MODELLING AND MEASUREMENT OF THE CONTINUOUS-COOLING-PRECIPITATION KINETICS OF Nb(CN) IN HSLA STEELS

by

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ABSTRACT

The addition of Nb significantly retards recovery and recrystallization through solute drag and precipitation pinning effects. It is important to describe the precipitation behaviour precisely because finely distributed precipitates retard the restoration process abruptly. The isothermal precipitation behaviour has been studied frequently. However, during industrial hot deformation processing, the temperature decreases continuously, so that isothermal data cannot be applied directly to predict the precipitation under these conditions. The focus of this study is therefore on the CCP (Continuous-Cooling-Precipitation) behaviour of Nb carbonitride in austenite.

To calculate the CCP behaviour, isothermal PTT (Precipitation-Time-Temperature) data in terms of the P_s (precipitation start) and P_f (precipitation finish) times are first required. In 1987, Dutta and Sellars developed a thermodynamic model to predict P_s times for the precipitation of niobium carbonitride, and in 1989, Liu and Jonas developed a model for titanium carbonitride. In the present work, the L-J (Liu-Jonas) model is used to calculate the P_s time at a given temperature from experimental data. Since the prediction models are only limited to the P_s times, a new calculation method for the P_f time, based on reaction kinetics and classical nucleation and growth theory, is proposed in this study. Two models are developed to follow the precipitation process, and the time exponent and rate constant for the kinetics are formulated for each model. The additivity rule, which was developed by Scheil in 1935, is then used to calculate the extent of precipitation during continuous cooling.

Isothermal precipitation rates for 0.040% Nb steels are measured experimentally by the stress relaxation method. The CCP behaviour is then calculated and is then examined by continuous cooling testing, using a hot deformation dilatometer. Precipitates are observed by transmission electron microscopy of specimens quenched after a period of cooling at various cooling rates. The P_s and P_f times estimated from the particle size data show good agreement with the calculated CCP behaviour.

RESUME

L'addition du niobium retarde de manière significative la restauration et la recrystallisation par les effets de trainage du niobium en solution et d'ancrage du niobium précipité. La description précise des réactions de précipitation est importante car une fine distribution de précipités peut retarder brutalement le processus d'adoucissement. La précipitation isotherme a fait l'objet de nombreuses études. Cependant, lors d'un procédé industriel de déformation à chaud, la température décroit continuellement, de sorte que les données obtenues pour un comportement isotherme ne peuvent pas être directement utilisées pour prédire la précipitation dans ces conditions. Le but de cette étude est donc la précipitation lors d'un refroidissement continu CCP (Continuous-Cooling-Precipitation) du niobium dans l'austénite.

Pour calculer le comportement CCP. des données isothermes PTT (Precipitation-Time-Temperature) en fonction de P_s (temps de début de précipitation) et P_f (temps de fin de précipitation) sont d'abord requises. En 1987, Dutta et Sellars ont développé un modèle thermodynamique pour prédire les temps P_s de précipitation du niobium, et en 1989, Liu et Jonas ont développé un modèle pour le titane. Dans le travail présent, le modèle L-J (Liu-Jonas) a été utilisé pour calculer les temps P_s à une température donnée à partir de données expérimentales. Puisque les prédictions sont limitées au seul calcul du temps P_s , une nouvelle méthode de calcul pour les temps P_f , basée sur la théorie de cinétique et la théorie classique de nucléation et de croissance, est suggérée dans cette étude. Deux modèles sont proposés pour suivre le processus de précipitation, et l'exposant temps et la constante de vitesse des cinétiques ont été exprimés pour chacun des modèles. La régle d'additivité, qui a été développe par Scheil en 1935 a été ensuite utilise pour calculer l'étendue de la précipitation lors du refroidissement continu.

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Les vitesses de précipitations isothermes pour des aciers contenant 0.04% de niobium ont été mesures expérimentalement par la méthode de relaxation de contrainte. Le comportement CCP a été calculé et par la suite étudié par des tests de dilatométrie à chaud durant refroidissement continu. Les précipités d'échantillons trempés, aprés une certaine durée de refroidissement selon différentes vitesses de refroidissement, ont été observés par microscopie électronique en transmission. Les temps P_s et P_f estimés à partir des données des tailles des précipités, sont en bon accord avec ceux calculés par la méthode du comportement CCP.

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CHAPTER I INTRODUCTION

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Niobium is one of the most commonly used microalloying elements in steels. It is used primarily in hot rolled products, where it retards the restoration process and produces fine and elongated austenite structures. The retardation of recrystallization due to Nb has been discussed by many investigators and it is attributed to i) solute drag and ii) precipitation of fine Nb(CN). The recrystallization retardation behaviour changes drastically when Nb forms precipitates. Thus, PTT (Precipitation-Time-Temperature) diagrams were introduced to show the exact relationship between the appearance of precipitates and time and temperature. These diagrams have been widely used to verify that the abrupt retardation of recrystallization occurs after the start of precipitation. They have also been instrumental in the optimum design of controlled rolling schedules.

In the past, isothermal studies were used to approximate the microstructural changes taking place during industrial hot deformation processing. With the need for increasing precision, such approximations are inadequate. For example, for the phase transformation of austenite, CCT (Continuous-Cooling-Transformation) diagrams are frequently referred to instead of the IT (Isothermal-Transformation) diagrams. The CCP (Continuous-Cooling-Precipitation) behaviour is therefore necessary to accurately predict the precipitation process characteristics of industrial hot deformation procedures. However, until now, few attempts have been made, either experimentally or theoretically, to understand and model precipitation during continuous cooling. Therefore, the main objective of this study is to generate a relationship between isothermal (PTT) and continuous cooling (CCP) precipitation behaviour, analogous to the case of austenite transformation. The present thesis is divided into the following chapters:

In Chapter 2, the role of Nb in austenite and the modes and kinetics of precipitation of Nb(CN) in austenite are reviewed.

In Chapter 3, methods for predicting the P_s times and a new model for predicting the P_f times during isothermal holding are described. A theoretical model to predict the continuous cooling behaviour from isothermal data based on the additivity rule is proposed.

In Chapter 4, the experimental materials and methods used to observe the precipitation behaviour during isothermal holding and continuous cooling are outlined.

In Chapter 5, the isothermal P_s and P_f times obtained from the experimental measurements are shown, along with the particle size evolution observed by TEM during continuous cooling testing.

In Chapter 6, the relevant thermodynamic parameters are calculated using the present model and are compared to the experimentally determined values. The mechanisms associated with the various stages of relaxation behaviour are discussed. The method used of determining the P_s and P_f times from the experimental particle size evolution data is also described and the results are compared to the predicted values.

Finally, the general conclusions of this study are summarized in Chapter VII.

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CHAPTER II

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THE PRECIPITATION OF NIOBIUM CARBO-NITRIDE IN AUSTENITE

The addition of transition metals, such as Nb, Ti and V, improves the mechanical properties and microstructure of hot rolled steel. These are called microalloying elements because small additions can greatly change the properties and microstructures of such steels.

In the temperature range of hot rolling, microalloying elements can be dissclved during reheating and then reprecipitated during subsequent hot rolling. The finely distributed precipitates are responsible for the retardation of recrystallization and the consequential accumulation of strain leading to a pancaked austenite grain structure. The pancaked austenite structure has a high value of effective surface area per unit volume (S_v) , which increases the ferrite nucleus density, and results in the formation of a highly desirable fine ferrite and pearlite microstructure after transformation. Even when the microalloying elements do not precipitate, the substitutional atoms still affect the properties and microstructures of the steel through the solute drag effect. However, the influence of precipitates is much greater than that of the solute.

In this chapter, the effect of Nb addition in steel is reviewed. The process of Nb carbonitride precipitation and general aspects of precipitates are also summarized.

II.1. Nb IN STEEL

In the early 20th century, the most important property of steel was its tensile strength. At the time, C was usually employed as an inexpensive alloying element to produce high strength levels [1]. During World War II, the use of welding became widespread and one of the problems that most frequently occurred was brittle fracture of the heat affected zone (HAZ). Carbon additions were recognized as being harmful to the HAZ fracture properties. Therefore, a high manganese-to-carbon ratio was adopted to lower the carbon contents. As early as 1924, Arrowsmith [2] pointed out the advantage of grain refinement for strength and toughness. Following Fickering [1], grain refinement has been found to be the only method of increasing both the yield stress and toughness of materials, as shown in Fig. 2.1.

To produce fine grained ferrite, the austenite grain size must be controlled because the ferrite grain size is closely related to the austenite grain size [3, 4]. During hot rolling, two methods are usually applied to refine the grain size of ferrite; i) control of the austenite microstructure during rolling, and ii) control of the cooling rate after rolling

During hot rolling, control of the austenite microstructure is important because it dictates the number of nucleation sites available for the phase transformation. In the case of C-Mn steels, recrystallization after deformation is so fast that the rolling must be done at very low temperatures to obtain a deformed grain structure before transformation. This requires increases in mill power and causes the products to have nonuniform gauge. Niobium is used mainly to overcome this kind of shortcoming because it expands the region of non-recrystallization [9] (Fig. 2.2). During the late 50's and early 60's, Nb bearing steel was developed [7] and controlled rolling was introduced to increase the toughness of the steel. The objective of controlled rolling is to increase the number of nucleation sites before transformation. This is achieved in the Nb steels by suppressing recrystallization and rolling at a relatively low temperature with an increased reduction at the final pass [8].

The cooling rate after rolling is also critical in the control of ferrite grain size. When a fast cooling rate is used, grain growth is suppressed and a fine grain structure is obtained [5, 6]. The cooling rate should therefore be kept as high as possible to produce a refined ferrite grain structure, provided it does not reach the point where diffusionless phase transformations, i.e. bainitic and martensitic transformations, occur. The critical cooling rate depends on chemical composition and initial austenite grain size.

The reason why Nb retards recrystallization has been discussed many times, and it has been established that the basic mechanisms are solute drag



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Fig. 2.1 The factors affecting yield strength and impact transition temperature (ITT). The numbers refer to the change in transition temperature per 15 MPa increase in yield strength [1].



Fig. 2.2 Effect of deformation temperature and initial grain size on critical reduction required for recrystallization in plain carbon and niobium steels [9].

[10-15] and precipitation pinning [11-13, 16-19]. A diagram which shows these effects clearly is shown in Fig. 2.3 [13]. At high temperatures, there is no Nb(CN) precipitation and the retardation is attributed to solute drag. At lower temperatures, precipitation occurs, recrystallization is delayed and the pinning effect is much stronger than solute drag.

Elements such as Nb and Ti are easily precipitated in the temperature range of hot rolling and are thus used frequently to control austenite recrystallization. The solubility products of various carbides and nitrides found in the literature are summarized in Table 2.1 and in Fig. 2.4 [35]. It can be seen from this diagram that complete solution can be obtained for most microalloy precipitates at high temperatures in the austenite range. The exceptions are VC, which is taken into solution at relatively low temperatures, and TiN, which is extremely stable and is only soluble in austenite at very high temperatures.

Two species of niobium precipitate, NbC and NbN, are formed in HSLA steels. However, Nb(CN) is frequently used to denote the precipitating species because NbC and NbN are known to be completely mutually soluble. In most cases, the atomic ratio between substitutional solute atoms (Nb) and interstitial atoms (C, N) in Nb(CN) is assumed to be stoichiometric. However, the combination of Nb and C, N is found in practice to be non-stoichiometric because of vacancies in the interstitial sites of the Nb(CN) crystal lattice [25].

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Fig. 2.3 Recrystallization/precipitation diagram for plain carbon and niobium steels [13].

Species of	Temp. range	$\log[M][I] = A + B/T$			
precipitate	(°C)	А	В	reī.	
	1050~1150	3.31	-7970	20	
	1050~1300	3.42	- 79 00	21	
	1000~1300	3.18	-7700	22	
NbC	1000~1300	3.70	-9100	23	
	950~1050	4.37	-9290	24	
	$1000 \sim 1250^{*}$	3.40	-7920	25	
	900~1300*	2.81	-7020	26	
	900~1200*	3.11	-7520	27	
	1190~1330	2.80	-8500	24	
NbN	1100~1300	2.89	-8500	27	
	_*	2.86	-7927	26	
Nb(CN)	900~1300	2.26	-6770	28	
	1000~1250	4.03	-8720	29	
TiC	950~1350	2.75	-7000	28	
	900~1300	5.33	-10475	30	
	1000~1300	4.94	-14400	31	
TiN	1100~1350	5.19	-15490	32	
	1200~1300	3.82	-15020	33	
AlN	1050~1350	1.95	-7400	34	
	950~1300	1.48	-7500	74	
	950~1350	1.03	-6770	28	
VC	-	6.72	-9500	24	
VN	900~1100	3.46	-8330	28	

Table 2.1Solubility products of Nb, Ti, Al and V carbide,
nitride and carbonitrides.

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*carbide or nitride assumed to be $MI_{0.87}$ in the analysis.



Fig. 2.4 The solubility products of Nb, Ti, Al and V carbides and nitrides [35].

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II.2. CHARACTERISTICS AND PROPERTIES OF Nb CARBONITRIDES

II.2.1. Structure of Nb Carbonitride

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Niobium shows a strong tendency to form carbonitrides, but relatively little tendency to form oxides or sulfides [78]. Cubic forms of Nb carbonitrides have been frequently reported in steels with low niobium content (0.04%). However, steels containing 0.1% C, high niobium contents (0.1%), or high nitrogen contents (0.012%) give rise to the formation of non-cubic compounds after long austenitizing treatments (150 hrs) [36-38]. Some of these have been identified as hexagonal NbN or as tetragonal Nb-O-N precipitates. When NbN precipitates in the Fe-Nb-N system, it usually has the hexagonal structure. However, when C is also present in the concentration range of typical microalloyed steels, Nb(CN) precipitates in the cubic form. Here, nitrogen substitutes randomly for carbon in the NbC lattice [26]. Nb mono carbides and nitrides exhibit complete intersolubility because carbon is randomly replaced by nitrogen. Most of the Nb compounds which can be found in HSLA steel have the NaCl type structure with Nb atoms occupying one fcc lattice and C and N occupying the other fcc lattice.

In Figs. 2.5 (a) and (b), the equilibrium diagrams of Nb-C and Nb-N, respectively, are shown. These systems display the presence of an M₂I phase in addition to the MI phase. Here, M and I represent the metal and interstitial atoms, respectively. Although the equilibrium diagram of Nb-C is generally accepted, the Nb-N phase diagram is very complex and still questionable in terms of chemical compositions and phases [39]. In the Nb-N phase diagram, detailed phases proposed by Brauer and Esselborn [40] are shown. The crystal structures and lattice parameters for the NbC and NbN phases are summarized in Table 2.2.

Lattice parameters change with the ratio of interstitial to metal atoms and decrease with increasing vacancy of interstitial sites [48]. The lattice parameter of pure stoichiometric NbC is 4.470Å and this decreases to 4.431Å for NbC_{0 77}. Pure NbN has a lattice parameter of about 4.38Å. For Nb(CN)





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Phase diagram for niobium-carbon [41].





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) Phase diagram for niobium-nitrogen [40, 42].

Phase	hase Structure Lattice parameter (Å)		Ref.
β -Nb ₂ C	Hex	a = 5.417, c = 4.974	43
γ-Nb₂C	Hex	$a = 3.127, c = 4.965 at NbC_{0.49}$ $a = 3.127, c = 4.972 at NbC_{0.50}$	44
NbC	B1	a = 4.431 at NbC _{0 77} a = 4.470 at NbC _{0 99}	44
β-Nb2N	НСР	a = 3.056, c = 4.957 at N-poor boundary a = 3.056, c = 4.995 at N-rich boundary	45
y-NbN	Distorted B1.(Tetrag.)	a = 4.385, c = 4.310 at N-poor boundary a = 4.386, c = 4.335 at N-rich boundary	40
δ-NbN	B1	a=4.381~4.392	45
δ'-NbN	Anti-NiAs	a = 2.968, c = 5.535	46
ε-NbN	TiP	a = 2.958, c = 11.272	47
TiC	B1	$a = 4.328 \text{ at TiC}_{1 0}$ $a = 4.317 \text{ at TiC}_{0 61}$	39 48
TiN	B1	a=4.24	39
VC	B1	$a = 4.131 \text{ at VC}_{0.73}$ $a = 4.166 \text{ at VC}_{0.87}$	49
VN	B1	$a = 4.066 \text{ at VN}_{0.72}$ $a = 4.140 \text{ at VC}_{1.0}$	50

Table 2.2Crystal structure and lattice parameter of several
niobium carbides and nitrides.

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precipitates, the lattice parameter has a value between those of NbC and NbN, according to the composition.

II.2.2. Nonstoichiometry

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It is a characteristic of many carbides and nitrides, and of interstitial compounds more generally, that they are liable to vary from stoichiometry. This is particularly so within the cubic (NaCl type) group. Thus, the compound is very often symbolized as MI_x , where M is the transition metal element (Nb, Ti or V), I is the interstitial element (C or N), and x (≤ 1) is the atomic ratio of I to M in the compound. Nb(CN) can be written as Nb(C_yN_{1-y})_x and this means that the fraction of interstitial sites occupied by interstitial atoms is x, which is in the range of 0.75~0.98 [25].

