 3 than in steel 1.



Figure 6.79: Transformation kinetics of continuous cooling at 5°Cs<sup>-1</sup> for steels 1 and 3 with austenitisation at 1250°C for 5 seconds and 300 seconds respectively. Samples were quenched to 900°C after the austenitisation at 1250°C and then continuously cooled at 5°Cs<sup>-1</sup>.



Figure 6.80: Optical micrographs of steels 1 and 3 with 5 seconds and 300 seconds austenitisation at 1250°C, respectively. Samples were quenched to 900°C after the austenitisation at 1250°C and then continuously cooled at 5°Cs<sup>-1</sup>.

The transformation kinetics curves for steels 1 and 3 with 10°Cs<sup>-1</sup> cooling are plotted in Figure 6.81. Steel 3 still has a lower transformation start and finish temperature

than steel 1. Although the transformation start temperature of steel 1 is still above 700°C, there are only a few ferrite grains present in the optical microscopy image shown in Figure 6.82, and there is nearly all bainite with a small amount of ferrite present in steel 3.



Figure 6.81: Transformation kinetics of continuous cooling at 10°Cs<sup>-1</sup> for steels 1 and 3 with austenitisation at 1250°C for 5 seconds and 300 seconds respectively. Samples were quenched to 900°C after the austenitisation at 1250°C and then continuously cooled at 10°Cs<sup>-1</sup>.



Steel 1

Steel 3

Figure 6.82: Optical micrographs of steels 1 and 3 with 5 seconds and 300 seconds austenitisation at 1250°C, respectively. Samples were quenched to 900°C after the austenitisation at 1250°C and then continuously cooled at 10°Cs<sup>-1</sup>.

From the transformation rate curves of steels 1 and 3 with 20°Cs<sup>-1</sup> shown in Figure 6.83, it can be seen that steels 1 and 3 have almost the same transformation start and finish temperatures, but the whole curve of steel 3 is slightly lower than that of steel 1. At this cooling rate, steels 1 and 3 have quite similar microstructure. Bainite is the main phase present in both samples, with little ferrite or martensite, as shown in Figure 6.84.



Figure 6.83: Transformation kinetics of continuous cooling at 20°Cs<sup>-1</sup> for steels 1 and 3 with austenitisation at 1250°C for 5 seconds and 300 seconds respectively. Samples were quenched to 900°C after the austenitisation at 1250°C and then continuously cooled at 20°Cs<sup>-1</sup>.



Steel 1

Steel 3

Figure 6.84: Optical micrographs of steels 1 and 3 with 5 seconds and 300 seconds austenitisation at 1250°C, respectively. Samples were quenched to 900°C after the austenitisation at 1250°C and then continuously cooled at 20°Cs<sup>-1</sup>.

Samples of steels 1 and 3 with 50°Cs<sup>-1</sup> continuous cooling also have similar transformation start and finish temperatures, as shown in Figure 6.85. However, the transformation start and finish temperatures are about 100°C lower than those with 20°Cs<sup>-1</sup> cooling. The low transformation start temperature enables the martensitic transformation, which can be seen from the optical microscopy images in Figure 6.86. Both steels 1 and 3 have mainly martensite, with some bainite present.



Figure 6.85: Transformation kinetics of continuous cooling at 50°Cs<sup>-1</sup> for steels 1 and 3 with austenitisation at 1250°C for 5 seconds and 300 seconds respectively. Samples were quenched to 900°C after the austenitisation at 1250°C and then continuously cooled at 20°Cs<sup>-1</sup>.



Steel 1

Steel 3

Figure 6.86: Optical micrographs of steels 1 and 3 with 5 seconds and 300 seconds austenitisation at 1250°C, respectively. Samples were quenched to 900°C after the austenitisation at 1250°C and then continuously cooled at 50°Cs<sup>-1</sup>.

The 0.1% transformed temperature was chosen as the transformation start temperature. The 0.1% transformed temperatures and the 50% transformed temperatures of steels 1 and 3 are plotted against the cooling rates in Figure 6.87. It can be seen that steel 3 with 0.029 wt. % Nb always has a lower transformation start temperature and 50% transformed temperature than the Nb free steel 1 at each cooling rate. However, the differences in T0.1% and T50% between steels 1 and 3 become smaller with increasing the cooling rate. This is because Nb can delay the transformation kinetics, and thus steel 3 always has a lower transformation start temperature than steel 1, but the retardation of effect of Nb is much more significant in slow cooled samples than fast cooled samples. In fast cooling, the displacive transformation is very fast, and indeed is sometimes finished in a few seconds. The fast transformation rate easily overcomes the delay effect caused by Nb. Another reasonable explanation is that the solute drag effect caused by Nb reduces the interface mobility during transformation, because solute Nb atoms which prefer to segregate at grain boundary, have a lower diffusion coefficient. However, the displacive transformation which occurs during fast cooling does not rely on the diffusional interface movement, and thus there is little difference in transformation start temperature during fast cooling.



Figure 6.87: Transformation start time and 50% transformation time of steels 1 and 3 at various cooling rates.

It has been shown that 5 minutes austenitisation at 1100°C for steels 3 and 6 cannot fully dissolve pre-existing Nb(C,N) particles, and the prior austenite grain size is ~ 30  $\mu$ m for both samples. The transformation kinetics for 0.5°Cs<sup>-1</sup> continuous cooling of the samples have been compared with a sample of steel 1 with a similar prior austenite grain size and cooled at 0.5°Cs<sup>-1</sup>. From Figure 6.88, steel 6 with 0.067 wt. % Nb, can be seen to have the lowest transformation start temperature, and the Nb free steel 1 has the highest transformation start temperature. Figures 6.89 and 6.90 are FEGSEM images of steels 3 and 6, respectively. Using the backscatter mode, many Nb(C,N) particles which are white particles can be observed. It can be seen that there are many more particles in steel 6 than in steel 3, and therefore, steel 6 has a slightly lower transformation start temperature than steel 3.



Figure 6.88: Transformation kinetics of continuous cooling at 0.5°Cs<sup>-1</sup> for steel 1 with 5 minutes austenitisation at 1000°C, and for steels 3 and 6 with 5 minutes austenitisation at 1100°C.

The effect of Nb(C,N) particles on continuous cooling and the effect of solute Nb atoms on continuous cooling are compared in Figure 6.91. It can be seen that the transformation start temperature in steel 3 is only slightly lower than that in steel 1 after the austenitisation below 1200°C, but there is a large difference in transformation start temperatures between steels 1 and 3 after austenitisation at 1250°C. 1250°C austenitisation allows all pre-existing Nb(C,N) particles to dissolve

as solute Nb atoms, and 1100°C allows only a few of the pre-existing Nb(C,N) particles to dissolve. Therefore, the delay effect on transformation start temperature caused by pre-existing Nb(C,N) particles is less than that caused by solute Nb atoms. This conclusion is consistent with the results from the isothermal transformation kinetics of samples held at 900°C.



Figure 6.89: FEGSEM images using the backscatter mode of steel 3 with 5 minutes austenitisation at 1100°C, and then quenched to 900°C and followed by 0.5°Cs<sup>-1</sup> continuous cooling.



Figure 6.90: FEGSEM images using the backscatter mode of steel 6 with 5 minutes austenitisation at 1100°C, and then quenched to 900°C and followed by 0.5°Cs<sup>-1</sup> continuous cooling.



Figure 6.91: A comparison between the effects of solute Nb atoms and Nb(C,N) precipitates on the continuous cooling kinetics.

#### 6.8 Discussion

All of the dilatometer results and microscopy images indicate that Nb has a retardation effect on transformation kinetics. For the samples directly quenched from 1250°C to the isothermal transformation temperatures, it is reasonable to assume all Nb atoms are in solid solution at the beginning of the isothermal transformation, because no Nb(C,N) particles have been found using TEM in samples directly quenched from 1250°C to room temperature.

During the isothermal transformations, a steel with a high Nb content was always found to have a slower transformation rate than a steel with a low Nb content, and the delay on transformation kinetics typically happened in the first few minutes. At the beginning, the transformation was delayed by solute Nb atoms, because all the Nb atoms were still in solid solution. Nb atoms and iron atoms have a large misfit [1, 17, 63], which is ~16%, and therefore solute Nb atoms preferred to segregate at prior austenite grain boundaries, where a large amount of defects are typically present. As a result, the interfacial energy at prior austenite grain boundaries is reduced, and thus less energy is available for ferrite nucleation [63]. Optical microscopy images of the interrupted isothermally transformed samples show that steel 3 has a much slower nucleation progress than steel 1.

Even for the nucleated ferrite grains, many solute Nb atoms remain at the interface between the ferrite and austenite, because the newly formed ferrite grains are quite thin (as shown in the FEGSEM images of interrupted isothermally transformed samples in Figures 6.22 and 6.23), and the diffusion of solute Nb atoms in iron matrix is quite slow. Nb is a ferrite stabiliser, and thus the chemical potential of solute Nb in ferrite is lower than that in austenite [77]. In addition, there should be a potential well at the interface to explain the attraction of solute atoms. A schematic diagram of Nb concentration profile across a ferrite/austenite interface is shown in Figure 2.33 (a), and the solute chemical potential profile across ferrite/austenite interface is schematically shown in Figure 2.33 (b). For the sample isothermally transformed at 750°C, the prior austenite grain size is chosen as 80 µm, and the

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ferrite grain size after 15 minutes transformation is ~20  $\mu$ m. It is reasonable to estimate that the ferrite/austenite interface moves at a rate of a few microns per minute from microstructural observations. However, the diffusion of solute Nb atoms at this temperature is much slower than this rate. As a result, it takes extra energy to 'drag' these solute Nb atoms to move with the interface, and therefore the transformation rate is slowed down. From literature [e.g. 64, 65], some researchers attribute the retardation effect caused by solute Nb atoms to the increase in the activation energy of carbon diffusion, and thus the ferrite growth rate is reduced.

It is quite difficult to characterise the distribution of solute Nb atoms across a ferrite/austenite interface even using advanced high resolution TEM. However, solute Nb atoms began to precipitate as Nb(C,N) particles simultaneously as the transformation progresses from austenite to ferrite. Therefore, the distribution of solute Nb atoms at the ferrite/austenite interface can be represented by the distribution of Nb(C,N) particles. From the carbon extraction replica images of steel 3 with 60 seconds or 180 seconds interrupted isothermal transformation at 750°C, many small Nb(C,N) particles which are typically ~5 nm, are found across an interface. There are more Nb(C,N) particles in the sample with 180 seconds transformation than the sample with 60 seconds transformation. This indicates that many solute Nb atoms precipitate during the transformation from austenite to ferrite, and therefore, the retardation effect on the transformation caused by solute Nb atoms should become less and less. On the other hand, the Nb(C,N) particles also have a particle pinning effect on the interface [79, 86, 89]. The newly formed Nb(C,N) particles are small but there are many of them, and thus the particle pinning effect is unlikely to be negligible. From the dilatometer curves for samples isothermally transformed at 750°C, it can be seen that after 180 seconds, the delay effect on the transformation rate of steel 3 is not significantly reduced, because solute Nb atoms have not been fully precipitated, and the particle pinning effect of Nb(C,N) particles also has a retardation effect on the transformation kinetics. From TEM images for the FIB lift out samples of steel 3 with 180 seconds interrupted isothermal transformation, a high density of dislocations can be found around Nb(C,N) particles near grain boundaries.