The degree of nonstoichiometry, i.e. the value of x, depends on the equilibrium activity of I in the compound. For example, x values as high as 0.98 in Nb carbide can be achieved when the carbide is in equilibrium with pure carbon, that is when the activity of carbon is 1.0. Since the carbon activity in microalloyed steel is generally less than 1.0, the precipitating carbide cannot be stoichiometric. The concentration of interstitial in NbC varies from $0.7 \sim 1.0$ and in Nb₂C, from $0.35 \sim 0.5$. For hexagonal carbides of the M₂I type, the non-stoichiometry is considerably smaller than for the cubic ones. As in the nitride, the composition is in the range of 0.29-0.33 N for Nb₂N, 0.4-0.5 N for NbN and 0.445-0.475 for ε -NbN [48].

Since the deviation from stoichiometry is due to the vacancies in the interstitial sites [39], the lattice parameter of the compound is a function of the degree of its non-stoichiometry. The lattice parameters of Nb(CN) are much larger than that of γ -Fe (3.54 Å). This difference causes a significant lattice mismatch between the precipitates and the austenite matrix. The free energy of formation of these compounds also varies with the non-stoichiometry. However, according to the thermodynamic analysis of Balasubramanian and Kirkaldy [51], the effect is not strong. For example, the variation in the molar free energy of NbC_x is only about 5% when the value of x is changed from 1.0 to 0.75 at 1273K. Thus, Nb(CN) is frequently used to describe precipitation despite its non-stoichiometric nature.

II.2.3. Crystallography

The shape, size and orientation of the precipitate depends on whether precipitation occurs in austenite or ferrite. There are two relevant aspects of the crystallography of precipitation to discuss; i) the orientation relationship and ii) the degree of lattice mismatch (the degree of lattice disregistry).

Davenport et al. [52] have shown that, in stainless steel, strain induced precipitates of Nb(CN) in austenite have a cube-cube relationship, i.e.:

(100)ppt//(100)_y [010]ppt//[010]_y

When Nb(CN) is precipitated in ferrite or martensite, it exhibits the Baker-Nutting orientation relationship [52, 53]:

> (100)ppt//(100)a [011]ppt//[010]a

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~₩ ∕_> The austenite transforms to ferrite with the Kurdjumov-Sachs (K-S) orientation relationship.

 $(111)_{\gamma}//(110)_{\alpha}$ $[110]_{\gamma}//[111]_{\alpha}$

Consequently, precipitates formed in γ would be related to the ferrite by the K-S relationship when observed at room temperature. If the orientation of austenite grains changes after precipitation has occurred, e.g. by grain rotations accompanying deformation or recrystallization, there would be no rational crystallographic relationship between the Nb(CN) that had formed in the γ and the final ferrite matrix. A change in the austenite grain orientation after precipitation usually cannot occur because most of the precipitation that forms in γ is strain induced, and these precipitates act to suppress subsequent recrystallization of the deformed austenite. The precipitates formed during the y to a transformation are very small in size and have a planar distribution. The ledge mechanism is often employed to explain this arrangement of precipitates. The other distinction of these interphase precipitates is their prominent contribution to the strength of the material. If a large amount of precipitation takes place in the austenite, then the amount of solute atoms which can precipitate during transformation decreases, thus the strengthening effect of the precipitates decreases.

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DeArdo et al. [54] calculated the lattice mismatch between precipitate and matrix by calculating the percent increase in the matrix lattice parameter that would be required to bring the two lattices into coincidence at the matrix/precipitate interface, i.e.

$$\% Mismatch = 100 \left(\frac{L_p - L_m}{L_m} \right)$$
 (2.1)

where L_p and L_m are the lattice parameters of the precipitate and matrix, respectively.

As seen in Table 2.3, the magnitudes of the elastic matrix strain $(\varepsilon = 0.255$ for NbC in y and $\varepsilon = 0$ 105 and 0.563 in a) required for lattice registry would appear to rule out any large degree of coherency between precipitate and matrix. However, the elastic strains required for the matrix to achieve lattice registry could be easily accommodated by the presence of a few interfacial dislocations for a precipitate of dimension 100Å. (A first order approximation indicates that about seven and three dislocations would be required to cancel the lattice mismatch for a precipitate of NbC of size 100 Å in austenite and ferrite, respectively.)

Table 2.3	Lattice mismatch for Nb(CN) precipitates in
	austenite and ferrite [54]. Value means required
	distortion to maintain lattice coherency.

Matrix	Orientation relationship	Required distortion of matrix (%)		
		NbC	NbC ₀₈	NbN _{0.8}
Ŷ	$[100]_{PPT}$ // $[100]_{Y}$	25.5	26.6	23.0
	$[010]_{PPT}$ // $[101]_{Y}$	25.5	26.6	23.0
	$[001]_{PPT}$ // $[001]_{Y}$	25.5	26.6	23.0
α	[100] _{PPT} // [100] _a	56.3	57.7	53.1
	[011] _{PPT} // [010] _a	10.5	11.5	8.4
	[011] _{PPT} // [001] _a	10.5	11.5	8.4

All matrix strains are tensile.

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II.3. PRECIPITATION OF Nb(CN) IN SUPERSATURATED AUSTENITE

The precipitation of Nb(CN) in austenite and ferrite generally occurs at crystalline defects. The main reason why the precipitates are formed in this fashion is the rather large mismatch between the lattice of Nb(CN) and the matrix (Table 2.3). This increases the probability of nucleation at lattice defects where part of the strain energy can be reduced. Four sites of precipitation have been reported frequently, these being grain boundaries, dislocations, stacking faults as well as the matrix.

II.3.1. Precipitation on Grain Boundaries

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When a nucleus forms at a grain boundary, a small part of the boundary disappears and the energy released reduces the total energy associated with the formation of the nucleus. Suppose that the nucleus forms as an oblate spheroid of equatorial radius (a_e), the area of boundary destroyed is πa_e^2 and the corresponding loss in austenite grain boundary energy is $\pi a_e^2 \gamma_{GB}$, where γ_{GB} is the grain boundary energy per unit area. Taking $\gamma_{GB} = \gamma_{PM} (\gamma_{PM})$ is the surface energy of the precipitate/matrix interface) because of its incoherent nature, the surface energy increase due to grain boundary precipitation is half that of matrix precipitation [55]. Further reductions in free energy occur at junctions where 3 or 4 grains meet. Clemm and Fisher [56] showed that the activation energy for nucleation at the latter can be reduced to about 1/2000th of that of homogeneous nucleation. Other reasons for preferred nucleation at grain boundaries are solute atom segregation to grain boundaries and more rapid diffusion along boundaries.

J.W. Cahn [57] studied the kinetics of grain boundary nucleation systematically and reported a free energy decrease in the case of heterogeneous nucleation compared to homogeneous nucleation as shown in Fig. 2.6. In this diagram, the vertical axis is the ratio of the free energy of formation for heterogeneous nucleation to that for homogeneous nucleation. When the ratio of grain boundary energy to nucleus surface energy increases, i.e. when the contact angle of the nucleus decreases, the energy needed for
heterogeneous nucleation decreases. Nucleation at a grain edge or grain corner decreases the free energy further.

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Fig. 2.6 Relative nucleation energy for nucleation at a grain boundary (a), grain edge (b) and grain corner (c) [57].

II.3.2. Precipitation on Dislocations and Dislocation Substructures.

It is well known that dislocations are preferred sites for precipitation from solid solution. Cahn [58] calculated the activation energy for the nucleation of a second phase on a dislocation, assuming an elastic model of a dislocation and an incoherent precipitate, and found that the nucleation energy decreases even more rapidly with increasing thermodynamic driving force than does the nucleation energy for homogeneous nucleation. According to Cahn, it was explained that the volume strain energy term in the free energy of formation is negative on account of the release of the strain energy of the dislocation.

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There are several experimental observations which confirm the occurrence of precipitation on dislocations and dislocation substructures. It is often reported that the repeated precipitation of Nb(CN) along dislocation lines forms chain-like precipitates [59-61] and repeated precipitation on climbing dislocations produces planar particle arrays [62]. Davenport et al. [17] and Brown et al. [63] employed dark field electron microscopy to reveal a cell like distribution of Nb(CN) precipitates in hot rolled microalloyed steels. Chandra et al. [64] and Liu [65] also showed that strain induced precipitation occurs preferentially on the dislocation substructures developed during deformation.

Two models have been proposed for the mechanism of precipitation on dislocations and these are the dislocation climb model and the dislocation sweep model. The first was developed by Silcock and Tunstall [66] for the precipitation of NbC on partial dislocations and stacking faults. The model was improved by Nes [67] who extended it to the case of nucleation on edge dislocations. This model is based on the observation that the significant volume increase involved in precipitate formation requires a vacancy flux toward the growing particle to reduce the local internal stresses resulting from particle growth. Consequently, it was assumed that the nucleation and growth of precipitates is controlled by the supply of vacancies provided by the climbing dislocations.

Kesternich [68] pointed out that the dislocation climb model neglects the long range diffusion of solute atoms to the precipitation sites, and concluded that there are always sufficient vacancies to reduce the strain energy between the precipitates and the matrix. Consequently, the lack of vacancies for balancing the lattice mismatch cannot be a factor limiting the growth of MI type precipitates. The proposed model, based on the observation of TiC precipitation, has the following characteristics: a) Interfacial reactions limit growth so strongly that growth is practically not observable, unless an aiding mechanism becomes operative.

b) Such an aiding mechanism is initiated through annealing of preexisting dislocations. The moving dislocations may sweep along solute atoms and increase the concentration of solute atoms.

c) The concentration is increased, particularly at locations where two dislocations react with or annihilate each other. The Cottrell atmospheres from both interacting dislocations are united and a locally enhanced supersaturation is created. This supersaturation drives interfacially controlled growth.

d) Since the growth is assisted by the mobile dislocations, precipitates stop growing as soon as the particles have grown to sufficient size to effectively pin the dislocations.

This model consists of two basic stages. The high stability of small precipitates is due to a strong interfacial barrier against growth and coarsening. Therefore, the first stage is the initial rapid growth regime due to an extra driving force emanating from dislocation reactions, leading to enhanced local supersaturation. The second stage is the termination of the growth regime by immobilization of the dislocation network, once the precipitates have grown sufficiently to pin the dislocations.

II.3.3. Precipitation on Stacking Faults

A perfect dislocation may decrease its strain energy by dissociating into two partial dislocations separated by a planar stacking fault. The fault represents an interruption in the crystal stacking and, as such, has a positive energy associated with it, which tends to draw the two partial dislocations back together. Such stacking faults are good nucleation sites, especially for semi coherent phases, where the interruption in stacking may provide part of the rearrangement needed to nucleate the new phase. Rate equations for this important type of nucleation event have not yet been derived [69]. Kesternich [68] assumed that stacking faults are not preferable precipitation sites for MI type carbides. However, there are many experimental data which show preferential precipitation at stacking faults. Honeycombe et al. [70, 71] observed NbC particles at stacking faults in austenitic stainless steel and others have reported the presence of planar arrays of precipitates in the stacking fault plane [62, 66, 67, 72]. Silcock and Tunstall [66] have shown that the stacking fault {111} extra plane, in which the precipitation of NbC occurs, is formed by the dissociation of the sessile dislocation 1/2 < 110 > into Frank and Shockley partial dislocations.

The stages in the growth of an NbC precipitate on an extrinsic stacking fault due to dislocation climb are illustrated in Fig. 2.7. First, precipitates are nucleated on the Frank partial or on an undissociated edge dislocation (a), jog movement provides vacancies to enable particle growth (b), and the Frank or undissociated edge dislocation moves forward by climb (c). Eventually, the dislocation pinches off around the particle and becomes available for the fresh nucleation of precipitates.

II.3.4. Precipitation in the Matrix

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Random matrix precipitation not nucleated on dislocations has been observed in Nb [73], V [61, 72, 75] and Ti [76] containing austenitic steels where a cube/cube orientation relationship exists. However, compared with the other modes of precipitation, matrix precipitation is the most difficult to produce.

The matrix precipitates are probably semi-coherent in the early stages of growth, but because of a 25% mismatch between the lattices of matrix and carbide, a substantial strain field is present. The strain field of a large particle is much smaller than that of a small particle, which suggests that much of the strain has been eliminated by the absorption of vacancies in the early stages and also by the generation of interfacial dislocations during growth [77].



Fig. 2.7 Stages in the growth of NbC precipitates on a stacking fault due to climb of a Frank partial dislocation [66]. E: extrinsic stacking fault, F: Frank partial, J: jog emitting vacancies.

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II.4. EFFECTS OF Nb ON ROLLING OF STEELS

II.4.1. Effect of Nb on Reheated Grain Size

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The initial grain size of steel after reheating depends on the temperature and holding time. During the reheating stage, the grain size of austenite increases to lower the total surface energy. Grain growth can be divided into two regions according to temperature; normal grain growth and abnormal grain growth [79]. In the former, the average grain size increases continuously, whereas in the later, certain grains increase their sizes abruptly above a certain temperature, resulting in a mixed grain structure. The latter is frequently seen in Al-killed steel, and this mixed grain structure decreases the workability of austenite and deteriorates the toughness remarkably. Under isothermal conditions, the grain size increases with time according to [80]:

$$d_t^2 - d_t^2 = k t (2.2)$$

where d_i is the initial grain diameter, d_f the grain diameter at a certain time, t is the time and k is the constant. The effect of reheating temperature on grain size increase is stronger than that of time.

It was observed that niobium containing steels produced coarser grains than plain carbon steels at very high temperatures (>1300°C) because of abnormal grain growth [81, 82]. However, within the range of reheating temperatures of hot rolling (1150~1250°C), the reheated grain size of niobium containing steels is generally much smaller than that of C-Mn steel for the same reheating condition. Zener [83] showed that the restraining effect of grain growth is attributed to grain boundary pinning by particles. The austenite grain size is then controlled by the mean diameter and the volume fraction of precipitates, as follows:

$$d^{\rm Y} = \frac{4}{3} \frac{d^p}{f_v} \tag{2.3}$$

where d^{γ} and d^{p} are the mean diameters of the austenite grains and the precipitates, respectively, and f_{v} is the volume fraction of precipitates.

Gladman [84] developed his grain growth theory in the presence of second phase particles on the basis of the energy change during grain growth:

$$d^{Y} = \frac{\pi}{6} \left(\frac{3}{2} - \frac{2}{\zeta}\right) \frac{d^{p}}{f_{v}}$$
(2.4)

where ζ is the ratio of the radii of the growing grain and its neighbor. This equation shows good agreement with experimental data, when the value of ζ is in the range 2- $\sqrt{2}$.

Hellman and Hillert [85] also obtained relationships between the diameter of the austenite grains and the diameter and volume fraction of the precipitates by modifying Zener's theory. The relationships can be written as:

$$d^{\rm N} = \frac{4}{9} \frac{d^{\rm p}}{f_{\rm v}} - - normal grain growth$$

$$d^{\rm N} < \frac{4}{3} \frac{d^{\rm p}}{f_{\rm v}} - - abnormal grain growth$$
(2.5)

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From the above equations (eqns. (2.4) and (2.5)), it can be seen that the austenite grain diameter is linearly dependent on the size of precipitate and the inverse volume fraction of precipitates. Therefore, the formation of finely distributed particles is effective in suppressing grain growth during reheating.

The movement of the grain boundary away from the particle would result in a local energy increase, and therefore there is a drag effect on the migrating boundary. The critical size of the particle arresting the migration of a pinned boundary can be estimated simply by inverting eqn. (2.4).

$$d^{p} = \frac{6 d^{\gamma} f_{v}}{\pi} (\frac{3}{2} - \frac{2}{\zeta})^{-1}$$
(2.6)

From this equation, the critical particle size increases with an increase either in the volume fraction of the particles or the matrix grain size. Increasing the grain size heterogeneity decreases the critical particle radius. At the critical particle size, the driving force for grain growth equals the pinning force exerted by the particle. If the particle size increases further, the driving force will exceed the pinning force and thus lead to grain growth.

II.4.2. Effect of Nb on Recrystallization

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Recrystallization is usually observed during the hot deformation of fcc metals with intermediate or low stacking fault energies. It has also been reported that recrystallization occurs in bcc metals such as very high purity α -Fe. During deformation, dynamic recrystallization takes place when a critical strain (ε_c) is reached. This ε_c is somewhat less than ε_p (strain to peak stress), which is related to the Zener-Hollomon parameter (Z), as follows [96];

$$\varepsilon_p = A \ d_1^{1/2} \ Z^n$$
 (2.7)

where A and n are constants. For C-Mn and low alloy steels, the value of n varies from 0.125 to 0.175. Le Bon et al. [16] reported that the deformation needed to initiate dynamic recrystallization is higher for Nb steels than for Nb-free steels. Jonas et al. [10-12] showed that ε_p increases when Nb is present. The increase of ε_p by Nb is most effective when the Nb exists as fine precipitates. The Nb in solution in austenite also retards the onset of dynamic recrystallization. However, at very slow strain rates, precipitation can take place much earlier than dynamic recrystallization. Thus the retardation effect of Nb(CN) is not significant because it has coarsened prior to the onset of dynamic recrystallization [16].