From the dilatometer results for samples of steel 3 with various holding times at 900°C before isothermal transformation at 750°C, the transformation rate is decreased with increasing holding time at 900°C. From the thermodynamic calculation results, solute Nb atoms are precipitated at 900°C. With increasing holding time at 900°C, the amount of solute Nb atoms is decreased, and thus the solute drag effect will become less important, but the influence of the particle pinning effect will be increased. Therefore, it can be concluded that for the same sample, the solute Nb atoms have a greater retardation effect on the transformation rate than the particle pinning effect. For the sample of steel 3 with a 1 hour precipitation treatment at 900°C, the solute Nb atoms have almost been fully precipitated as particles, because further holding at 900°C has little effect on the transformation kinetics. The holding at 900°C also slightly reduces the solute carbon content, which should accelerate the transformation rate according to the results of steel 4. However, the isothermal transformation rate of steel 3 with 1 hour holding at 900°C is still slower than steel 1, because of the particle pinning effect. For steels 3 and 6 with the austenitisation at 1100°C, pre-existing Nb(C,N) particles have not yet been fully dissolved. From the FEGSEM images of the as-received samples, many pre-existing Nb(C,N) particles are quite large, sometimes with a diameter of hundreds of nanometres. Considering the relationship between the pre-existing particles and dislocations, it appears that the pre-existing particles have little contribution to the particle pinning effect.

From the particle size study of steel 5, the particles formed during isothermal transformation are typically less than 20 nm, because the coarsening of particles is difficult at a relatively low temperature and during a short time. However, after 1 hour holding at 900°C, the particles have a wide size distribution with the main peak happens at about 35 nm, and there are some particles with a size of ~100 nm. This is because the long time holding at 900°C allows Nb(C,N) particles to grow. If the sample undergoes an isothermal transformation at 750°C after 1 hour holding at 900°C, a large amount of small (< 20 nm) particles will appear. This is possibly because solute Nb atoms have not yet been fully precipitated during 1 hour holding at 900°C for steel 5. From the dilatometer study of steel 3 with various holding times at 900°C, it seems that the solute Nb atoms have been fully precipitated after 1 hour

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holding at 900°C, because there is little acceleration in the subsequent transformation rate after 1 hour holding at 900°C compared with the sample after 20 minutes holding at 900°C. Steel 5 has a higher Nb content than steel 3, and thus it is not surprising that there is still a large amount of solute Nb atoms left after 1 hour holding at 900°C. The particle size distribution curve of the sample with 1 hour holding at 900°C followed by the isothermal transformation at 750°C appears to be a the summation of the curve for the sample only with 1 hour holding at 900°C and the curve for the sample only with 15 minutes isothermal transformation, exhibiting a bimodal particle size distribution. This is clear evidence for the fact that particles formed at different temperatures have different average particle sizes.

The microstructure of samples after isothermal transformation varied with the transformation temperature. Steels with different Nb contents also have different microstructures after isothermal transformation at the same temperature. From the optical microscopy images, steels 1-3 are all ferrite and martensite after isothermal transformation at 750°C, because 750°C is above the A<sub>1</sub> temperature, and the retained austenite transformed to martensite during quenching after the isothermal holding. Similar results can be found for samples after isothermal transformation at 725°C. When the transformation temperature is reduced to 700°C, pearlite is formed in all the steels. When the transformation temperature decreases further to 675°C, there are a number of displacive transformation products in steels 1 and 2, but steel 3 is still mainly ferrite with some martensite and pearlite. For samples isothermally transformed at 650°C, steel 1 is nearly all displacive transformation products, but steel 3 is still mainly ferrite and pearlite, with only a few displacive transformation products. It can be seen that a steel with a high Nb content has a wider temperature range for diffusional transformation.

From the continuous cooling results, steel 3 always has a lower transformation start temperature than steel 1, especially at a cooling rate slower than 10°Cs<sup>-1</sup>, and thus it is easier for steel 3 to start bainitic and martensitic transformations than steel 1 at the same cooling rate. The nucleation of ferrite is suppressed by solute Nb atoms which are segregated at prior austenite grain boundaries, and the grain growth rate is also

slowed, therefore the transformation start temperature in steel 3 is lower than that in steel 1. However, the solute drag effect has a strong effect on the diffusional transformation, but the martensitic transformation is very fast, and is typically finished in a few seconds. The large driving force makes the solute drag effect negligible. When the cooling rate is faster than 20°Cs<sup>-1</sup>, both steels have nearly all martensite, and there is little difference in transformation start temperature. For steels 3 and 6 with an austenitisation at 1100°C, their transformation start temperature is not much lower than steel 1 with the same prior austenite grain size during 0.5°Cs<sup>-1</sup> cooling. It is because few of the pre-existing Nb(C,N) particles are dissolved as solute Nb atoms in steels 3 and 6 after 5 minutes austenitisation at 1100°C, and thus the nucleation rate is not significantly affected.



Figure 6.92: Optical microscopy images. (a) As-received sample of steel 1; (b) homogenised and air cooled sample of steel 1; (c) as-received sample of steel 5; and (d) homogenised and furnace cooled sample of steel 5.

From the microscopy images of the samples after transformations, it can be seen that the banded microstructure which is caused by hot rolling has not been fully removed. In order to fully remove the banded microstructure and ensure the alloying elements are homogeneously distributed, a homogenisation heat treatment with 2 hours holding at 1250°C followed by air cooling or furnace cooling were both carried out for steels before austenitisation, as shown in Figure 6.92. It can be seen that after air cooling, there is a significant amount of bainite present in the sample, but the ferrite grain size becomes significantly coarser after furnace cooling. The homogenisation heat treatment changes the time for the re-austenitisation to achieve the standard prior austenite grain size. The optical microscopy images of as-received samples and homogenised samples of steels 1 and 3 isothermally transformed at 675°C are shown in Figure 6.93, and the isothermal transformation kinetics for homogenised samples are compared with the as-received samples, as shown in Figures 6.94 – 6.97. It can be found that for both the Nb free steel and the Nb containing steel, the 2 hour homogenisation heat treatment at 1250°C has little influence on the transformation kinetics and final microstructure. Therefore, it is reasonable to use the as-received samples to study the effect of Nb on transformation kinetics, even if the banded microstructure has not been fully removed. In addition, the effect of pre-existing Nb(C,N) particles formed during hot rolling can be studied and compared with the solute Nb atoms and Nb(C,N) particles formed at 900°C.