Figure 2.8 shows the critical temperature below which complete static recrystallization is arrested, taken from the experimental results of Cuddy, who used multi-pass rolling tests [86]. From the figure it can be seen that Nb is the element that most effectively retards recrystallization. The order of effectiveness of microalloying elements with respect to the retardation of recrystallization is Nb, Ti, Al and V [81, 86, 89].

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Fig. 2.8 The increase in recrystallization stop temperature with increase in the level of microalloy concentration [86].

The types of precipitates in austenite can be separated into precipitates which are not dissolved during reheating, precipitates formed dynamically during deformation, strain induced precipitates formed in the deformed matrix, and precipitates formed in recrystallized austenite. Non-dissolved precipitates show little effect on the retardation of recrystallization because of their coarse size. Since the kinetics of static precipitation from recrystallized austenite are extremely slow, the effect of Nb on the retardation of recrystallization can be mainly attributed to small strain induced precipitates [13, 16-19, 81, 86, 87, 93] and dynamically formed precipitates [10, 12, 88]. The solute drag effect is also important because it retards recrystallization until precipitation occurs [11, 92]. For instance, vanadium is not as effective in retarding recrystallization because solute vanadium atoms cannot delay recrystallization until precipitation starts. Therefore, precipitation will not affect recrystallization because recrystallization will finish before precipitation takes place.

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Precipitation drag forces were estimated by Cuddy [86] using three models, i) a rigid boundary model, ii) a flexible boundary model, and iii) a subboundary model. The calculated results gave much smaller values than the driving force for recrystallization. However, the retardation of recrystallization by precipitates is clearly observed experimentally. The discrepancy between the calculated and experimental values was attributed to the assumption that the particles are distributed uniformly, whereas they are precipitated in a highly localized manner. Kwon and DeArdo [94] evaluated the pinning force in specific local sites by combining the drag force equations and the volume fraction equation of Ashby and Ebeling [95]. The resulting force relations are as follows:

For the case of the rigid boundary model in which the boundaries are not deformed by particle drag [94];

$$F_{PRB} = \frac{6\gamma f_v}{\pi r} = 2d^p \gamma N_p \left(1 + (\frac{o}{d^p})^2\right)$$
(2.8)

In the flexible boundary model, in a boundary which interacts with every particle in the 3-D array until it is fully pinned [94];

$$F_{pFB} = \frac{3\gamma f_v^{3/2}}{\pi r} = 6\gamma \left(\frac{N_p^2 ((d^p)^2 + \sigma^2)^2}{36\pi}\right)^{1/3} / d^p$$
(2.9)

and in the sub-boundary model, in which precipitates are formed on the substructure [97];

$$F_{PSB} = \frac{3\gamma f_v}{2\pi r^2} = 2\gamma d^p N_p \qquad (2.10)$$

where d^p (=2·r) is the particle diameter, σ the standard deviation of the particle size and N_p is the number of particles per unit area of extraction replica.

The calculated pinning forces have the same order of magnitude as the driving force for recrystallization. For example, if it is assumed that d=4.7nm, $\sigma=3.5nm$, $N_p=2.98 \times 10^{14}/m^2$ and $\gamma=0.8 J/m^2$, then the calculated local pinning forces are 3.48, 9.95 and 2.24MN/m² for the rigid boundary, flexible boundary and sub-boundary models, respectively [94], as compared to recrystallization driving forces which have been found to be in the range 9.0-14.0MN/m² [94, 97]. This result implies that particles formed in the early stages of precipitation can retard recrystallization significantly.

II.4.3. Effect of Nb on Strength and Toughness

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Stress-strain curves in the work hardening region can be described by the following general relationship:

$$\sigma = \sigma_0 \varepsilon^n \tag{2.11}$$

where σ is the true stress, ε is the true strain and σ_0 and n are constants. Nb only increases σ_0 and does not affect the n value [91]. The strengthening effects of microalloying elements are due to grain refinement and solution and precipitation hardening [90].

The dependence of yield stress on grain size is given by the Hall-Petch relationship.

$$\sigma_{v} = \sigma_{t} + k_{v} d^{-1/2}$$
 (2.12)

where d is the grain diameter, σ_y is the yield stress, σ_i is the friction stress opposing the movement of dislocations in grains and k_y is a constant. Refining the grain size of metals and alloys results in an increase in the yield stress. The impact transition temperature of ferrite can be described quantitatively by an equation of the form [98]:

$$\beta T = ln\beta - lnC - lnd^{-1/2}$$
 (2.13)

where β and C are constants and T is the ductile-brittle transition temperature. The transition temperature decreases when the grain size is decreased.

Solid solution strengthening generally is not very effective and often expensive. This strengthening is related to the difference in atomic size between the solute and the solvent. All solutes, particularly those of the interstitial type, are detrimental to the impact transition temperature [1].

In the case of precipitation hardening, for a given precipitate volume fraction, small particles impart significant strengthening. Particles which remain undissolved during the reheating stage are relatively large and thus do not contribute to precipitation hardening. The strengthening effect is remarkable when precipitates are small and coherent with the matrix. In the initial stages of precipitation, where particles are small and coherent with the matrix, dislocation lines can cut the particles. At the later stages of precipitation, the particles become semi-coherent and/or incoherent with the matrix and, in this case, dislocations only circumvent the particles. When the dislocations bow around precipitates, shear loops remain around the particles and, for this reason, materials are strengthened by precipitates. In the case of Nb precipitates, the lattice mismatch is large enough to develop an incoherent boundary even at the early stages of precipitation.

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Ardell [99] classified several mechanisms by which the critical resolved shear stress could be increased by precipitates: 1) chemical strengthening is associated with the increasing energy due to the formation of additional precipitate/matrix interfaces when particles are sheared by dislocations; 2) stacking fault strengthening is taking place when the stacking fault energy of the precipitate differs from that of the matrix. The force required to free the dislocation from the precipitate depends upon the difference between the stacking fault energies; 3) modulus strengthening occurs when the elastic constants of the precipitate and matrix phases are different. The increment of the critical resolved shear stress is related to this difference; 4) coherency strengthening is brought about because the strain field of a coherent precipitate, which arises from the lattice mismatch with respect to the matrix, interacts with the strain field of a dislocation; 5) order strengthening occurs because antiphase boundaries are created when dislocations shear ordered coherent precipitates; 6) strengthening by spinodal decomposition; and 7) Orowan strengthening takes place when the dislocations bow and bypass impenetrable precipitates.

Gladman et al. [100] analyzed precipitation strengthening in terms of a simplified Ashby-Orowan equation:

$$\sigma(MPa) = \frac{5 9 f_v^{1/2}}{\overline{L}} ln\left(\frac{\overline{L}}{2 5X10^{-4}}\right)$$
(2.14)

where f_v is the particle volume fraction and \tilde{L} is the mean planar intercept length of precipitates. According to the above equation, precipitation hardening increases as the particle size decreases and volume fraction increases. This quantitative expression shows good agreement with experimental measurements for several microalloyed steels, as can be seen schematically from Fig. 2.9.

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Fig. 2.9 The dependence of precipitation strengthening on precipitate size and fraction according to the Ashby-Orowan model, compared with experimental observations for given microalloying additions [100].

II.5. KINETICS OF Nb(CN) PRECIPITATION

II.5.1. Kinetics of Precipitation

The precipitation kinetics of Nb(CN) have been measured in several investigations [13, 97, 101-106]. Isothermal precipitation from supersaturated austenite can be interpreted in terms of the Johnson-Mehl-Avrami equation:

$$Y = 1 - exp(-bt^{n})$$
 (2.15)

Here Y is the fraction precipitated, b and n are constants and t is the precipitation time. This equation was initially developed to explain the observed kinetics of phase transformation by Johnson and Mehl [107] and Avrami [108, 109]. That this rule applies well to the behaviour of precipitation was confirmed by DeSorbo and Turnbull [110]. The theoretical values of n for the case of diffusion controlled growth have been estimated and are summarized in Table 2.4 [111].

The kinetics of precipitation are influenced by several factors including the temperature, deformation and chemical composition. These effects are briefly summarized below.

II.5.1.1. Influence of temperature

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A useful method of displaying the effect of temperature is by the Precipitation-Time-Temperature diagram, usually referred to as the P'I'I' diagram. The rate of nucleation of solid particles from a supersaturated solid solution is a function of both ΔG^* , the free energy of formation of a critical sized nucleus, and of D, the diffusion coefficient of the solute in the matrix phase. The equilibrium number of clusters consisting of i atoms in a system containing a total of N atoms is given by:

Table 2.4Values of the time exponent (n) in the Johnson-
Mehl-Avrami equation for the case of diffusion
controlled growth [111].

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Conditions	n
All shapes growing from small dimensions, increasing nucleation rate	>2.5
All shapes growing from small dimensions, constant nucleation rate	2.5
All shapes growing from small dimensions, decreasing nucleation rate	1.5-2.5
All shapes growing from small dimensions, zero nucleation rate	1.5
Growth of particles of appreciable initial volume	1-1.5
Needles and plates of finite long dimensions, small in comparison with their separation	1
Thickening of long cylinders (needles), e.g. after complete end impingement	1
Thickening of very large plates, e.g. after complete edge impingement	0.5
Growth on dislocations (very early stages)	~2/3

$$n(i) = N \exp\left(-\frac{\Delta G^{i}}{kT}\right)$$
(2.16)

where ΔG^i is the free energy of formation of a cluster containing i atoms. The temperature dependence of D is known to be of the form:

$$D = D_{c} exp\left(-\frac{Q}{R T}\right)$$
(2.17)

where D_0 is a frequency factor and Q is the activation energy for solute diffusion. The variations of the thermodynamic term and the kinetic term with temperature are drawn schematically in Fig. 2.10. The rate of nucleation at any temperature is given by the product of above two terms, and this value can be expressed as the dotted line in the figure.



Fig. 2.10 Temperature dependence of the thermodynamic term (n(i)), the kinetic term (diffusion coefficient) (D), the rate of nucleation (I) and time for nucleation (N(t)).

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Once stable nuclei are formed, then the rate of precipitation is determined by the rate of interface migration (i.e. growth). The rate of interface migration of a diffusion controlled transformation is determined by a combination of the thermodynamic driving force, which is the volume free energy change (ΔG_v) between the reacted and unreacted regions, and the diffusion coefficient, D. As in the nucleation process, the thermodynamic driving force for growth is a function of the supersaturation, and thus increases with decreasing temperature. Therefore, the rate of growth is also represented as an inverse C shaped curve.

The rate of precipitation is a function of both the nucleation rate and the interface migration rate. The reaction occurs most rapidly at certain intermediate temperatures (as for the variation of N(t) in Fig. 2.10); it is sluggish at higher temperatures because the driving force for the reaction is small, and sluggish at lower temperatures because the rate of diffusion drops to a very low value [112, 113].

For most PTT curves reported in the literature, the temperature where the highest rate of precipitation takes place, i.e. the nose temperature, falls in the range 875-1000°C. It has been found that, in typical microalloyed steels, the PTT curves determined for the Nb bearing steels have higher nose temperatures than those for the V bearing steels, but are lower than those for the Ti containing steels [11, 114].

II.5.1.2. Influence of deformation

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Precipitation is accelerated by deformation because dislocations increase the density of nucleation sites and the effective diffusion rate of the solute atoms [65]. Le Bon et al. [16] reported that both the precipitation start times and finish times decreased with increasing amounts of deformation. They also pointed out that the particles precipitated after deformation are much smaller than those obtained from the undeformed condition. Speer and Hansen [115] observed precipitates which were formed after 20 and 50 pct deformation, and found fewer precipitates after the lower reduction. These observations can be explained in terms of dislocation densities, because a greater degree of deformation results in a higher dislocation density and a greater number of favorable nucleation sites. The effect of deformation on precipitation was systematically studied by Weiss and Jonas [12]. In this work, precipitation behaviour during and after deformation was followed by measuring the variation of the strain to the peak stress as a function of strain rate and holding time, respectively. The PIT diagrams obtained by this technique for three conditions are compared in Fig. 2.11. The imposition of a 5 pct prestrain accelerates the rate of static precipitation by about one order of magnitude and decreases the nose temperature. The rate of dynamic precipitation is more than an order of magnitude faster than that of the static precipitation induced by a 5 pct prestrain.



Fig. 2.11 Comparison of the PTT curves obtained during dynamic precipitation, strain induced precipitation (5 pct prestrain) and static precipitation (no predeformation) [12].

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II.5.1.3. Influence of alloying elements

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The PTT curve moves to higher temperatures and shorter times when the amount of Nb increases [116]. The presence and concentration of other elements, such as Mn, Si, Cr and Ni can also have significant effects on the precipitation kinetics of microalloying elements. Koyama et al. [20, 117] reported that Mn, Cr and Ni increase the solubility of carbides and nitrides and decrease the diffusivities of the precipitate forming elements. These effects on the solubility were recently confirmed experimentally for low carbon high manganese steels [118]. On the contrary, the addition of silicon showed the opposite effect. The accelerating effect of the latter is perhaps easier to rationalize since the diffusion of Si is relatively fast and its addition, therefore, leads to an increase in the self diffusivity of the matrix [122].

Akben et al. have studied the effect of Mn [11, 114], Mo [119, 120] and Al [121] on the precipitation kinetics of Nb and Ti microalloyed steels, and found that all these elements retard precipitation, i.e. shifted the C curve to the right. This was attributed to a decrease in the carbon and nitrogen activity coefficients associated with the presence of other alloying elements, which, in turn, led to an increase in the solubilities of the particles and to a decrease in the driving force for precipitation. The effect of Mn and Si additions on the diffusion of Nb in austenite was investigated experimentally [123], and the results demonstrated that the addition of 1.5 pct Mn decreased the diffusivity of Nb in austenite by about 11 pct and 0.6 pct Si increased it by about 5 pct.

The influence of alloying elements on the diffusivity of precipitating elements in the steel can be expressed by the following equation [124]:

$$D_{i} = D^{o} exp(\varepsilon_{i}^{\prime} X_{i})$$
(2.18)

where D_i is the effective diffusivity of element i (i=C, N, Nb, Ti,V) in the presence of element j (j=Mn, Si, Mo, Cr, Ni, Al), D^o is the diffusivity of element i in the absence of element j, ε_i^{j} is the Wagner interaction parameter and X_j is

the atom fraction of j. The activity of element i can be written according to the Wagner formalism [125] as:

$$lna_{l} = lnX_{l} + \varepsilon_{l}^{J}X_{l} \qquad (2.19)$$

According to the above two equations, the elements (Mn, Mo, Cr, Ni, Al) which increase the solubility of the carbide or nitride in austenite, will decrease the diffusivity and activity of the precipitating species. By contrast, Si, which decreases the solubility of carbides and nitrides, is expected to increase both the diffusivity and the activity.

II.5.2. Kinetics of Coarsening

The mean size of precipitates continuously increases even after the solute concentration of the matrix has decreased to near the equilibrium level, because the interfacial energy for smaller particles is higher for a given volume fraction of precipitates. The driving force of particle coarsening is, therefore, the decrease of interfacial energy of the particle precipitated.

The first detailed theory for particle coarsening was developed independently by Lifshitz and Slyozov [126] and Wagner [127] (the LSW theory). The kinetics can be described as:

$$r^n - r_o^n = Kt \tag{2.20}$$

where r and r_0 are the average particle radius at time t and t=0, respectively, and n and K are constants which depend on the process that is controlling the rate of particle coarsening.

When interface migration is controlling the coarsening process [127], n=2 and

$$K = \alpha \frac{V_m^2 C_e k \gamma}{RT}$$
(2.21)

Here, V_m is the molar volume of the precipitates, C_e is the concentration of the rate controlling element in equilibrium, k is the rate constant of the phase boundary reaction, y is the interfacial energy and a is a constant.

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When coarsening is controlled by bulk diffusion processes [126, 127], n=3 and

$$K = \beta \frac{V_m^2 C_e D_v \gamma}{RT}$$
(2.22)

where D_v is the diffusion coefficient of the metal element in the matrix and β is a constant.

When grain boundary diffusion is the controlling process [128], n = 4 and

$$K = \kappa \frac{V_m^2 C_e D_{gb} Y W}{GRT} f(\phi)$$
 (2.23)

Here, W is the grain boundary width, G is a parameter associated with the shape of the precipitates and the angle between the particle/matrix interface and the grain boundary, $f(\phi)$ is a parameter associated with the volume fraction of precipitates (ϕ) , $D_{g b}$ is the diffusion coefficient of the metal element along the grain boundary and κ is a constant.