Figure 6.93: Optical microscopy images of samples after transformation at 725°C. (a) as-received sample of steel 1; (b) homogenised sample of steel 1; (c) as-received sample of steel 3; and (d) homogenised sample of steel 3.





Figure 6.94: Comparison of isothermal transformation kinetics at 675°C between as-received and homogenised samples of steel 1.

Figure 6.95: Comparison of isothermal transformation kinetics at 700°C between as-received and homogenised samples of steel 1.



Figure 6.96: Comparison of isothermal transformation kinetics at 675°C between as-received and homogenised samples of steel 3.

Figure 6.97: Comparison of isothermal transformation kinetics at 700°C between as-received and homogenised samples of steel 3

#### 6.9 Summary

This chapter has presented a large number of dilatometry results and microscopy images concerned with the transformation behaviours of samples with different Nb contents. The mechanisms of the retardation effect of solute Nb atoms and Nb(C,N) particles on transformation kinetics have also been discussed in detail. From the interrupted isothermal transformation study, the solute drag effect caused by Nb appears to be the major factor in delaying the isothermal transformation kinetics and reducing the transformation start temperature during continuous cooling. Many solute Nb atoms segregate at prior austenite grain boundaries, reduce the nucleation rate and the mobility of interface. Particle pinning can also apply a retardation effect, but this has been shown to be much smaller than the solute drag effect. In many cases, the differences in transformation kinetics are caused by the combination of the two effects. The presence of Nb also affects the final transformation products. It enlarges the temperature range for diffusional transformation. However, the decrease in the transformation start temperature during continuous cooling makes it easier to form bainite and martensite in Nb containing steels. After isothermal transformation at 750°C, solute Nb atoms precipitate as Nb(C,N) particles, with a typical size of ~10 nm. Nb(C,N) particles formed during different heat treatments have been shown to have different particle size distributions and different average particle sizes. The distribution of particles near grain boundaries or inside grains indicates their different roles during the austenite to ferrite transformation. The preexisting banded microstructure caused by hot rolling has little influence on studying the effect of Nb, and is likely to be present in commercial steels. From all of these results, insight has been obtained on the effects of Nb on transformation, and therefore it is possible to incorporate these effects into metallurgical models of phase transformations, which will be discussed in the next chapter.

# 7 Modelling of the effects of Nb on transformation kinetics from austenite to ferrite

## 7.1 Introduction

It has been established that Nb has a delaying effect on the transformation kinetics from austenite to ferrite. It is therefore beneficial for industry to be able to utilise a metallurgical model to predict the transformation behaviour of Nb containing steels, thereby optimising the heat treatment parameters to improve the mechanical properties and reduce the cost. Chapter 6 has presented a systematic and careful investigation of the effects of Nb on both isothermal transformation kinetics and continuous cooling kinetics. It has been found that solute Nb atoms can delay both the nucleation rate and the grain growth rate during the transformation from austenite to ferrite. In Chapter 4, several existing models were utilised to predict the TTT and CCT diagrams of steels, and it was demonstrated that CamModel seems to be one of the best phase transformation models in the case of Nb containing steels. In this Chapter, the experimental results obtained are compared with CamModel predictions to investigate the applicability of CamModel for Nb containing steels of different compositions. The effects of Nb on the ferrite nucleation rate and grain growth rate are discussed and quantified. A new model is then developed by incorporating the Nb factors for the ferrite nucleation rate and grain growth rate. Dilatometry results from both isothermal transformation and continuous cooling experiments for different steels are then utilised to check the applicability and accuracy of the new model.

## 7.2 Comparisons between experimental data and CamModel predictions

CamModel has been briefly introduced in Chapter 4. A flowchart describing the model is shown in Figure 7.1. Chemical compositions, prior austenite grain size, and cooling parameters are from input files. It firstly carries out thermodynamic calculations to determine phase boundaries. At each temperature step and each time step, the free energy is calculated, and nucleation and growth rates of each

phase are calculated. Then the calculation comes to the next temperature and time step, until the transformation is finished.



Figure 7.1: Flowchart illustrating the basic structure of the CamModel [4].

In order to check the accuracy of the model, its predictions for the isothermal transformation kinetics at 750°C and 700°C for steels 1-5 have been compared with the experimental data, which have already been described in Section 6.3, as shown

in Figures 7.2 and 7.3. The Nb contents of steels 1-5 are 0, 0.009 wt. %, 0.028 wt. %, 0.029 wt. %, and 0.045 wt. % respectively. In addition, the carbon contents in steels 1, 2, 3, and 5 are all ~ 0.1 wt. %, but it is ~ 0.2 wt. % in steel 4. Before the isothermal transformations at 750°C or 700°C, steels 1-4 were austenitised at 1250°C for 5 seconds, 60 seconds, 300 seconds, and 150 seconds, respectively, and thus their average prior austenite grain sizes were all ~80  $\mu$ m. However, steel 5 with the highest Nb content was austenitised at 1250°C for 300 seconds before the isothermal transformations, in order to fully dissolve the pre-existing Nb(C,N) precipitates, and its average prior austenite grain size was ~200  $\mu$ m.



Figure 7.2: Comparisons of isothermal transformation kinetics of steels 1, 2, 3 and 5 at 750°C between dilatometer data and the existing CamModel predictions.



Figure 7.3: Comparisons of isothermal transformation kinetics of steels 1, 2, 3 and 4 at 700°C between dilatometer data and the existed CamModel predictions.

From Figures 7.2 and 7.3, it can be seen that the existing CamModel predictions are faster than the experimental results for the Nb free steel 1 at both 750°C and 700°C. However, for transformation in the Nb containing steels at 750°C, the CamModel predictions are much slower than the experimental results, and the final ferrite fractions are also significantly lower than the experimental results. For isothermal transformation at 700°C, the predictions are much better, but there are still large differences for steels 2 and 3. It can be seen that the existing CamModel underestimates the effects of Nb on transformation kinetics at 750°C and 700°C. However, steel 1 is Nb free, and thus this indicates that some other parameters in the model may also need to be modified. Nucleation and grain growth are the two stages of a typical diffusional transformation, and the nucleation rate and the grain growth rate are the key factors which affect the transformation kinetics. Therefore, it is clear that the existing CamModel requires further development, especially for the effects of Nb on transformation rate and the grain growth rate.

### 7.3 Modification of the nucleation rate

The experimental results presented in Chapter 6 have indicated that steels with a higher Nb content have a slower nucleation rate. If all Nb atoms are in solid solution at the beginning of the phase transformation, they are likely to be present at higher concentrations at prior austenite grain boundaries. From classic solute drag theory, if many solute atoms are segregated at a boundary, there is a solute-boundary interaction energy  $E'_0$ . It is reasonable to assume the solute-boundary interaction energy increases the critical energy for ferrite nucleation. As a result, the ferrite nucleation rate is decreased due to the presence of solute Nb atoms. The effect of solute Nb atoms on the nucleation rate can be expressed by adding a 'Nb factor',  $E_{Nb}$ , to the classic nucleation rate used in this research can be expressed in the following equation:

$$I_b^j = \frac{k_B T}{h} \frac{K_1^J}{\delta^2} exp\left[-\frac{\left(K_2^j [G^* + E_{Nb}] + Q\right)}{k_B T}\right]$$
Equation 7.1

where  $E_{Nb}$  is the Nb factor which influences the critical energy for ferrite nucleation. From classic solute drag theory [75, 77],  $E'_0 \sim k_B T$ , therefore, the Nb effect on the critical energy for ferrite nucleation is proposed in this work as:

$$E_{Nb} = \frac{\alpha k_B T}{\kappa_2^j} C_{Nb}$$
 Equation 7.2

where  $C_{Nb}$  is the Nb content in weight percent, and  $\alpha = -75$  is a constant chosen to fit the experimental results. The values of the other constants remain the same as in CamModel.

In the pre-existing CamModel, the effect of Nb on the nucleation rate is not considered, and the nucleation rate is merely calculated using the classic Equation 2.21, without the Nb factor,  $E_{Nb}$ . The calculated nucleation rates for steels 1-3 during isothermal holding at 750°C are shown in Figure 7.4. It can be seen that steel 3 with the highest Nb content has the fastest nucleation rate in the three steels. However, if the effect of Nb is incorporated, i.e. the Equations 7.1 and 7.2 are applied, the modified nucleation rates for steels 1-3 can be calculated and have been plotted in Figure 7.5. The Nb free steel 1 has a much faster ferrite nucleation rate than steels 2 and 3, and is much more consistent with the experimental results shown in Chapter 6. Modified nucleation rates at the beginning of an isothermal transformation at a temperature between 675°C and 750°C for steels 1-3 have also been calculated and plotted in Figure 7.6. Steel 3 with a higher Nb content always has the slowest nucleation rate, and steel 1 always has the fastest nucleation rate. After incorporation of the Nb effect, the critical energy for nucleation has been changed to  $(G^* + E_{Nb})$ , therefore the curves of the modified critical energy for nucleation as a function of temperature for steels 1-3 have been calculated and plotted in Figure 7.7. The presence of solute Nb atoms segregated at prior austenite grain boundaries increases the critical energy for nucleation, and thus steel 3 requires more energy for ferrite nucleation than steels 1 and 2.



Figure 7.4: Calculated ferrite nucleation rate as a function of holding time at 750°C for steels 1-3 using the pre-existing CamModel without the incorporation of the Nb factor (Equation 2.21).



Figure 7.5: Calculated ferrite nucleation rate as a function of holding time at 750°C for steels 1-3 using the modified nucleation model with the effect of Nb being taken into account (Equations 7.1 and 7.2).



Figure 7.6: Calculated ferrite nucleation rate as a function of temperature for steels 1-3 using the modified nucleation model with the effect of Nb being taken into account (Equations 7.1 and 7.2).



Figure 7.7: Calculated critical energy for ferrite nucleation as a function of temperature for steels 1-3 using the modified nucleation model with the effect of Nb being taken into account (Equations 7.1 and 7.2).

However, Equation 7.1 was derived from the reconstructive transformation from austenite to ferrite. The nucleation rates for other phases e.g. Widmanstätten ferrite, bainite and martensite should be calculated separately. Therefore, the application range for Equation 7.1 has a minimum temperature limit. From the optical microscope images for steels 1 and 3 after 15 minutes isothermal transformations at 650°C or 600°C shown in Figure 7.8, many displacive transformation products can

be seen. This research has focussed on the effect of Nb on the transformation from austenite to ferrite because that is of most importance to the range of industrial steels considered. It has been discussed in Chapter 6 that the effect of Nb on displacive transformations should be different from that on reconstructive transformations, and therefore, the new model developed should only be applicable for isothermal transformation above 650°C.



Steel 1 at 650°C

Steel 3 at 650°C



Steel 1 at 600°C

Steel 1 at 600°C

Figure 7.8: Optical microscopy images of steel 1 with 5 seconds austenitisation at 1250°C and then isothermally transformed at 650°C or 600°C for 15 minutes, and steel 3 with 5 minutes austenitisation at 1250° and then isothermally transformed at 650°C or 600°C for 15 minutes.

# 7.4 Effects of Nb on grain growth

The retardation effects of Nb on ferrite grain growth have already been discussed in Chapter 6. The solute drag effect caused by solute Nb atoms is the major reason for the retardation of ferrite grain growth in Nb containing steels, and the particle pinning effect caused by Nb(C,N) particles has a much smaller contribution. Solute Nb atoms segregated at prior austenite grain boundaries can reduce the mobility of the austenite/ferrite interface. The reconstructive transformation is controlled by carbon diffusion, and therefore, the solute drag effect can be considered to be a reduction in the carbon diffusion coefficient. Sellars [76] proposed a constant factor, f, to the activation energy for the carbon diffusion to describe the effect of Nb on carbon diffusion during recrystallisation, and the value of f was chosen to be 5000. Lee [64] applied this model to the phase transformation from austenite to ferrite in Nb containing steels, as shown in Equation 7.3:

$$D = D_C \times e^{\left(-\frac{Q}{RT}\right)} = D_C \times e^{\left(-5000X_{Nb}\left(\frac{2750}{T} - 1.85\right)\right)}$$
 Equation 7.3

where  $D_C$  is the diffusion coefficient of carbon,  $X_{Nb}$  is the mole fraction of Nb, and T is the temperature (K).