Finally, when diffusion along dislocations is controlling [128, 129], n=5and

$$K = \eta \frac{V_m^2 C_e D_d Y N q}{RT}$$
(2.24)

In this equation, N and q are the number of dislocations intersecting each particle and the effective cross sectional area of dislocation pipe diffusion path, D_d is the diffusion coefficient of the metal element along dislocations and η is a constant. In all the above equations, R and T have their usual meanings.

An alternative theory for particle coarsening, which considers that coarsening occurs primarily by particle coalescence, has been developed [130-132]. However, this theory has not been further developed because coarsening behaviour can be adequately explained by the LSW theory [64, 88, 133-136].

Particle coarsening is affected by deformation. Weiss and Jonas [88] reported that the coarsening rate under dynamic deformation conditions is accelerated by about three orders of magnitude when compared to the static rate of Ostwald ripening. In a related paper [64], it was observed that the lower the temperature of deformation, the greater the rate of particle coarsening. This was interpreted in terms of the higher dislocation densities generated at lower temperatures of deformation. The reported n values for precipitates in commercial HSLA steels are listed in Table 2.5. The most frequently observed n value is 3 and this implies that matrix diffusion is mainly controlling the rate of particle coarsening.

Table 2.5Experimentally determined n values of the Lifshitz-
Slyozov-Wagner equation for particle coarsening.

Species of precipitate	n value	Experimental conditions	ref.
Nb(CN)	3, 5	Dynamic coarsening	64, 88, 133
Ti(CN)	3	5 pct predeformation	65
VN	3	no deformation	134
Complex	3	no deformation	135

CHAPTER III MODELLING OF CCP DIAGRAMS

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Many researchers [10-13, 16, 92, 102, 114, 119, 121] have studied precipitation behaviour during isothermal holding and have produced PTT diagrams to show the relationship between precipitation. time and temperature. However, PTT data cannot be directly applied to predict the precipitation behaviour in industrial hot rolling processes because the temperature continuously decreases during the process. Therefore, the focus of this work is the examination and prediction of precipitation behaviour under continuous cooling conditions.

To calculate continuous-cooling-precipitation (CCP) diagrams, prediction of the precipitation start (P_s) and precipitation finish times (P_f) during isothermal holding is first necessary. Unfortunately, the two prediction methods currently available are limited to P_s times. In 1987, Dutta and Sellars [137] developed a thermodynamic model (the D-S model) to predict P_s times for niobium carbonitrides, and in 1989, Liu and Jonas [138] developed another model (the L-J model) for titanium carbonitrides. A new calculation method for the P_f time is proposed in this thesis, based on reaction kinetics and classical nucleation and growth theory. Thus the P_s and P_f times during isothermal holding at any temperature can be calculated if certain thermodynamic factors and PTT data are available.

The precipitation behaviour during continuous cooling can then be constructed using the additivity rule developed by Scheil [139] in 1935. The additivity rule has often been employed to predict phase transformation behaviour during continuous cooling from isothermal data [140-145].

III.1. METHODS OF PREDICTING P_s TIMES DURING ISOTHERMAL HOLDING

III.1.1. Comparison of D-S Model and L-J Model

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In the D-S model, P_s times were derived as the time when a critical number of nuclei are reached assuming a steady state nucleation rate. The steady state nucleation rate can be written as [69]:

$$I = Z \beta^* N \exp\left(-\frac{\Delta G^*}{kT}\right)$$
(3.1)

where Z is the Zeldovich non-equilibrium factor, which is less than 1, β^* is the rate at which atoms are added to the critical nucleus, N is the number of nucleation sites per unit volume, ΔG^* is the critical free energy to form a nucleus and k is Boltzmann's constant. Russell [69] has shown that the product of $Z\beta^*$ in the above equation can be approximated as:

$$Z\beta^* = \frac{DX}{a^2} \tag{3.2}$$

where a is the lattice parameter, and D and X are, respectively, the effective diffusivity and concentration of the element which controls the rate of the nucleation process. Since the diffusivity of interstitial atoms in austenite is much faster than that of substitutional atoms, the rate controlling element for Nb(CN) precipitation is niobium. The steady state nucleation rate is thus given as:

$$I = N \frac{DX}{a^2} \exp\left(-\frac{\Delta G^*}{kT}\right)$$
(3.3)

The critical free energy is related to the supersaturation ratio and can be expressed as:

$$\Delta G^* = \frac{16\pi \gamma^3 V_m^2 \xi}{3 (RT \ln K_s)^2}$$
(3.4)

where y is the particle/matrix interfacial energy, V_m is the molar volume of Nb(CN), ξ is the modifying factor that arises for nucleation at dislocations, R is the gas constant and K_s is the supersaturation ratio, which is defined as the ratio of the actual amount of solubility product in solution to that of the equilibrium condition.

The critical number of nuclei per unit volume (N_c) that must be formed for precipitation to be detected is then;

$$P_s = \frac{N_c}{I} \tag{3.5}$$

Therefore, the precipitation start time in the D-S model can be expressed as:

$$P_{s} = C[X_{Nb}]^{-1} exp\left(\frac{27000}{RT}\right) exp\left(\frac{B}{T^{3}(lnK_{s})^{2}}\right)$$
(3.6)

Here, C is N_c/α , and B is $16\pi\gamma^3 V_m^2 N_o/(3R^3)$.

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Several modifications were made by Liu and Jonas [138] to the D-S theory because it did not lead to satisfactory results when applied to titanium carbonitride precipitation. In the D-S model, the chemical driving force for nucleation is simply related to the solubility product of the precipitating species. By contrast, in the L-J model, the chemical driving force was derived from the free energy change during precipitation. The resulting model for P_s in Ti microalloyed steel can be written as:

$$P_{s} = H \left(\rho X_{T_{l}} \right)^{-1} exp\left(\frac{Q}{RT} \right) exp\left(\frac{\Delta G^{*}}{kT} \right)$$
(3.7)

where H is $N_c a^{3/D_0}$, a is the interatomic spacing of Ti(CN), D_0 is the frequency factor, X_{Ti} is the concentration of Ti in solution and Q is the activation energy for the diffusion of solute atoms. The main difference between the D-S and L-J model is the second exponential term. ΔG^* in the L-J model can be expressed as:

$$\Delta G^* = 16\pi (\xi \gamma)^3 / (3 (\Delta G_{chem} + \Delta G_{c})^2)$$
 (3.8)

where ΔG_{ϵ} is the volume strain energy. To compare the two models, the precipitation of Nb(CN) can be considered. The chemical free energy (ΔG_{Chem}) can then be expressed as:

$$\Delta G_{chem} = \frac{RT}{2\Omega} \left\{ ln\left(\frac{X_{Nb}^{e}}{X_{Nb}^{o}}\right) + y ln\left(\frac{X_{C}^{e}}{X_{C}^{o}}\right) + (1-y) ln\left(\frac{X_{N}^{e}}{X_{N}^{o}}\right) \right\}$$
(3.9)

where Ω is the molar volume of precipitates (=No $a_{Nb(CN)}^3$), y is the volumetric ratio of NbC in Nb(CN) and X^e, and X^o, are equilibrium and overall concentrations of solute i in the steel, respectively. ΔG_{ϵ} can be neglected when Nb(CN) is precipitated in the austenite, as will be discussed in the next section, leading to:

$$\Delta G^{*} = \frac{16\pi (\xi \gamma)^{3}}{3 \left[\frac{4RT}{No \, a_{Nb(CN)}^{3}} \left\{ ln \left(\frac{X_{Nb}^{e}}{X_{Nb}^{o}} \right) + y \, ln \left(\frac{X_{C}^{e}}{X_{C}^{o}} \right) + (1-y) \, ln \left(\frac{X_{N}^{e}}{X_{N}^{o}} \right) \right\} \right\|^{2}}$$
(3.10)

Dividing both sides by $kT(R/N_0 = k)$ gives:

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$$\frac{\Delta G^{*}}{kT} = \frac{16\pi (\xi \gamma)^{3} (2\Omega)^{2} N_{o}}{3R^{3}T^{3} \left\{ ln\left(\frac{X_{Nb}^{e}}{X_{Nb}^{o}}\right) + y ln\left(\frac{X_{C}^{e}}{X_{C}^{o}}\right) + (1-y) ln\left(\frac{X_{N}^{e}}{X_{N}^{o}}\right) \right\}^{2}}$$
(3.11)

If this term is compared to the last exponential term in the D-S model, it can be seen that those two equations have similar structures except for the expression of the chemical driving force. In this work, the L-J model was chosen to calculate P_s times because every term in the L-J model has a clear physical and thermodynamic meaning.

III.1.2. Determination of Critical Free Energy

The L-J model can be rewritten for niobium precipitation as follows:

$$P_{s} = \frac{N_{c} a_{Nb(CN)}^{3}}{D_{o} \rho} (X_{Nb})^{-1} exp\left(\frac{Q}{RT}\right) exp\left(\frac{\Delta G^{*}}{kT}\right)$$
(3.12)

Therefore, to calculate the P_s times, it is necessary to define the value of the thermodynamic and physical factors. From the literature:

$$a_{Nb(CN)} = 4.445 \times 10^{-10} m$$

 $Q = 266.5 \text{ kJ/mole} (lattice diffusion) [146]$
 $Do = 0.83 \text{ cm}^2/\text{s} [146]$
 $\gamma = 0.5 \text{ J/m}^2 [137]$

The dependence of P_s with temperature shows a C shape because of the competition of the two exponential terms in the model. They represent conflicting trends with temperature, i.e. $\exp(Q/RT)$ decreases as the temperature increases, but $\exp(\Delta G^*/kT)$ increases with increasing temperature because the change of ΔG^* with temperature is much faster than the temperature change itself, as will be shown in Chapter VI. The parameters, such as volume strain energy, chemical driving force and interfacial energy modifying factor, should be calculated to evaluate the critical free energy of Nb(CN) precipitation. The following subsections describe the method used to determine the parameters contained in ΔG^* (eqn. 3.8).

III.1.2.1. Volume strain energy

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Following Barnett [147], the total elastic strain energy per unit volume of precipitate, when precipitation occurs in the absence of dislocations, can be expressed as eqn. (3.13), below, if the matrix and precipitates are elastically different, i.e.

$$\Delta G_{e} = \frac{2}{3} \,\mu_{M} \,\epsilon_{D}^{2} \,\frac{\eta}{\eta + (1 - \eta) \,K_{M}/K_{P}} \tag{3.13}$$

Here, μ_M is the shear modulus of the matrix, ϵ_D is the pure dilatation, v_M is the Poisson's ratio of the matrix and K_M , K_P and η are elastic parameters:

$$K_{M} = 3\lambda_{M} + 2\mu_{M}$$

$$K_{P} = 3\lambda_{P} + 2\mu_{P}$$

$$\eta = (1 + v_{M})/\{3(1 - v_{M})\}$$

where λ_M and λ_P are the Lamé constants of the matrix and precipitate, and μ_M and μ_P are the shear modulus of the matrix and precipitate, respectively. Pure dilatation during precipitation depends on the lattice mismatch between the matrix and precipitate, and can be expressed as:

$$\varepsilon_{D} = \frac{a_{Nb(CN)}^{3} - a_{Fe}^{3}}{a_{Fe}^{3}}$$
(3.14)

where $a_{Nb(CN)}$ and a_{Fe} are the lattice spacings of niobium carbonitride and iron, respectively.

Employing values of $a_{Nb(CN)} = 4.445$ Å, $a_{Fe} = 3.54$ Å, $\mu_M = 4.5 \times 10^4$ MPa, $\mu_P = 1.3 \times 10^5$ MPa, $v_M = 0.30$ and $v_{Nb(CN)} = 0.26$, the estimated strain energy when forming a coherent Nb(CN) nucleus in austenite is about 2×10^{10} J/m³. Since this value is greater than the chemical free energy term, the strain energy term must be relaxed simultaneously with nucleation, otherwise precipitation cannot take place. To initiate the relaxation, the nucleus/matrix interface must lose its coherent nature.

Liu and Jonas [148] described the effective cubic dilatation associated with the elastic component δ_e (elastic lattice disregistry) as follows:

$$\varepsilon_D^* = \delta_e^3 + 3\,\delta_e^2 + 3\,\delta_e \tag{3.15}$$

where the elastic component of lattice disregistry can be expressed as:

$$\delta_e = (1 - C)\delta \tag{3.16}$$

where C is the coherency loss parameter, which varies from 0 to 1, and δ is the lattice disregistry. The value of C represents the fraction of the lattice mismatch which is relaxed by the presence of interface dislocations. When C=0, the interface is fully coherent; when C=1, the lattice mismatch between the two phases is completely relaxed by the presence of a sufficient number of interfacial dislocations and a fully incoherent interface is obtained. The coherency loss parameter depends strongly on the chemical driving force and the value can be represented as [65, 148]:

$$C = 1 - 1.66X 10^{-11} \Delta G_{Chem} - 2.18X 10^{-22} \Delta G_{Chem}^2 - 2.56X 10^{-32} \Delta G_{Chem}^3$$
(3.17)

The chemical driving force for Nb(CN) precipitation when the Nb content is less than 0.1 is less than $3 \times 10^9 \text{J/m}^3$. The coherency loss parameter is thus greater than 0.95. This relatively large C value implies that the interface between austenite and precipitate is predominantly incoherent.

The ΔG_{ϵ} values for niobium carbonitride precipitation in austenite have been calculated and the results, with respect to C, are shown in Fig. 3.1. In the range of coherency loss parameter for the precipitation of Nb(CN), the elastic strain energy is very small compared to the chemical driving force for nucleation. Therefore, in this calculation, the volume strain energy was neglected.

III.1.2.2. Chemical driving force

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From the equilibrium condition between the austenite (y) and the Nb(CN) precipitates, the partial molar free energy or chemical potential of each species should be the same in both phases (y and precipitate), i.e.:



Fig. 3.1 The variation of strain energy according to the coherency loss parameter.

$$\overline{G}_{Nb}^{Y} = \overline{G}_{Nb}^{Nb(CN)}$$

$$\overline{G}_{C}^{Y} = \overline{G}_{C}^{Nb(CN)}$$

$$\overline{G}_{N}^{Y} = \overline{G}_{N}^{Nb(CN)}$$
(3.18)

where ${\bf \check{G}}_j{}^{_1}$ is the partial molar free energy of element j in phase i.

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If the niobium carbonitride is assumed to have the composition $Nb(C_yN_{1,y})$, then the total free energy of the precipitates can be described as:

$${}^{"}G_{N\flat(CN)} = \overline{G}_{N\flat}^{N\flat(CN)} + y \overline{G}_{C}^{N\flat(CN)} + (1-y) \overline{G}_{N}^{N\flat(CN)}$$
$$= \overline{G}_{N\flat}^{Y} + y \overline{G}_{C}^{Y} + (1-y) \overline{G}_{N}^{Y}$$
(3.19)

The partial free energy of element i in austenite is given as:

$$\overline{G}_{i}^{\mathrm{Y}} = {}^{\mathrm{o}}G_{i} + RT \ln a_{i}^{\mathrm{Y}} \tag{3.20}$$

where ${}^{o}G_{i}$ is the free energy of one mole of pure element i and a_{i}^{γ} is the activity of element i in austenite. Substituting eqn.(3.20) into eqn.(3.19) gives:

$$\ln a_{Nb}^{\gamma} + y \ln a_{C}^{\gamma} + (1 - y) \ln a_{N}^{\gamma} = \Delta^{o} G_{Nb(CN)} / (RT)$$
 (3.21)

where $\Delta^{0}G_{Nb(CN)}$ is the free energy of formation of Nb(CN) from the austenite, and is expressed as:

$$\Delta^{o}G_{Nb(CN)} = {}^{o}G_{Nb(CN)} - {}^{o}G_{Nb} - y \,{}^{o}G_{C} - (1-y) \,{}^{o}G_{N}$$
(3.22)

The mass balance of each element can be given as:

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$$X_{Nb}^{o} = F/2 + (1 - F) X_{Nb}^{Y}$$

$$X_{C}^{o} = F/2 + (1 - F) X_{C}^{Y}$$

$$X_{N}^{o} = F/2 + (1 - F) X_{N}^{Y}$$
(3.23)

where X_{i^0} is the overall concentration of element i in the steel, $X_{i^{\gamma}}$ the concentration of solute element i in austenite, and F is the equilibrium mole fraction of precipitate.

Hudd et al. [149] calculated the solubility and composition of carbonitride precipitates in steel on the basis of the complete solid solution model, which assumes that the carbide and nitride are completely mutually soluble. This ideal solution model was applied to the Fe-Nb-C-N system and led to good agreement with experimental results. Introducing the ideal solution model to calculate $\Delta^{0}G_{Nb(CN)}$ gives:

$$\Delta^{o}G_{Nb(CN)} = y\Delta^{o}G_{NbC} + (1-y)\Delta^{o}G_{NbN} + RT\{y \ln y + (1-y)\ln(1-y)\}$$
(3.24)

Substituting $\Delta^{\circ}G_{Nb(CN)}$ from eqn.(3.24) into eqn.(3.21) produces:

$$lna_{Nb}^{Y} + y lna_{C}^{Y} + (1 - y) lna_{N}^{Y}$$

$$= \frac{y \Delta^{0} G_{NbC}}{R T} + \frac{(1 - y) \Delta^{0} G_{NbN}}{R T} + \{y lny + (1 - y) ln(1 - y)\}$$
(3.25)

Rearranging the above equation with respect to y gives:

$$y(\ln a_{Nb}^{\vee} + \ln a_{C}^{\vee}) + (1 - y)(\ln a_{Nb}^{\vee} + \ln a_{N}^{\vee})$$

1.5

$$=y\left(\frac{\Delta^{o}G_{NbC}}{RT}+lny\right)+(1-y)\left(\frac{\Delta^{o}G_{NbN}}{RT}+ln(1-y)\right)$$
(3.26)

If eqn.(3.26) is applicable for any value of y between 0 and 1, then the two sides of the equations should be identical, i.e.:

$$\ln a_{Nb}^{\gamma} + \ln a_C^{\gamma} = \Delta^o G_{NbC} / RT + \ln y$$
(3.27a)

$$lna_{Nb}^{Y} + lna_{N}^{Y} = \Delta^{0}G_{NbN}/RT + ln(1-y)$$
(3.27b)

$$ln(a_{Nb}^{\gamma}a_{C}^{\gamma}) = \Delta^{o}G_{NbC}/RT$$
 (3.28a)

$$ln(a_{Nb}^{Y} a_{N}^{Y}/(1-y)) = \Delta^{0} G_{NbN}/RT$$
 (3.28b)

The five variables, X_{C}^{γ} , X_{N}^{γ} , X_{Nb}^{γ} , F and y, can be determined from the three mass balance equations (eqn. 3.20) and the two equations for thermodynamic equilibrium (eqn. 3.28 (a) and (b)).

According to the Wagner formalism [125],

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$$\ln a_{\mu}^{\gamma} = \ln X_{\mu}^{\gamma} + \varepsilon_{\mu}^{\gamma} X_{\mu}$$
 (3.29)

where $\varepsilon_i^{\ j}$ is the Wagner interaction parameter between elements i and j, i.e. $\varepsilon_i^{\ j}$ is the effect of element j on the activity of element i. The effect of element j on the activity of i should be considered for all j elements in austenite. However, only selected elements were considered to simplify the calculation. When the Wagner formalism is applied to calculate the activity:

$$lna_{N}^{Y} = lnX_{N}^{Y} + \varepsilon_{N}^{N}X_{N}^{Y} + \varepsilon_{N}^{Nb}X_{Nb}^{Y} + \varepsilon_{N}^{C}X_{C}^{Y}$$

$$lna_{C}^{Y} = lnX_{C}^{Y} + \varepsilon_{C}^{C}X_{C}^{Y} + \varepsilon_{C}^{Nb}X_{Nb}^{Y} + \varepsilon_{C}^{N}X_{N}^{Y}$$

$$lna_{Nb}^{Y} = lnX_{Nb}^{Y} + \varepsilon_{Nb}^{Nb}X_{Nb}^{Y} + \varepsilon_{Nb}^{C}X_{C}^{Y} + \varepsilon_{Nb}^{N}X_{N}^{Y}$$
(3.30)

The Wagner interaction parameters for C, N and Nb in austenite are summarized in Table 3.1. Note that there is a general relationship $\varepsilon_{j}^{1} = \varepsilon_{i}^{1}$ between two elements i and j.

From equations (3.23), the solute concentration of precipitating elements can be expressed as:

$$X_{Nb}^{Y} = (X_{Nb}^{o} - F/2) / (1 - F)$$

$$X_{C}^{Y} = (X_{C}^{o} - yF/2) / (1 - F)$$

$$X_{N}^{Y} = (X_{N}^{o} - (1 - y)F/2) / (1 - F)$$
(3.31)

Parameter	Value	ref.
٤ _C C	8890/T	150
ϵ_N^{N}	6294/T	151
٤ _{Nb} ^{Nb}	-2	152
٤ _C ^N	5790/T	153
ϵ_{C}^{Nb}	-66257/T	154
ε _N ^{Nb}	-66257/T	26

Table 3.1Wagner interaction parameters for
C, N and Nb in austenite.

Assuming the equilibrium composition of Nb(CN) to be Nb($C_yN_{1\ y}$)_{0.87} (this can be considered as a solid solution of NbC_{0.87} and NbN_{0.87}) [25-27, 38], the thermodynamic equations (3.28) become:

$$\ln a_{Nb}^{\gamma} + 0.87 \ln a_{C}^{\gamma} - 0.87 \ln y = \frac{\Delta^{0} G_{NbC_{0.87}}^{\gamma}}{R T}$$
(3.32a)

$$\ln a_{Nb}^{\gamma} + 0.87 \ln a_{N}^{\gamma} - 0.87 \ln(1-y) = \frac{\Delta^{o} G_{NbN_{0}87}^{\gamma}}{R T}$$
(3.32b)

Following the results of Kirkaldy et al. [25, 26], who obtained the free energy of formation of NbC_{0 87} ($\Delta^{\circ}G_{NbC_{0}87}$) by means of a least squares fit:

$$\Delta^{\circ} G_{NbC_{0,87}}^{\vee} = -136 \ 8 - 0 \ 011 \ T \qquad (kJ/mole) \tag{3.33}$$

The average value of the free energy difference between niobium carbide and niobium nitride determined from the literature, i.e. $\Delta^{0}G_{NbC_{0.87}}$ - $\Delta^{0}G_{NbN_{0.87}}$ is 15.7kJ/mole. Thus, the free energy of formation of NbC_{0.87} can be expressed as the following:

$$\Delta^{0}G_{NbN_{0.87}}^{Y} = -152\ 5 - 0\ 011\ T \qquad (kJ/mole)$$
(3.34)

For these precipitate chemical compositions, the mass balance of each element also changes:

$$X_{Nb}^{Y} = \frac{X_{Nb}^{o} - \frac{1}{187}F}{1 - F}$$

$$X_{C}^{Y} = \frac{X_{C}^{o} - \frac{087}{187}yF}{1 - F}$$

$$(3.35)$$

$$X_{N}^{Y} = \frac{X_{N}^{o} - \frac{087}{187}(1 - y)F}{1 - F}$$

From equations (3.30), (3.32) and (3.35), two master equations can be derived:

$$ln\left(\frac{X_{Nb}^{0} - \frac{1}{1.87}F}{1 - F}\right) + 0\ 87\ ln\left(\frac{X_{C}^{0} - \frac{0.87}{1.87}yF}{1 - F}\right) + \left(\frac{X_{Nb}^{0} - \frac{1}{1\ 87}F}{1 - F}\right)\left(-2 - \frac{57644}{T}\right)$$
$$+ \left(\frac{X_{C}^{0} - \frac{0.87}{1\ 87}yF}{1 - F}\right)\left(-\frac{58523}{T}\right) + \left(\frac{X_{N}^{0} - \frac{0.87}{1\ 87}(1 - y)F}{1 - F}\right)\left(-\frac{61220}{T}\right)$$
$$- 0\ 87\ lny + \frac{16454}{T} + 1.32 = 0$$
(3.36a)

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$$ln\left(\frac{X_{C}^{o} - \frac{0.87}{1.87}yF}{1 - F}\right) + \left(\frac{X_{C}^{o} - \frac{0.87}{1.87}yF}{1 - F}\right)\left(\frac{3100}{T}\right) + \left(\frac{X_{N}^{o} - \frac{0.87}{1.87}(1 - y)F}{1 - F}\right)\left(-\frac{504}{T}\right)$$
$$-ln\left(\frac{X_{N}^{o} - \frac{0.87}{1.87}(1 - y)F}{1 - F}\right) + ln\left(\frac{1 - y}{y}\right) - \frac{2170}{T} = 0$$
(3.36b)

These equations enable the calculation of the equilibrium mole fraction of precipitate and fraction of carbide in carbonitride to be performed at any temperature. The two unknowns, y and F, were calculated from the above master equations, for specific temperatures, by the Newton-Raphson method. Once these values are obtained, the equilibrium concentrations of solute atoms at this temperature can then be determined, using the mass balance equations (eqn. 3.35).

III.1.2.3. Modifying factor

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The other problem concerning the solution of ΔG^* is the determination of the interfacial energy modifying factor (ξ), which is the reduction factor associated with the presence of dislocations. This is unity when nucleation is homogeneous and less than unity when nucleation is heterogeneous. ξ values in the range from 0.19 to 0.55 were reported for Nb(CN) nucleation [137] and the value fell between 0.38 and 0.51 for Ti(CN) [138]. To determine ξ , calculations were carried out for various ξ values in the range of 0.1~0.5. Since the nose temperature of the C curve varies according to ξ , the ξ value chosen was the one that most closely fit the experimental nose temperature.

The calculated results of the precipitation start times, using the L-J model, are shown in Fig. 3.2 for various ξ values. The experimental data used for this calculation are from the work of Akben et al. [11]. At $\xi = 0.42$, the nose temperature is located at approximately 900°C, which shows good agreement with the experimental data. The same result can be seen for the analysis of other experimental results [121]. Therefore 0.42 was selected as the value of the modifying factor for the interfacial energy between precipitate and matrix. This value is within the range of that calculated for Nb(CN) in the D-S model.



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Fig. 3.2 Variation of P_s curves with the modifying factor.



Fig. 3.2 Variation of P_s curves with the modifying factor.

III.1.3. Ps Calculation

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In the L-J model, two parameters are still unknown; the critical number of nuclei (N_c) and the dislocation density (ρ). Here, the ratio N_c/ ρ was assumed to be constant in the test temperature range used. This ratio is then obtained as part of the P_s calculation using experimental data.

Once the N_c/ρ values have been determined from each PTT data point, the average is taken as being constant for the temperature range investigated. The calculated P_s times from PTT data, along with the experimental data and the ratio of N_c/ρ , will be shown later.

III.2. METHODS OF PREDICTING P_f TIMES DURING ISOTHERMAL HOLDING

The various types of kinetic rule applied to precipitation and phase transformation are summarized in Table 3.2.

Various kinetic rules for

precipitation transformation.	and	phase
Kinetic equation		ref.
$Y = 1 - \exp(-b t)^n$		105
$Y = 1 - \exp\{-(t/\tau)^n\}$		104
$Y = 1 - \exp(-b(T) t^n)$		142
$Y = 1 - exp(-b t^n)$		110

Table 3.2

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In this study, the original Johnson-Mehl-Avrami (J-M-A) type equation is employed, i.e.:

$$Y = 1 - exp(-b t^{n})$$
 (2.15)

To use this equation to describe a certain reaction, the rate constant (b) and time exponent (n) must be derived.

III.2.1. Derivation of Rate Constant and Time Exponent

Here it is assumed that the particles are growing spherically. In this case, the expected concentration distribution along the radial direction of a particle is shown in Fig. 3.3. C_P, C_M and C_I are the solute concentrations in the precipitate, matrix and at the interface, respectively, and R_1 is the radius of the precipitate.



Fig. 3.3. Actual concentration distribution along the radial direction of the precipitate.

If the volume increase of a precipitate during the time interval dt is dV, then the concentration of solute atoms which is removed from the matrix through the interface is dV(CP-CI). The number of solute atoms supplied to the interface from the matrix by diffusion is determined by Fick's first law:

$$J dt = 4nR^2 D\left(\frac{\partial C}{\partial r}\right)_{r=R_1} dt$$
(3.37)

where J is the flux, D the diffusivity and C is the concentration of solute in the matrix.

Equating the concentration of solute atoms removed from the matrix with that supplied to the interface from the matrix by diffusion, yields:

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$$\frac{dR}{dt} = D\left(\frac{\partial C}{\partial r}\right)_{r=R_1} \frac{1}{C_P - C_I}$$
(3.38)

To calculate the concentration gradient $(\partial C/\partial r)$ at the interface, Zener's approximation was used.

III.2.1.1. Zener's approximation

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The real concentration gradient beyond the precipitate/matrix interface is shown in Fig. 3.3. However, in this calculation it is assumed that the gradient is simplified, as shown in Fig. 3.4. The solute concentration at a distance R ($R_1 < R < R_2$) from the interface is:

$$C_{R} = C_{I} + (C_{M} - C_{I}) \frac{R - R_{1}}{R_{2} - R_{1}}$$
(3.39)



Fig. 3.4. Simplified concentration profile between precipitate and matrix along the radial direction.

where R_2 is the radius of the solute depleted zone. At R, the solute depletion which contributes to the precipitate is C_M - C_R , and is expressed as:

$$C_{M} - C_{R} = (C_{M} - C_{I}) \frac{R_{2} - R_{I}}{R_{2} - R_{I}}$$
(3.40)

The volume of a shell of small distance dR is $4\pi R^2 dR$. Therefore the number of solute atoms (dm) which contributes to that volume of precipitate is:

$$dm = 4\pi R^2 dR \left(C_M - C_I \right) \frac{R_2 - R}{R_2 - R_1}$$
(3.41)

The total number of solute atoms in the precipitate is equal to the integrated value of dm from R_1 to R_2 .

$$\int_{R_{1}}^{R_{2}} 4\pi R^{2} (C_{M} - C_{I}) \frac{R_{2} - R}{R_{2} - R_{1}} dR = \int_{0}^{R_{1}} 4\pi R^{2} (C_{P} - C_{M}) dR \qquad (3.42)$$
$$\cdot \left(\frac{R_{2}}{R_{1}}\right)^{3} + \left(\frac{R_{2}}{R_{1}}\right)^{2} + \left(\frac{R_{2}}{R_{1}}\right) - \left(3 + \frac{4(C_{P} - C_{I})}{C_{M} - C_{I}}\right) = 0 \qquad (3.43)$$

The above equation has only one root and it can be determined numerically. Setting $R_2/R_1 = r_s$, then $R_2 = r_s R_1$.

$$\frac{dR}{dt} = D \frac{C_M - C_I}{R_2 - R_1} \frac{1}{C_P - C_I}$$
$$= D \frac{C_M - C_I}{C_P - C_I} \frac{1}{(r_s - 1)R_1}$$
(3.44)

Integration of the above equation gives:

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$$R^{2} = \frac{2D}{(r_{s}-1)} \frac{C_{M} - C_{I}}{C_{P} - C_{I}} t$$
(3.45)

$$\therefore R = c (Dt)^{1/2}$$
 (3.46)

where

$$c = \left(\frac{2}{r_s - 1} \frac{C_M - C_l}{C_P - C_l}\right)^{1/2}$$

The growth coefficient of this derivation is somewhat different from Zener's, which was derived under the assumption of one-dimensional growth. In this three-dimensional solution, the factor of $1/(r_s-1)^{1/2}$ is included in the growth coefficient. The ratio of precipitate radius to that of the solute depleted zone is around 25 in the composition range of HSLA steels. This implies that the growth rate for the three-dimensional case is about 5 times slower than that of one-dimensional growth.

III.2.1.2. Growth only model for precipitation kinetics

Here, it is assumed that the precipitation process is governed only by the growth of the precipitates, which is applicable when site saturation occurs in the early stages of precipitation. Suppose that N particles per unit volume have been randomly nucleated at time t_0 and the mean radius of the particles at time t is R. Then the number of atoms (N_P) removed from the unit volume of matrix (i.e. the number of atoms which form the precipitates) at time t is:

$$N_p = N \frac{4}{3} \pi R^3 (C_p - C_i)$$
 (3.47)

The total number of solute atoms which can be precipitated per unit volume is C_{M} - C_{I} . Therefore the fraction transformed, Y, can be expressed as:

$$Y = N \frac{4}{3} \pi R^3 \frac{C_P - C_I}{C_M - C_I}$$
(3.48)

and from eqn. (3.45):

$$R^{3} = \left(\frac{2D}{r_{s}-1} \frac{C_{M}-C_{I}}{C_{P}-C_{I}}\right)^{3/2}$$
(3.49)

Substituting this expression for \mathbb{R}^3 in eqn.(3.48) gives:

$$Y = N \frac{8\sqrt{2}}{3} \pi \left(\frac{D}{r_s - 1}\right)^{3/2} \left(\frac{C_M - C_I}{C_P - C_I}\right)^{1/2} t^{3/2}$$
(3.50)

Differentiating the above equation with respect to time t yields:

$$\frac{dY}{dt} = 4\sqrt{2}ND^{3/2} \left(\frac{C_M - C_I}{(r_s - 1)^3 (C_P - C_I)}\right)^{1/2} t^{1/2}$$
(3.51)

The effect of competition for solute atoms during the later stages of precipitation is allowed for by putting a factor (1-Y) into eqn.(3.51) [55].

$$\frac{dY}{dt} = 4\sqrt{2} N D^{3/2} \left(\frac{C_M - C_I}{(r_s - 1)^3 (C_P - C_I)}\right)^{1/2} t^{1/2} (1 - Y)$$
(3.52)

Integrating the above equation gives:

$$Y = 1 - exp\left\{-\frac{8\sqrt{2}}{3}\pi ND_{o}^{3/2}exp\left(-\frac{\frac{3}{2}Q}{RT}\right)\left(\frac{C_{M}-C_{I}}{\left(\frac{R_{2}}{R_{1}}-1\right)^{3}(C_{P}-C_{I})}\right)^{1/2}t^{3/2}\right\}$$
(3.53)

From the above equation it can be seen that the time exponent is 1.5 when the reaction is controlled only by the growth of particles after nucleation. This result agrees with early investigations into precipitation continuing with a zero nucleation rate, for the case of diffusion controlled growth (Table 2.4). The rate constant b is a complicated expression which is a function of the temperature.