The values of the solute drag factor  $e^{\left(-5000X_{Nb}\left(\frac{2750}{T}-1.85\right)\right)}$  for steels 2 and 3 between 675°C and 750°C have been calculated and are listed in Table 7.1. The Nb solute drag factor has been incorporated into the CamModel, and then the predicted isothermal transformation kinetics curves for steels 2 and 3 at 750°C, 725°C and 700°C are compared with experimental results, as shown in Figures 7.9-7.11, respectively. It can be found that the predictions are then much faster than the experimental results at these temperatures.

	Steel 2	Steel 3
750°C	0.798	0.496
725°C	0.784	0.469
700°C	0.769	0.442
675°C	0.754	0.416

Table 7.1: Values of the Nb solute drag factor from Lee's model [64] for steels 2 and 3



Figure 7.9: A comparison of the predictions made after Incorporating Lee's Nb solute drag factor into the CamModel with the experimental data from steels 2 and 3 isothermal transformations at 750°C.



Figure 7.10: A comparison of the predictions made after Incorporating Lee's Nb solute drag factor into the CamModel with the experimental data from steels 2 and 3 isothermal transformations at 725°C.



Figure 7.11: A comparison of the predictions made after Incorporating Lee's Nb solute drag factor into the CamModel with the experimental data from steels 2 and 3 isothermal transformations at 700°C.

Militzer and Fazeli [30, 31] also incorporated a constant to modify the ferrite growth rate in Nb containing steels, as shown in Equation 7.4:

$$\frac{dR_f}{dt} = D_C \frac{C^{\gamma} - C_0}{C^{\gamma} - C^{\alpha}} \frac{1}{R_f} \left( 1 + \frac{D_C \alpha C_{Nb}}{R_f} \right)^{-1}$$
 Equation 7.4

where  $R_f$  is the radius of the growing ferrite grain,  $D_c$  is the carbon diffusion coefficient in austenite,  $C_{Nb}$  is the Nb concentration, and  $\alpha$  is a constant to describe the solute drag effect.

In both Equations 7.3 and 7.4, a Nb solute drag factor was used as a multiplier on the value of the carbon diffusion coefficient, and thus both of them can be mathematically considered as an increment of the activation energy for carbon diffusion. The factor in Equation 7.3 varies with both temperature and Nb content, but it is a constant in Equation 7.4. Table 7.1 shows that the solute drag factor in Equation 7.3 decreases with decreasing temperatures and increasing Nb content, but it still underestimates the solute drag effect on grain growth rate, as shown in Figures 7.9-7.11. As a result, the solute drag factor for steels at various temperatures should be accurately calculated, and then a suitable expression for it can be obtained.

In this research, the solute drag effect of Nb is expressed as f(Nb,T), because it is affected by Nb content and temperature, as shown in the new Equations 7.5 and 7.6:

$$D = D_C \times f(Nb, T) = D_0 \times e^{\left(-\frac{Q_C}{RT}\right)} \times e^{\left(-\frac{E_{Nb,T}}{RT}\right)} = D_0 \times e^{\left(-\frac{Q_C + E_{Nb,T}}{RT}\right)}$$
Equation 7.5
$$f(Nb, T) = \exp\left[\frac{f_1(T) + RT \cdot f_2(Nb)}{RT}\right]$$
Equation 7.6
$$= \exp\left[\frac{f_1(T)}{RT} + f_2(Nb)\right]$$

where  $f_1(T)$  is a function of temperature, and  $f_2(Nb)$  is a function of Nb content.

Since the f(Nb,T) expresses the delay effect of Nb, its value should be positive but less than 1. In order to accurately determine the value of f(Nb, T), many isothermal transformation kinetic curves for steels 2 and 3 at various temperatures have been calculated using different values of f(Nb,T) between 0 and 1, and the predicted curves were then compared with the experiment results. Figures 7.12-7.15 are tests of f(Nb,T) values for steel 2 at different temperatures. Figures 7.16-7.19 are tests for steel 3 at different temperatures. From these curves, the values f(Nb, T) at each temperature have been determined and then plotted as points in Figure 7.20. Using these points, the relationships between the solute drag factor f(Nb,T) and temperatures for steels 2 and 3 can be extrapolated as solid lines. Since the value of f(Nb,T) was chosen to be between 0 and 1, a higher value indicates a weak solute drag effect, and a low value represents a strong solute drag effect. At the same temperature, a higher value of f(Nb,T) also indicates a faster transformation rate. From Figure 7.20, it can be seen that the relationship between the solute drag factor and temperature also has the typical C shape. At a high isothermal transformation temperature, the reconstructive transformation is slow, and thus the solute drag effect which delays the transformation has a small influence on the kinetic curve. With decreasing isothermal transformation temperature, the transformation becomes faster and faster because there is more supercooling, and the solute drag effect becomes more important. However, when the temperature continues to decrease, displacive transformations become possible which are much faster than the reconstructive transformation. The solute drag effect has a much weaker effect on a displacive transformation, because the large stored energy makes displacive

transformation products much easier to 'break through' the clusters of solute Nb atoms. A new equation can therefore be generated to describe the effects of Nb content and temperature on the solute drag factor f(Nb,T), as shown in Equation 7.7:

$$f(Nb,T) = \text{EXP}\left[\frac{a_{n}T^{n} + \dots + a_{2}T^{2} + a_{1}T + a_{0} + bRT\ln(C_{Nb})}{RT}\right]$$
Equation 7.7

where  $a_0$ ,  $a_1$ ,...,  $a_n$ , and b are all constants, T is the temperature (K), and  $C_{Nb}$  is the Nb content.