III.2.1.3. Nucleation and growth model for $\mathbf{k} = \mathbf{c}$ -station kinetics

In this model, it is assumed that the rate of nucleation per unit volume (I) is constant during the whole precipitation process. At time t, the radius of a particle nucleated at time t_1 ($0 < t_1 < t$) is expressed by eqn. (3.43). If v is the volume of this particle, the rate of volume increase at time t is:

$$\frac{dv}{dt} = 4\sqrt{2\pi} \left(\frac{D}{r_s - 1} \frac{C_M - C_I}{C_P - C_I}\right)^{3/2} (t - t_1)^{1/2}$$
(3.54)

The number of nuclei formed between t_1 and $t_1 + dt_1$ is I dt₁ and the rate of volume increase of this group of particles at t is Idt₁dv/dt. The rate of increase in volume V of all particles formed from t=0 to $t=t_1$ is:

$$\frac{dV}{dt} = \frac{8\sqrt{2}}{3} \ln D^{3/2} \left(\frac{1}{r_s - 1} \frac{C_M - C_I}{C_P - C_I}\right)^{3/2} I t^{3/2}$$
(3.55)

To convert volume of precipitate to fraction precipitated, the above equation must be multiplied by $(C_P-C_I)/(C_M-C_I)$. This, plus the consideration of the competition factor (1-Y), yields:

$$\frac{dY}{dt} = \frac{8\sqrt{2}}{3} \pi D^{3/2} \left(\frac{1}{(r_s - 1)^3} \frac{C_M - C_I}{C_P - C_I}\right)^{1/2} I t^{3/2} (1 - Y)$$
(3.56)

Integrating the above equation gives:

$$Y = 1 - exp\left\{-\frac{16\sqrt{2}}{15} \pi D^{3/2} \left(\frac{1}{(r_s - 1)^3} \frac{C_M - C_I}{C_P - C_I}\right)^{1/2} I t^{5/2}\right\}$$
(3.57)

The steady state nucleation rate is given by eqn. (3.3). In the case of nucleation on dislocations, the nucleus site density, N, is the product of the dislocation line density, p, and the number of sites per unit length [69]:

$$N = \frac{\rho}{a} \tag{3.58}$$

Thus, the nucleation rate of eqn. (3.57) can be rewritten as:

$$I = \frac{D X_{Nb}}{a^3} \rho \exp\left(-\frac{\Delta G^*}{kT}\right)$$
(3.59)

Substituting the nucleation rate in eqn. (3.57) for the expression in eqn. (3.59) gives:

$$Y = 1 - exp \left\{ -\frac{16\sqrt{2}}{15} \ln \frac{X_{Nb}\rho}{a^3} D_o^{5/2} \left(\frac{C_M - C_I}{\left(\frac{R_2}{R_1} - 1\right)^3 (C_P - C_I)} \right)^{1/2} exp \left(-\frac{5}{2} \frac{Q}{RT} \right) exp \left(-\frac{\Delta G^*}{kT} \right) t^{5/2} \right\}$$
(3.60)

The resulting kinetic equation shows that the time exponent is 2.5 when the reaction is controlled by a constant rate of nucleation and the growth of these nuclei. This also agrees with work associated with precipitation due to a constant nucleation rate and diffusion controlled growth (Table 2.4). As before, the rate constant b is a complex equation and is a function of the temperature.

111.2.2. Evaluation of Time Exponent from PTT Data

It is very important to know the time exponent and rate constant accurately to predict the kinetics of the reaction. However, n and b values can vary with the temperature and fraction precipitated, respectively. Therefore much kinetic data are needed to precisely evaluate the rate constant and time exponent. Unfortunately, kinetic studies for Nb(CN) precipitation are scarce and inconsistent [101-105].

The very early stages of strain induced precipitation involve elemental segregation. This was considered by Cottrell and Bilby [155], who determined that the time exponent for the rate of atoms moving toward a dislocation was 2/3 (Table 2.4). This calculation was performed under the assumption that the dislocation lines are effectively sinks for solute atoms, which are removed from the matrix. The diffusion current was neglected and only the strain field of the dislocation was considered to produce a net drift or flow of the solute atoms.

Harper [156] proposed a generalization of their result, which attempted to take into account the competition between adjacent dislocations, and expanded their equation to the overall process of precipitation on dislocations. He suggested that an n value of 2/3 was a good estimate of the overall process of precipitation on dislocation. A more detailed analysis was carried out by Ham [157], in which he concluded that the time exponent 2/3 is not accurate over the range of time during which most of the precipitation occurs. Instead, it was found that n=1 gave a good agreement with experimental data after long times. Barford [104] studied the kinetics of NbC precipitation in austenitic stainless steel in the temperature range 685-825°C, and found that the n value was around 0.7 at the early stages of precipitation (within 10% of the fraction precipitated) and close to unity at the later stages of precipitation (10-95% fraction precipitated).

At the same time as Cottrell and Bilby, Wert [158] studied the formation of precipitates from solid solutions of C and N in a-iron by means of the internal friction method. The average n values he obtained for the precipitation of Fe₃C and Fe₄N at various temperatures were 1.45 and 1.6, respectively. The n value for Fe₄N was 2.5 in its initial stage and it decreased to 1.0 at the later stages of precipitation. Wert and Zener [159] developed a theory of the rate of growth of spherical precipitates and found good agreement for up to 95% completion for both precipitates using an n value of 1.5. It was also proposed by Ham [160] that if the particle grew from initially negligible dimensions, and growth was entirely diffusion limited, then the n value was 1.5 for all spheroids, including rods and disks.

III.2.2.1. Variation of time exponent with temperature

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Although the previous analysis indicates that there is no effect of temperature on n, the kinetic studies of Watanabe et al. [102] and Barford [104] reveal that the n values vary slightly with temperature; however, there is no clear dependence of n value on the temperature. From the analysis of the experimental results of Harris and Nag [105], it appears that the n value increases as the temperature decreases. This means that the reaction rate decreases as the temperature increases, which is a questionable result. The time exponent in the J-M-A equation determines the interval of the logarithmic reaction start and finish times. When the n value increases, the logarithmic time interval between reaction start and finish decreases. Generally, the reaction time is dependent on the temperature, i.e. at a high temperature, the reaction finishes in a shorter logarithmic time interval because of a high diffusion rate, even though the incubation time for the reaction is longer than that in the lower temperature region because of the diminished driving force.

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The n value for the precipitation of Nb(CN) can be analytically evaluated from the PTT diagram. If it is assumed that the overall kinetics can be well described by the J-M-A equation for the progress of Nb(CN) precipitation, then the mean value of the rate constant and time exponent can be estimated from PTT data.

The Johnson-Mehl-Avrami equation can be rewritten as:

$$lnln\frac{1}{1-Y} = lnb + n \, lnt \tag{3.61}$$

In the PTT curves, it is generally accepted that the P_s and P_f times correspond to precipitate volume fractions of about 5% and 95%, respectively [161]. When the J-M-A equation is applied to the precipitation start and finish times, this equation can be rewritten as:

$$\ln \bar{b} + \bar{n} \ln P_{s} = \ln \ln \frac{1}{1 - Y_{s}}$$
(3.62 (a))

$$ln \,\overline{b} + \overline{n} \, lnP_f = lnln \, \frac{1}{1 - Y_f}$$
 (3.62 (b))

where \bar{b} and \bar{n} are the mean values of the rate constant and time exponent during precipitation, and Y_s and Y_f are the volume fractions of precipitate at the P_s and P_f times, respectively. Y_s , Y_f , P_s and P_f can be obtained from the literature, and using the above two equations, values for \bar{b} and \bar{n} can be simply calculated. Three PTT data sets [11, 12, 121] were analyzed, and the \bar{b} and \bar{n} values are listed in Table 3.3. From this analysis, it can be seen that the \bar{n} value does not change significantly with the temperature. Therefore, in this study, the value of \bar{n} is assumed to be constant in the test temperature range.

Temp. (°C)	Akben et al.		Weiss	and Jonas	Wang and Akben		
	ň	Ď	ñ	b	ñ	b	
875	1.41	3.90X10 ⁴	0.80	5.13X10 ²	1.78	2.14X10 ⁴	
900	1.74	3.46X10 ⁻⁴	0.88	7.60X10 ⁻²	1.65	1.04X10 ⁻³	
925	1.67	2.72X10 ⁻⁴	0.87	5.13X10 ⁻²	1.69	6.59X10 ⁻⁴	
950			0.87	2.53X10 ⁻²			
975			0.91	6.37X10 ⁻³			

Table 3.3The calculated mean values of rate constants and time
exponents from three sets of PTT data.

III.2.2.2. Variation of time exponent with fraction precipitated

To elucidate the dependence of the time exponent n on the fraction precipitated, a quadratic type formula was used to fit the ln(t) versus lnln(1/(1-Y)) data of eqn. (3.61). Using data from the literature [102, 104, 105], the error range of the calculated results is less than 5%. From Fig. 3.5, it can be seen that the n value decreases as the fraction precipitated increases.

The n value also varies significantly with the test conditions. Theoretically, the time exponent is determined by the mode in which precipitation progresses. The data of Harris and Nag imply that both nucleation and growth control the process initially, but that growth of the nuclei dominates the process at the later stages of precipitation.

The n value of the Watanabe et al. experiment is predominantly less than 1.5, which indicates that growth of the particles dominates the reaction



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Mole fraction of precipitate

Fig. 3.5 Dependence of time exponent n on the mole fraction of precipitate (a) data of Watanabe et al. and (b) data of Harris and Nag.

and that the number of nuclei is decreasing as they grow. However, a decreasing number of nuclei can only be observed in the coarsening stage of precipitation. The reason for these results is partly because the electrolytic extraction method, employed to measure the volume fraction of precipitates, cannot detect small precipitates. Therefore, the initial stage of precipitation may not have been detected accurately.

It is apparent, from the above survey, that the n value is changing continuously with the fraction precipitated. There are insufficient kinetic data on niobium precipitation to determine this variation systematically.

III.2.3. Evaluation of Rate Constant from PTT Data

The reaction starts and finishes in a short time when the b value is high. The rate constant mainly affects the incubation time of the reaction and does not change the logarithmic time interval between the reaction start and finish times.

III.2.3.1. Variation of rate constant w th temperature

The variation of the rate constant with temperature is characterized by an inverse C-shaped curve because the PTT behaviour exhibits a C-curve. Following Umemoto et al. [141], the rate constant corresponds to the shape and position of the C curve in a TTT diagram during phase transformation and, therefore, the constant generally follows a parabolic rule according to the temperature.

As already demonstrated, the b value can be explicitly formulated by considering growth only, or nucleation and growth. Almost all the parameters in the rate constant equation are dependent on temperature.

III.2.3.2. Variation of rate constant with fraction precipitated

Figure 3.6, which was obtained by curve fitting the data of Harris and Nag to the J-M-A equation, shows that the value of b increases as the mole fraction of precipitates increases. The reason for this is not obvious.



Mole fraction of precipitate

Fig. 3.6 Dependence of the rate constant on the mole fraction of precipitate.

III.2.4. Calculation of Pf

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As shown above, the precipitation process cannot be represented by a single value of rate constant and time exponent. Both values vary according to the test temperature and fraction reacted. However, because of the lack of kinetic data for precipitation and the inaccuracy of the existing data, the prediction of exact values of n and b from experimental data is almost impossible. Therefore, in this study, two boundary conditions, growth only and nucleation and growth, were assumed, and the time exponent and rate constant were derived for each condition. Almost all the parameters in the rate constant expression can be calculated from thermodynamic relationships. However, the number of nuclei per unit volume (N_c) in the growth only model and the dislocation density (p) in the nucleation and growth model are still unknown. These can be determined from the rate constant of each experimental PTT data set. The average value of these parameters is used to calculate the rate constant at any temperature.

Figure 3.7 shows the predicted P_s and P_f curves for both the growth only and nucleation and growth models, and demonstrates that the nucleation and growth model yields a better fit to the experimental data. The constants determined during the calculations are shown in Tables 3.4 to 3.6.

The unknown parameter in the nucleation and growth model is the dislocation density, which shows a strong dependence on temperature. The obtained values are correlated with temperature as a linear relationship between ln(p) and 1/T. The modified calculations are presented in Fig. 3.8, and the predictions are somewhat improved, except in the case of the analysis of the P_f data of Akben et al. It is perhaps notable that, in the case of the latter, the dependence of p on temperature is quite steep relative to the data of Wang and Akben, and Weiss and Jonas. It also should be noted that the experiments consist of only 3 sets of real data, which are insufficient to define the precise dependence of p on temperature.

from PTT data (P _s).					
Temp.(°C)	Akben et al.	Weiss and Jonas	Wang and Akben		
975		3.72X 10 ³			
950		1.38X104			
925	8.34X104	1.87X104	1.12X10 ⁵		
900	9.90X1 04		1.02X10 ⁵		
	I I I I I I I I I I I I I I I I I I I	I I	1		

1.97X104

1.66X105

1.69X105

875

Table 3.4Calculated constants (the ratio of the number of
nuclei per unit volume to the dislocation density)
from PTT data (P_s) .

Temp.(°C)	Akben et al.	Weiss and Jonas	Wang and Akben
975		3.11X1017	
950		2.26X1018	
925	4.72X10 ¹⁶	8.75X1018	9.60X10 ¹⁶
900	1.33X1017		3.34X1017
875	3.51X1017	4.39X1019	1.65X1017

Table 3.5	Calculated number of nuclei per unit volume (cm ⁻³)
	from PTT data (P_f) based on the growth only model.

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Table 3.6	Calculated dislocation densities (cm/cm ³) from PTT
	data (P_f) based on the nucleation and growth model.

Temp.(°C)	Akben et al.	Weiss and Jonas	Wang and Akben
975		2.09X10 ¹⁵	
950		9.44X1014	
925	3.26X1 013	1.28X1015	2.82X1013
900	5.98X1013		8.79X1013
875	1.63X1014	6.15X10 ¹⁵	5.39X1013



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Fig. 3.7 Calculated P_s and P_f times from experimental data; (a) data of Akben et al.; (b) data of Weiss and Jonas; (c) data of Wang and Akben.



Fig. 3.7 Calculated P_s and P_f times from experimental data; (a) data of Akben et al.; (b) data of Weiss and Jonas; (c) data of Wang and Akben.



Fig. 3.7 Calculated P_s and P_f times from experimental data; (a) data of Akben et al.; (b) data of Weiss and Jonas; (c) data of Wang and Akben.



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Fig. 3.8 The variation of Pf time when dislocation density is modified according to temperature; (a) data of Akben et al.; (b) data of Weiss and Jonas; (c) data of Wang and Akben.



Fig. 3.8 The variation of Pf time when dislocation density is modified according to temperature; (a) data of Akben et al.; (b) data of Weiss and Jonas; (c) data of Wang and Akben.

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Fig. 3.8 The variation of P_f time when dislocation density is modified according to temperature; (a) data of Akben et al.; (b) data of Weiss and Jonas; (c) data of Wang and Akben.

III.3. MODELLING OF CCP (Continuous-Cooling-Precipitation) DIAGRAMS

For phase transformations, the additivity rule [139] has been used to predict the continuous cooling behaviour from isothermal data [140-145]. In this work, the same approach is employed to predict the CCP behaviour from PTT data.

III.3.1. The Additivity Rule

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Figure 3.9 illustrates the concept of the additivity rule. Here, $\tau_x(T_i)$ is the time when the reaction reaches x% at temperature T_i and Δt_i is the incremental hold time at temperature T_i . In other words, the cooling curve is divided into a series of incremental isothermal steps. Scheil [139] originally proposed that the reaction starts when the sum of the ratios of reaction time to reaction start time (τ_0) reaches unity.

$$\sum_{i=1}^{n} \frac{\Delta t_{i}}{t_{o}(T_{i})} = 1$$
 (3.63)

Umemoto et al. [140-145] extended this to predict the time when the reaction reaches x%. The additivity rule, in this case, can be rewritten as:

$$\sum_{\iota=1}^{n} \frac{\Delta t_{\iota}}{v_{\iota}(T_{\iota})} = \sum_{\iota=1}^{n} \frac{1}{v_{\iota}(T_{\iota})} \frac{\Delta t_{\iota}}{\Delta T_{\iota}} \Delta T_{\iota} = 1$$
(3.64)

where $\Delta t_i / \Delta T_i$ is the inverse of the cooling rate. If the cooling curve is divided into sufficiently small steps, then the equation can be expressed as an integral:

$$\int_{T_{e}}^{T} \frac{1}{t_{r}(T_{i})} \frac{dt}{dT} dT = 1$$
(3.65)

where T_e is the equilibrium temperature at which the reaction is initiated.



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Fig. 3.9 A diagrammatic representation of the additivity rule concept.

The additivity rule can be applied when the reaction satisfies one of the following conditions.

i) It is isokinetic, i.e. the rate of nucleation is proportional to the rate of growth [108, 109]

ii) There is a site saturation, i.e. the nucleation sites are saturated early in the reaction [162]

iii) the reaction is nucleation controlled, i.e. the nuclei grow to a certain size quite rapidly and then stop growing [143].

It has been shown that the predicted CCT (continuous-coolingtransformation) behaviour from IT (isothermal-transformation) data using the additivity rule is very close to the experimental results when the calculations were carried out for the proeutectoid ferrite, pearlite and bainite transformations. These phenomena can be classified in terms of the above conditions as follows:

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a) Site saturation takes place in the proeutectoid ferrite transformation because the nucleation sites (mainly on grain boundaries of the austenite) are occupied at a very early stage in the transformation [143].

b) Bainite transformation is a nucleation controlled reaction because the growth rate of this reaction is very rapid [140].

c) Other diffusional transformations, e.g. pearlite formation from austenite, are also additive, even though they do not precisely satisfy any one of the above conditions. The calculated results, which were obtained by the additivity rule, show good agreement with experimental ones. This was explained in terms of two mechanisms [142]: firstly, the variation of the ratio of nucleation rate to growth rate is not large enough to produce a considerable difference in the transformed volume fraction; secondly, the cooling transformation nearly satisfies one of the following additivity conditions, i.e., when the cooling rate is slow, transformation occurs under nearly isokinetic conditions and when the cooling rate is fast, the condition of site saturation is nearly satisfied.

For the present work, it was assumed that the additivity rule can be applied to predict P_s and P_f times during continuous cooling. However, strictly speaking, not one of the above conditions can be applied. Instead, it is assumed that the reaction is nucleation controlled, as in iii) above, in the early stages of precipitation, and that it is mainly controlled by the growth of nuclei during its later stages, as in point ii).

III.3.2. Calculation of CCP Curves

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Using the thermodynamic equations, the precipitation start and finish times can be calculated continuously with temperature from isothermal data. These data are then the τ_x values for the additivity rule. The solution temperature (T_e) is defined as the temperature at which the precipitation start time is more than 10^{25} sec (near the real equilibrium solution temperature, the P_s and P_f times are so large that the calculation cannot be continued). This simplification introduces an error far less than 1%.

The cooling curves are divided into 1°C increments, and, at each temperature, τ_x and Δt_i are calculated. The precipitation start and finish times during continuous cooling are then determined from the time when the sum of the ratios of each reaction time (Δt_i) to τ_x reaches unity. The program which includes all the calculations for the P_x and P_f times at certain temperatures for isothermal and continuous cooling is listed in the appendix. Calculated CCP diagrams are shown in Fig. 3.10. The shapes of the CCP diagrams are similar to those of the PTT diagrams, except for the lower temperature region under the nose temperature. During continuous cooling, the precipitation start and finish times shift to the right and are lower, i.e. to longer times and lower temperatures compared to the PTT diagrams. This occurs because nucleation and growth of the precipitates are suppressed during cooling. This effect is prominent at the higher cooling rates.



Fig. 3.10 Calculated CCP behaviour from PTT data; (a) data of Akben et al.; (b) data of Weiss and Jonas; (c) data of Wang and Akben.



Fig. 3.10 Calculated CCP behaviour from PTT data; (a) data of Akben et al.; (b) data of Weiss and Jonas; (c) data of Wang and Akben.



Fig. 3.10 Calculated CCP behaviour from PTT data; (a) data of Akben et al.; (b) data of Weiss and Jonas; (c) data of Wang and Akben.

CHAPTER IV

EXPERIMENTAL MATERIALS AND METHODS

IV.1 EXPERIMENTAL MATERIALS

For the purpose of investigating the CCP behaviour, a Nb containing steel and a C-Mn steel were studied. The plain carbon steel was used for reference purposes. The steels used in the present study were prepared at the Metals Technology Laboratories of the Department of Energy, Mines and Resources, Ottawa, and their chemical compositions are given in Table 4.1

Table 4.1Chemical compositions of the experimental steels (wt%).

Steel	С	Mn	Si	S	Р	Nb	AI	N
C-Mn	0.060	1.31	0.25	0.008	0.013	-	0 020	0 0056
C-Mn-Nb	0.067	1.23	0.20	0.008	0.008	0.040	0.020	0.0060

IV.2 MECHANICAL TESTING EQUIPMENT

IV.2.1 MTS Testing System

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The isothermal precipitation behaviour was measured by a computerized material testing system set up for hot compression. This apparatus consists of a load frame, a hydraulic power supply, a closed loop servohydraulic system and a computerized outer loop system. The operation is controlled by means of the closed loop and the outer loop systems (Fig. 4.1). The hydraulic power supply provides a source of hydraulic fluid under pressure for the system. A hydraulic actuator generates the force and the linear displacement which are measured by the load cell and the LVDT (linear variable differential transformer), respectively.

The load cell provides an output voltage having a magnitude in direct proportion to the amount of applied force. The output voltage of the load cell is determined by the direction of the applied force, i.e., if a compressive force is applied, the output voltage is negative while a tensile force produces a positive output. Thus the output voltage of the load cell contains information about the amount and direction of the applied force. The LVDT is mounted in the base of the actuator and the movable core is positioned by the piston of the actuator. The output voltage increases linearly from zero as the piston is displaced from its mid-stroke position. In the present tests, the capacity of the load cell was 1000N and the range of 100% was selected. The gauge length of the LVDT was 100mm and the range selected was 10%.

The automation in this MTS system is through a computer/433 subsystem and data processing equipment, which forms an outer, supervisory loop around the closed loop. The computer/433 subsystem performs the functions of command generation, data acquisition and reduction, real time decision making and various other system control functions. The computer/433 subsystem consists of a Digital Equipment Corporation PDP-11/04 computer, a Tektronics graphics terminal, a series 433 processor interface unit, a DEC RX11 disk system with RX01 floppy disk drive, a Tektronics hard copy device and MTS-BASIC/RT-11 system software. An exterior view of the system is seen in Fig. 4.2.

IV.2.2 The High Temperature Vacuum Furnace

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The elevated temperature experiments were made possible by a high temperature, high vacuum furnace which was mounted on the MTS load frame. It consists of a 17 kVA CENTORR model M60 front loading furnace, with a high speed diffusion pump backed by a mechanical pump. A view of the test chamber of the furnace is presented in Fig. 4.3.

The furnace employs tungsten mesh resistance heating elements. The hot zone of the chamber, approximately 76 mm in diameter and 200 mm high, is surrounded by concentric multilayered tungsten and molybdenum radiation shields. The top and bottom ends of the furnace are similarly shielded. The



Fig. 4.1 Block diagram of the automated system.


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Fig. 4.2 An external view of the high temperature compression testing system: 1) MTS load frame; 2) Centorr vacuum furnace; 3) temperature and vacuum control console; 4) PDP 11/04 computer; 5) Tektronix terminal; and 6) Tektronics hard copy device.



Fig. 4.3 An internal view of the Centorr high temperature, high vacuum furnace: 1) vacuum chamber; 2) TZM anvils; 3) specimen; 4) thermocouples; 5) shields; and 6) tungsten mesh heating elements.

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upper and lower anvils (d=32mm, h=150mm) are made of the molybdenum alloy TZM and are fixed to the actuator piston and load cell, respectively, through internally water cooled stainless steel extension rods.

To control the temperature in the test chamber, a J-type Pt/Pt-10%Rh thermocouple was placed close to the center of the chamber, and linked to a current adjusting type (CAT) temperature controller made by Leeds & Northrup. The CAT controller provides an output current which is proportional to the temperature deviation from the set point. The temperature of the specimer was measured using a K-type chromel-alumel thermocouple which was placed in contact with the specimen. The other thermocouple, not in contact with the sample, was used for reference and for verification when the specimen contacting thermocouple was broken, or lost contact with the sample. For example, during cooling from the solutionizing to the test temperature, contact failure is indicated when the two cooling rates are similar. This is because the specimen and anvil have higher heat capacities than the reference thermocouple. Thus, the cooling rate of these parts should be lower than that of the self-standing thermocouple when the furnace is cooled down.

A vacuum of $2x10^{-5}$ to $1x10^{-4}$ torr was consistently attained by the vacuum system. All the present tests were carried out in vacuums better than $5x10^{-5}$ torr.

IV.2.3 Hot Deformation Dilatometer

Even though the maximum cooling rate of the specimen, when quenched in the MTS machine using helium gas, is up to 60° C/s, this cooling rate cannot be controlled properly in the high temperature vacuum furnace. In general, a reproducible maximum cooling rate is obtained when the furnace is turned off and is on average 2°C/s (Fig. 4.4). However, controlling the cooling rate beyond this level is very difficult in this furnace. Therefore, a computerized MMC quench hot deformation dilatometer was used to follow the precipitation behaviour during continuous cooling, the main advantage being the accuracy in controlling the cooling rate. An external view and the detailed configuration are shown in Fig. 4.5. The hot deformation dilatometer is frequently employed to observe phase transformation behaviour after deformation through measurement of the dimensional changes during phase transformation. A maximum cooling rate of up to 400° C/s can be obtained when the sample is quenched using helium gas. Specimens are heated to the solution temperature using induction and the temperature is continuously measured by a K-type thermocouple which is spot welded on the surface of the specimen.

IV.3 EXPERIMENTAL METHODS

IV.3.1 Specimen Preparation

IV.3.1.1 MTS test

Compression specimens were machined from the as-received 13mm thick plate with their longitudinal directions along the rolling direction. The specimen configuration for this test is shown in Fig. 4.6. As can be seen in this figure, both cylindrical ends were grooved to enhance uniform deformation by allowing the maximum retention of lubricants [163]. Fine glass powder was used as a lubricant between the tooling and the specimen and was applied as a slurry made up with alcohol. A height-to-diameter ratio of 1.5 was selected for the specimen dimensions to promote homogeneous deformation [164, 165]. The lubricants were chosen to have a viscosity of about 104 poise at the test temperature, according to suggestions made in a previous investigation [166]. The glasses used in this work were manufactured by the Corning Glass Co., Ltd.

IV.3.1.2 Hot deformation dilatometer

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Sample preparation followed the same pattern as for the MTS test. However, cylindrical specimens in this instance were 8mm long and 4mm in diameter. The specimens did not have grooves; instead, both ends were spot



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Fig. 4.4 Temperature-time relation obtained by shutting off the furnace; the maximum cooling rate and the repeatability of the temperature profile are illustrated.



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(a)

Fig. 4.5 The MMC quench hot deformation dilatometer (a) an external view of the MMC quench hot deformation dilatometer, (b) detailed view of measuring head, and (c) close up of (b) showing specimen positioning.



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(b)



(c)

Fig. 4.5 The MMC quench hot deformation dilatometer (a) an external view of the MMC quench hot deformation dilatometer, (b) detailed view of measuring head, and (c) close up of (b) showing specimen positioning.

Components of measuring head are; 1) LVDT, 2) induction coil, 3) specimen, 4) deformation pistons, 5) limit switch, 6) micrometer adjustment of limit switch, 7) platens, 8) extension rod to LVDT and 9) thermocouple.



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Fig. 4.6 Compression test sample geometry and groove design.

welded to thin, round molybdenum foils (t=0.06mm), which decreased the friction between the tooling and specimen.

IV.3.2 Stress Relaxation Testing

The stress relaxation method was employed to measure the isothermal precipitation behaviour. It was initially developed by Liu and Jonas [167, 168] to detect the precipitation of Ti(CN) precipitation in austenite and was subsequently used by Djahazi [169] for Nb precipitation investigations.

IV.3.2.1 Fundamentals of stress relaxation

Stress relaxation is the decrease in stress at constant deformation due to the conversion of elastic strain into inelastic strain. In the basic stress relaxation test, a specimen is deformed at a constant temperature and strain rate to some initial stress, σ_0 , and the actuator is then arrested and the subsequent stress relaxation is continuously monitored. When stress relaxation occurs, the stress needed to maintain a constant total deformation decreases as a function of time. For a specimen which is under a total strain ε at an elevated temperature where creep can occur:

$$\varepsilon = \varepsilon_e + \varepsilon_p = \frac{\sigma}{E} + \varepsilon_p \tag{4.1}$$

where ε_e is the elastic strain, ε_p is the plastic strain and E is the elastic modulus of the specimen. Stress relaxation curves at different temperatures are shown schematically in Fig. 4.7. The initial rate of decrease of stress is high, but the rate diminishes in the later stages. For the total strain to remain constant, the elastic strain decreases as the material creeps. This means that the stress required to maintain the total strain decreases with time as the creep strain increases. The plastic strain in the specimen during relaxation can be written as:

$$\varepsilon_p = \frac{\sigma_o - \sigma}{E} \tag{4.2}$$

Feltham [170] found the following empirical logarithmic relationship between stress and time:

$$\sigma_{\rho} = \sigma - S' \ln \left(1 + \beta t \right) \tag{4.3}$$

where S' is a time independent parameter and β is a constant. This empirical relationship has been observed in various materials including a-iron [171], plain carbon steels [172, 174], stainless steels [173], nickel [175] and niobium [176]. Although most of these experiments were carried out at room temperature or elevated temperatures ($<0.5T_m$), for the present study, this stress relaxation method was employed in the high temperature austenite region to observe precipitation behaviour.



Fig. 4.7 Typical stress relaxation curves at different temperatures.

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IV.3.2.2 Length change of the compression tooling

When the temperature is decreased from the solution temperature to the test temperature, a constant level of deformation is not easy to attain because dimensional changes of both the tooling and specimen are involved which are associated with thermal contraction. The amount of thermal contraction of both the tooling and the specimen should be compensated for during the stress relaxation test, to maintain a constant strain.

In this study, the amount of contraction of the tooling was measured using a ceramic (Al_2O_3) dummy sample with the same dimensions as the steel specimen. The length change with time, using the same thermal history as each stress relaxation test, was continuously monitored under a load of between 1.5 and 5.0kg. Since both the thermal contraction and the creep of ceramic dummy sample are negligible, the displacement data give the length decrease of the compression tooling.

The length changes with time determined during cooling to and holding at various test temperatures are shown in Fig. 4.8. The results were fitted to the following equation by the least squares method:

$$\Delta l = \Delta l_{\mathcal{A}} \{1 - exp(-h t^n)\}$$
(4.4)

where Δl is the current length change, Δl_{∞} is the maximum length decrease attained by the tooling at a given temperature, and k and n are constants. This was then used to control the actuator piston to keep the specimen deformation constant.

IV.3.2.3 Stress relaxation testing details

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The thermal profiles of the stress relaxation tests are presented in Fig. 4.9. The samples were reheated to the solutionizing temperature, held for 30 min. and then cooled down to test temperature by switching off the furnace.



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Fig. 4.8 Length change of the compression tooling with time during cooling to and holding at different test temperatures.

The sample was held for 1min at the test temperature to stabilize the temperature, and a 5 % deformation was then executed using a strain rate of 0.1/s. The stress decrease with time was monitored while the strain level after deformation was kept constant.

Before deformation, the piston is positioned automatically such that the anvil is in contact with the specimen surface prior to testing. In this positioning period, 20 load and displacement data are transferred from the MTS machine in a time interval of 0.169 s, and the mean values of load and displacement are used to follow the contraction of the specimen and tooling. Depending on the load value, the piston moves either 1 machine unit down or up or remains stationary (1 machine unit is 1/2047 of the set range, i.e. in the present experiment, this represents 1/204.7 mm because the range selected to measure the gauge length by the LVDT was 10 mm). The critical loads to control the piston were 0.5kg and 5kg, i.e. if the load is less than 0.5kg, the piston moves down 1 machine unit to increase the contact pressure between the anvil and the specimen; if greater than 5kg, the piston moves up, and between the two values it remains stationary. At the point of prestraining, the automatic positioning loop exits and the current position of the piston is taken as the reference position for the prestrain. The amount of prestrain was chosen in order to avoid the initiation of recrystallization during the stress relaxation test.

To maintain a constant true strain rate, the sample is deformed at a rate which is proportional to its instantaneous height, h:

$$\frac{dh}{dt} = -\dot{\varepsilon} h \tag{4.5}$$

where $\dot{\epsilon}$ is the strain rate. By integrating the above equation and setting $h = h_0$ at t = 0, the following relation is obtained.





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Fig. 4.9 Experimental schedule for stress relaxation tests.

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$$\Delta h = h - h_o = h_o \{1 - \exp(-\dot{\varepsilon}t)\}$$
(4.6)

With a computer controlled system, true strain rate tests are produced by dividing the entire deformation time into n steps (n=50 in the present test) with intervals of constant Δt . The deformation time at the end of the i-th interval is:

$$t_i = i \Delta t = \frac{i}{n} \frac{\varepsilon}{\dot{\varepsilon}}$$
(4.7)

Thus, eqn (4.6) can be rewritten as:

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$$\Delta h_{\iota} = h_{o} \left\{ 1 - exp\left(-\frac{i}{n} \varepsilon \right) \right\}$$
(4.8)

where Δh_i is equivalent to the actuator displacement in the i-th step during the deformation. This equation was employed to deform the specimen at a constant strain rate.