From the experimental results, n=3,  $a_3$ =0.0504,  $a_2$ =-142.9764,  $a_1$ =134939.18,  $a_0$ =-42390786.19, and b=-0.321568.



Figure 7.12: Modified CamModel predictions of the isothermal transformation kinetics at 750°C with different f(Nb,T) values for steel 2 using Equation 7.7.



Figure 7.13: Modified CamModel predictions of the isothermal transformation kinetics at 725°C with different f(Nb,T) values for steel 2 using Equation 7.7.



Figure 7.14: Modified CamModel predictions of the isothermal transformation kinetics at 700°C with different f(Nb,T) values for steel 2 using Equation 7.7.



Figure 7.15: Modified CamModel predictions of the isothermal transformation kinetics at 675°C with different f(Nb,T) values for steel 2 using Equation 7.7.



Figure 7.16: Modified CamModel predictions of the isothermal transformation kinetics at 750°C with different f(Nb,T) values for steel 3 using Equation 7.7.



Figure 7.17: Modified CamModel predictions of the isothermal transformation kinetics at 725°C with different f(Nb,T) values for steel 3 using Equation 7.7.



Figure 7.18: Modified CamModel predictions of the isothermal transformation kinetics at 700°C with different f(Nb,T) values for steel 3 using Equation 7.7.



Figure 7.19: Modified CamModel predictions of the isothermal transformation kinetics at 675°C with different f(Nb,T) values for steel 3 using Equation 7.7.



Figure 7.20: The relationship between f(Nb, T) and temperature for steels 2 and 3 in the new model which contains the modified factor for the influence of Nb taking into account temperature and Nb concentration.
## 7.5 Accuracy of the new model

The new equations for nucleation rate and ferrite grain growth rate developed in this research have been incorporated into the previous version of CamModel. The equations are based on the isothermal transformation results of steels 1-3. In order to check their accuracy, the new model has been used to predict the isothermal transformation kinetics for steels 4 and 5, and the kinetic curves for isothermal transformation for steels 1-3 at 735°C which is a new temperature, have also been predicted. All of these predictions have then been compared with their experimental results, as shown in Figures 7.21-7.24. It can be seen that the predictions are quite consistent with the experimental results for all the steels at these temperatures. However, there is only a slightly deviation for steel 1 after isothermal transformation at 675°C shown in Figure 7.24. From the microstructural analysis in Chapter 6, there are some displacive transformation products in the sample of steel 1 which has been isothermally transformed at 675°C. From Figure 7.24, the experimental curve appears to be a straight line at the beginning of the transformation, which looks like the typical displacive transformation curve, however, the predicted curve looks more parabolic, which indicates that there are mainly reconstructive transformation products present. Therefore, the problem in this case has possibly arisen from the thermodynamic calculations for the phase boundary temperatures. For Nb containing steels, there are mostly reconstructive transformations at 675°C, and in those cases the new model works guite successfully.



Figure 7.21: Comparisons between new model predictions and experimental data for steels 1, 2, 3 and 5 after isothermal transformations at 750°C.



Figure 7.22: Comparisons between new model predictions and experimental data for steels 1, 2, and 3 after isothermal transformations at 735°C.



Figure 7.23: Comparisons between new model predictions and experimental data for steels 1, 2, 3 and 5 after isothermal transformations at 700°C.



Figure 7.24: Comparisons between new model predictions and experimental data for steels 1, 2, 3 and 5 after isothermal transformations at 675°C.

The new model has also been utilised to predict the continuous cooling kinetics for the steels, and the predictions have been compared with the dilatometry data and the old CamModel predictions. Both the 0.1% transformation temperature (T0.1%) and the 5% transformation temperature (T5%) can indicate the transformation start temperature during continuous cooling. The 50% transformation temperature (T50%) is another important parameter to describe the continuous cooling kinetics, and it is also quite important for steels which contain multiple phases, e.g. dual phase steels. Comparisons of T0.1%, T5%, and T50% for steel 1 using various cooling rates are plotted in Figures 7.25-7.27, respectively. It can be seen that the new model predictions are quite similar to the pre-existing CamModel when the cooling rate is quite slow. Since steel 1 is Nb free, both the new model and the pre-existing CamModel predictions are not far away from the experimental results. Comparisons of T0.1T, T5%, and T50% for steel 3 using various cooling rates are plotted in Figures 7.28-7.30, respectively. For the Nb containing steel 3, the new model predictions are nearly overlapped with the experimental results, which is a significant improvement when compared to the pre-existing CamModel. These successful predictions on the continuous cooling transformations validate and indicate the accuracy of the new model.



Figure 7.25: Comparison of the 0.1% transformation temperatures of steel 1 between the dilatometer data and model predictions.



Figure 7.26: Comparison of the 5% transformation temperatures of steel 1 between the dilatometer data and model predictions.



Figure 7.27: Comparison of the 50% transformation temperatures of steel 1 between the dilatometer data and model predictions.



Figure 7.28: Comparison of the 0.1% transformation temperatures of steel 3 between the dilatometer data and model predictions.



Figure 7.29: Comparison of the 5% transformation temperatures of steel 3 between the dilatometer data and model predictions.



Figure 7.30: Comparison of the 50% transformation temperatures of steel 3 between the dilatometer data and model predictions.

Tata Steel RD&T has some previous dilatometry results for isothermal transformations carried out at various temperatures for Nb free and Nb containing steels, and the results have been compared with the new model predictions to provide an additional check of its accuracy. The Nb contents of the steels are 0 wt. %, 0.011 wt. %, and 0.05 wt. % respectively. The new model can accurately

predict the overall isothermal transformation kinetic curves, but Tata Steel's previous results only contain the interrupted dilatometer data, without any optical microscopy images to measure the final ferrite fraction. Therefore, only the isothermal transformation start times can be compared. The comparison of the TTT diagrams between the new model and the Tata Steel's previous data for the Nb free steel, the 0.011 wt. % Nb steel, and the 0.05 wt. % Nb steel are shown in Figures 7.31-7.33, respectively. It can be seen that the predicted TTT diagrams using the new model developed in this research are generally consistent with Tata Steel's previous experimental data.

After making a comparison with the isothermal transformation kinetic curves for steels 1-5 at various temperatures, the CCT diagrams for steels 1 and 3, and the Tata Steel previously unseen results, the new model has been validated and shown to be an accurate model to predict the transformation kinetics for these type of low alloy Nb containing steels, and the modifications on the nucleation rate and the grain growth rate calculations appear to be successful.



Figure 7.31: TTT diagrams of the new model predictions and Tata Steel previous results for a Nb free steel.



Figure 7.32: TTT diagrams of the new model predictions and Tata Steel previous results for a steel with 0.011 wt. % Nb.



Figure 7.33: TTT diagrams of the new model predictions and Tata Steel previous results for a steel with 0.05 wt. % Nb.

## 7.6 Summary

This chapter has presented the incorporation of the effects of Nb into the pre-existing CamModel via new equations which have been proposed in this research, and the subsequent validation of the new model. The retardation effect of Nb on transformation kinetics is caused by the effect on both the nucleation rate and the effect on the grain growth rate. The effect of Nb on the nucleation rate can be attributed to the increase in critical energy for ferrite nucleation. According to many previous researches, the solute drag effect of Nb on grain growth rate can be considered as an increment in the activation energy for carbon diffusion. After examining various values of the solute drag factor, the effects of temperature and Nb content on the solute drag factor have been investigated, and an equation has been generated to describe the relationships. The effects of Nb on nucleation rate and grain growth rate have been incorporated into the pre-existing CamModel, and the new model predictions are quite consistent with experimental results for different steels not used in the development of the modified model which were isothermally transformed at various temperatures. The accuracy of the new model has been proved by comparing the predictions are also quite consistent with Tata Steel's previous dilatometry data from another batch of steels with different chemical compositions.

## 8 Conclusions and Suggestions for Further Work

The effects of niobium on phase transformations from austenite to ferrite in low alloy steels have been investigated in this research. During austenitisation, both solute niobium atoms and niobium carbo-nitride precipitates inhibit austenite grain growth, however it has been shown that solute niobium atoms appear to have a stronger retardation effect on austenite grain growth than niobium carbo-nitride precipitates. For steels with different niobium contents, the same austenite grain size can be obtained by adjusting austenitisation time and temperature, and thus the influence of austenite grain size on subsequent phase transformation can be eliminated. For steels with different niobium contents but the same austenite grain size and the same heat treatment, their final ferrite grain sizes have been shown to be quite similar. Therefore, it has been demonstrated that niobium has a refinement effect on the austenite grain size, which thus results in an indirect refinement effect on the ferrite grain size.

Dilatometer results indicate that solute niobium atoms have a retardation effect on both isothermal transformations and continuous cooling from austenite to ferrite, via a solute drag effect. There is a significant effect on isothermal transformation above 650°C, and on continuous cooling transformations with a slow cooling rate. However, for a lower isothermal transformation temperature or a faster continuous cooling rate, the retardation effect is much reduced. From microstructural analysis of interrupted isothermally transformed samples, the solute drag effect caused by the segregation of niobium atoms at austenite/ferrite interface has been investigated. Both the ferrite nucleation rate and grain growth rate have been shown to be delayed by the presence of solute niobium atoms. Solute niobium atoms also enlarge the temperature range for diffusional transformation, and thus the final microstructure is affected. However, if solute niobium atoms are precipitated as niobium carbo-nitride particles before subsequent transformation, the particle pinning effect is much weaker than the solute drag effect. The particle size distribution is largely dependent on the precipitation heat treatment temperature and time, and particles with different sizes and locations have been shown to have different effects on the transformation.

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Most previous metallurgical models do not consider the effects of niobium on phase transformations. CamModel, which is one of the best metallurgical models in this respect, still required further development for niobium containing steels, because its predicted transformation kinetics did not agree with the experimental observations. In this research, the existing CamModel has been modified to better take into account the influence of niobium on phase transformations. Solute niobium atoms have been considered to result in a reduction in the nucleation rate and an increment in the activation energy for carbon diffusion. After incorporation of these effects of niobium into new equations which have been proposed in this research, the new model has been shown to accurately predict the transformation kinetics for all of the steels used in the research during both isothermal transformation and continuous cooling. Transformation kinetics data from another source have also been utilised for model validation, and then it has been shown that there is generally very good agreement between the model predictions and the experimental data. The improvements made to the model will allow industry to develop an improved predictive capability for transformations in Nb-containing low alloy steels, with a view to process optimisation, cost reduction and improvements in mechanical properties.

Current work does not measure the amount of solute Nb atoms after interrupted isothermal transformations, due to the limitation of equipment and time. It would be quite beneficial if it can be accurately measured in further work, and thus the solute drag force caused by Nb can be accurately calculated using the classic solute drag theory, and the precipitation kinetics of Nb(C,N) particles can also be analysed. During transformations from austenite to ferrite, Nb(C,N) particles are precipitated simultaneously as the transformation progresses, and therefore a precipitation kinetics model could be incorporated into the phase transformation model. Although the combination of the two models will be a quite complex, this is a worthwhile scientific endeavour and is likely to further improve the accuracy. Isothermal transformations at lower temperatures can also be tried in further work, and thus the effects of Nb on displacive transformation to bainite or martensite can be studied. Effects of hot rolling on Nb containing steels can be incorporated into the current

model, in order to expand its applications in industry. A subroutine for the prediction of mechanical properties could also be incorporated, because the final microstructure, grain size, precipitation strengthening can all be predicted based on the current research, and then the new model will be even more beneficial for industry. In addition, the current study on solute drag effect caused by niobium is based on 2-D microstructural analysis, but would be interesting to perform a high resolution 3-D microstructural characterisation for the solute drag effect in future work.

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