The monitoring of the stress relaxation experiments was divided into three time periods to conserve computer memory: i) 0.5s immediately after the prestrain, ii) the next 100s and iii) the remaining time. Within each period, a different data acquisition time interval was selected to obtain sufficient data points for a log scale of experimental time. A total of 4150 load and displacement data points was sampled during a stress relaxation experiment. The load data were converted into true stress by the following equation.

$$\sigma_{\iota} = \frac{load}{A_{\iota}}$$
(4.9)

where A_i is the instantaneous sample cross section which was calculated as $A_i = A_0 h_0/h_i$. Here A_0 and h_0 are the cross sectional area and height of the undeformed specimen, respectively, and h_i is the instantaneous height of the specimen. The true strain at t_i was converted from the recorded displacement data Δh_i by the inverse of eqn. (4.8), i.e.

$$\varepsilon_{i} = -\ln\left(1 - \frac{h_{i}}{h_{o}}\right) \tag{4.10}$$

The raw data determined from eqn. (4.9) involve significant scatter because the movement of the piston is digitized. This data scatter was smoothed by taking mean values of the stress over selected time intervals, which were defined so as to lead to an even distribution of the mean stress data points on the log time scale.

IV.3.3 Continuous Cooling Testing

To check the predicted CCP behaviour of the model, continuous cooling testing was performed by means of the hot deformation dilatometer. The schedule of thermal treatments is represented in Fig. 4.10. The solutionizing stage was the same as that of the stress relaxation test. The samples were then cooled down to 1000°C and deformed 5% at a strain rate of about 0.1/s. During cooling, using various cooling rates $(0.1°C/s\sim5°C/s)$, the samples were quenched at designated temperatures. The quenched samples were sectioned parallel to the deformation axis and the Nb precipitates were observed by transmission electron microscopy.

IV.4. ELECTRON MICROSCOPY

IV.4.1. Preparation of Carbon Replicas

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The specimens quenched during continuous cooling were sectioned and ground using silicon carbide papers and polished with $6\mu m$ diamond paste and $0.05\mu m$ alumina, in sequence. The polished specimens were lightly etched with 2% nital for about 5sec. Carbon was deposited on the etched surface using a vacuum evaporator in vacuums better than 5×10^{-4} torr. To obtain a uniform carbon film, the specimen stage was rotated continuously during deposition.

Squares of approximately 2x2 mm were scribed on the coated surfaces and removed by chemical etching using a solution of 10% nital. During the



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Time

Fig. 4.10 Experimental schedule for the continuous cooling tests.

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chemical etching, the solution was agitated mildly to improve the contact between the specimen and the clean solution. The removed carbon replicas were washed gently in a 50-50 mixture of ethanol and distilled water and then in distilled water. They were finally mounted on TEM copper grids (Cu, 3mm, 200 mesh) and dried.

IV.4.2. Transmission Electron Microscopy

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The carbon replicas were observed in a JEOL-100CX scanning transmission electron microscope operated at 80kV. Chemical analysis of the individual particles was performed by a PGT system IV energy dispersive Xray spectrometer (EDS).

IV.4.3. Particle Size Measurement

From the TEM micrographs, the particle size was measured with an accuracy of up to 10⁻¹mm, using a monocular. For each test condition, between 200 and 300 particles were observed. The particle size distribution and statistical parameters, such as mean particle size, standard deviation, etc., were then determined.

CHAPTER V EXPERIMENTAL RESULTS

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V.1. STRESS RELAXATION TEST RESULTS

A specimen is plastically deformed at a constant strain rate to a particular strain, which is then held constant during the test. The consequent continuous stress decrease under this condition is termed as stress relaxation. The stress change with time can generally be described by the logarithmic time dependence shown in eqn. (4.3).

V.1.1. Flow Behaviour During Prestraining

Figure 5.1 shows several true stress-strain curves as a function of temperature during prestraining. At small strains, the σ - ϵ curves coincide with each other and this phenomena is identified as an initial athermal hardening. In general, the flow curves at high temperatures are the result of athermal hardening and dynamic recovery when the strain is not sufficient for dynamic recrystallization.

The flow curve can be divided into a pre-yield and a work hardening region. In the pre-yield region, stress increases linearly with strain, while the rate of stress increase with strain decreases in the work hardening region. The yield stress (σ_y) and the maximum stress (σ_m) were determined by the 0.2% offset criterion and the flow stress at the end of the prestrain (5%), respectively. The two values are listed in Table 5.1.

The temperature dependence of the yield and maximum stress is usually described by an Arrhenius type equation, which follows the rate of a thermally activated process. Therefore, a plot of $\log(\sigma_y)$ and $\log(\sigma_m)$ with inverse absolute temperature (1/T) is widely used to characterize the temperature dependence of stress. The strain rate dependence on temperature can be expressed by the thermally activated rate equation:



Fig. 5.1 True stress-strain curves during prestraining.

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Temp. (°C)	Yield stress (σ _y) (MPa)	Maximum stress (σ _m) (MPa)
950	21.6	56.2
925	26.1	61.0
900	31.0	67.7
875	35.4	79.0
850	39.5	75.0

Table 5.1Yield and maximum stress during
prestraining.

$$\dot{\varepsilon} = K(\sigma) \exp(-\frac{Q}{RT})$$
(5.1)

where $K(\sigma)$ can be expressed in several ways, including $A\sigma^n$, $A'exp(\beta\sigma)$, and $A''(sinhao)^n$, where A, A', A'', a, β and n are constants. It has been often observed that $A\sigma^n$ generally describes creep conditions well, i.e. where the amount of stress is small. Since the strain rate, for this study, is constant:

$$ln\sigma = \frac{1}{n} \ln\left(\frac{\dot{\varepsilon}}{A}\right) + \frac{Q}{nRT}$$
(5.2)

As expected, the relationship between $ln\sigma$ and 1/T, which is shown in Fig. 5.2, is linear, and the slope of this graph is Q/nR.

V.1.2. Relaxation Behaviour of Plain Carbon Steel and Nb Steel

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The stress relaxation behaviours of the plain carbon steel and niobium containing steel at 900°C after 5% deformation are shown in Fig. 5.3. For the plain carbon steel, the time dependence of stress is well defined by eqn. (4.3) during the whole test period, i.e. the stress decreases linearly with logarithmic time. However, the later stages of relaxation behaviour of the Nb steel deviate



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Fig. 5.2 Temperature dependence of yield stress and maximum stress.



Fig. 5.3 Comparison of stress relaxation data for the Nb and base steel, deformed 5% at 900°C.

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from its initial time dependence. In this region, the stress versus logarithmic time relationship of the Nb steel can be described as a combination of the basic logarithmic curve plus a stress increment, $\Delta \sigma$; thus eqn. (4.3) can be expressed as:

$$\sigma = \sigma_{o} - S' \ln (1 + \beta t) + \Delta \sigma$$
(5.3)

The relaxation behaviour can be divided into three regions. In region I, $\Delta \sigma = 0$ and the relaxation behaviour is similar to that of plain carbon steel, except for the higher stress levels caused by the strengthening effect of solute niobium. In region II, $\Delta \sigma$ starts to increase due to precipitate formation, i.e. the rate of stress decrease with time is arrested because of the interaction of newly formed precipitates and moving dislocations. The curve diverges continuously until the stress increment reaches a maximum value, after which $\Delta \sigma$ starts to decrease. The points at which $\Delta \sigma$ deviates from zero and where $\Delta \sigma$ is a maximum are identified as the precipitation start (P_s) and finish (P_f) times, respectively. TEM examination of carbon extractions has confirmed this interpretation [65, 167-169].

The stress relaxation behaviour of the specimen which was held at 800° C differs somewhat from that of the other specimens (Fig. 5.4). The stress decreases linearly with logarithmic time, and then experiences a sudden drop. The latter is attributed to the γ -to- α phase transformation in the specimen, since the strength of ferrite is less than that of austenite at the same temperature.

Stress relaxation tests were performed to determine P_s and P_f times for the Nb steel during isothermal holding at several temperatures. The experimental results, which are presented in Fig. 5.5, indicate that the temperature at which precipitation is the fastest is near 900°C, which agrees well with the literature [11, 12, 16, 121].



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Fig. 5.4 Stress relaxation results of Nb steel when a phase transformation is involved (test temp; 800°C).





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V.1.3. Precipitation - Time - Temperature Diagrams

The P_s and P_f times determined from the stress relaxation method for the Nb steel are listed in Table 5.2. The results are also presented in the form of precipitation-time-temperature (PTT) diagrams in Fig. 5.6. From the five sets of experimental P_s and P_f times, PTT curves can be determined using the isothermal precipitation model which was described in chapter III. The P_s and P_f times calculated from experimental data using the nucleation and growth and growth only models are also presented in Fig. 5.6. From the diagram, it can be seen that the nucleation and growth model provides a slightly better fit compared to the growth only model.

Temp. (°C)	P _s (sec)	$\mathbf{P_{f}}(sec)$
950	48	440
925	38	345
900	32	295
875	44	395
850	62	540

Table 5.2Measured Ps and Pf times using the
stress relaxation method.

The calculated mean values of the rate constants and time exponents evaluated from the experimental PTT data are listed in Table 5.3. The unknown parameter (ρ) was determined from the experimental data (Table 5.4), and the mean value of ρ was applied for all test temperatures to calculate the P_s and P_f of Fig. 5.6. The dislocation density so determined seems to be an overestimate, when it is considered that the value of ρ in *highly deformed* metals is about 10¹²/cm². Since the rate constant is proportional to the activation energy, exponentially, a small change of this value leads to large differences in dislocation density. The value of the activation energy used in this calculation was determined experimentally under the condition that no deformation was employed [146]. However, stress is applied during testing, which can decrease the activation energy for the diffusion of solute atoms.

The logarithm of ρ calculated from the experimental data displays a linear dependence on the inverse absolute temperature, as shown in Fig. 5.7. This behaviour arises because the dislocation density is directly related to the applied load, which exhibits an Arrhenius type temperature dependence. From other data [11, 12, 121], this dependence is apparently not as strong, possibly because of insufficient data. The lines represent least square fits. The calculated P_f times are much closer to the experimental data, as shown in Fig. 5.8, when the dislocation density is modified according to the temperature.

All the PTT curves are classically C-shaped because of the competition between the driving force and diffusion rate. The driving force for precipitation is controlled by the degree of supersaturation of the precipitating element. Above the nose temperature, the lower supersaturation reduces the nucleation rate and longer times are then needed to start precipitation. On the other hand, below the nose temperature, the low diffusivity of the precipitating element causes an increase in the start times.

V.1.4. Prediction of CCP Curves from Isothermal Data

Once the isothermal precipitation kinetics have been determined, the CCP behaviour can be predicted using the model described in chapter III. The calculated CCP diagram is presented in Fig. 5.9. Here, two sets of calculations were carried out for different cooling start temperatures (CCP1: cooling from 1130°C, and CCP2: cooling from 1000°C). Small arrows indicate the calculated P_s and P_f times during continuous cooling on each cooling curve. As can be seen in the figure, the CCP behaviour is shifted to the right (longer times) compared to the PTT curves, because precipitation is delayed during continuous cooling. This is because a high degree of supercooling is needed to start precipitation when the material is continuously cooled. The degree of supercooling is dependent on the cooling rate, i.e. if the cooling rate is fast, then a larger amount of supercooling is necessary to start the reaction. Therefore the deviation between the CCP behaviour and the isothermal one is



Fig. 5.6 Calculated P_s and P_f times from experimental data on the basis of growth only model and nucleation and growth model.

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Temp. (°C)	ň	b
950	1.84	4.19X10-5
925	1.85	6.24X10-5
900	1.83	8.96X10-5
875	1.85	4.60X10-5
850	1.88	2.19X10-5

Table 5.3The calculated mean values of the rate
constant (b) and time exponent (n) at
different temperatures.

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Table 5.4Calculated dislocation densities
from measured Ps and Pf times.

Temp. (°C)	Dislocation Density (cm-2)
950	1.60X10 ¹²
925	2.69X10 ¹²
900	7.71X10 ¹²
875	1.16X10 ¹³
850	2.12X 10 ¹³



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Fig. 5.7 Temperature dependence of the dislocation density.



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Fig. 5.8 Calculated P_s and P_f times on the basis of the nucleation and growth model with and without modification of the dislocation density according to temperature.

greater in a higher cooling rate region (shorter time region) than in a lower cooling rate region (longer time region).

V.2. CONTINUOUS COOLING TEST RESULTS

The continuous-cooling-precipitation behaviour calculated from isothermal data is shown again with several cooling curves in Fig. 5.10. Continuous cooling tests were performed to check the accuracy of the CCP predictions. Quenching temperatures during cooling were selected from the calculated CCP and cooling curves, and are listed in Table 5.5.

V.2.1. Dilatation During Quenching

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During continuous cooling and quenching, the length of the specimen decreases linearly as the temperature drops, if no phase transformation is involved. When the temperature reaches any value where a transformation occurs, the rate of length decrease is changed because phase transformation is generally accompanied by a volume change. For example, in the case of the γ to-a transformation of steel, the length decrease with temperature is countered by an expansion when ferrite is formed from austenite. The length of the specimen decreases linearly again with temperature after the phase transformation is completed. Therefore the start and finish points of a phase transformation can be determined from the variation in the dilatation.

In the present study, the dilation was followed to ensure that the quenching was rapid enough to suppress the y-to-a transformation. As can be seen in Fig. 5.11, the temperature at which a phase transformation was detected was about 500°C, which corresponds approximately to the martensite start temperature. The micrograph in Fig. 5.12 shows the typical microstructure of a quenched specimen and it can also be identified as a martensite microstructure. The cooling rate of the hot deformation dilatometer is thus considered as sufficient to restrain the y-to-a transformation during quenching.



Fig. 5.9 Calculated P_s and P_f times during continuous cooling.



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Fig. 5.10 Schematic illustration of interrupted quenching temperatures during continuous cooling.

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Fig. 5.11 The variation of specimen length with temperature during cooling.
Cooling Rate (°C/s)	Interrupted Quenching Temp. (°C)					
0.1	975, 960, 940, 930, 890, 800					
0.2	965, 950, 930, 900, 860, 800					
0.5	955, 935, 905, 800					
1.5	930, 895, 800					
5.0	800					

Table 5.5 Interrupted quenching temperatures during continuous cooling.

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Fig. 5.12 Typical microstructure of the quenched specimen.

### **V.3. TEM OBSERVATIONS**

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Both extraction replica and thin foil TEM methods may be used to image particles. Extracted particles are normally visible in bright field images, but high resolution dark field imaging is often necessary to observe small particles in a thin foil, because they are easily obscured by contrast effects in the matrix. Wexler and Borland [177] compared the accuracy of the extraction replica and thin foil techniques for the quantitative analysis of small second phase particles, and the results indicated that the particle size distribution and estimated volume fractions were similar for both techniques. The main advantages of the thin foil method are that smaller particles may be detected and more information can be obtained concerning the shapes and orientation relationships of the precipitates. However, at present, the extraction replica technique is the most commonly used for quantitative particle measurements because of its simplicity.

In the present analysis, carbon extraction replicas were employed to observe the Nb(CN) particles in the interior of a specimen which was quenched during continuous cooling. Quantitative analysis, i.e. the particle size distribution, was employed to describe the progress of precipitation.

#### V.3.1. Identification of Niobium Carbonitrides

The precipitating species observed in commercial HSLA steels are MnS, AlN, Ti(CN), V(CN) and Nb(CN). The types and shapes of precipitates are, of course, dependent on the chemical composition and the thermomechanical treatment. In this investigation, the particles that were most frequently observed were MnS, AlN and Nb(CN) precipitates. Among these, manganese sulfide can easily be distinguished from the others because of its considerably larger size. The diameter of a MnS particle is as high as a few hundred nm and it is almost spherical in shape.

In contrast to MnS, the differentiation of AlN from Nb(CN) by their morphological characteristics is somewhat more difficult. It has been reported that the kinetics of AlN precipitation in austenite are generally slow and dependent upon thermal history [178, 179]. Two nose points are observed in isothermal AlN precipitation, one in austenite and the other in ferrite. This is because the diffusion of Al in ferrite is much faster than in austenite. When compared to Nb, it can be seen that Al precipitation is delayed by almost an order of magnitude. However, the deformation of austenite significantly accelerates the kinetics of AlN precipitation [178, 180]. Following Michel and Jonas [180], the dynamic precipitation kinetics of AlN have been shown to be close to those of Nb(CN). They determined the start and finish times for the dynamic precipitation of AlN using a mechanical testing technique [10, 12], and found that the  $P_s$  and  $P_f$  times at 875°C, where the reaction was most rapid in this investigation, were in the range 6-11 sec and 45-130 sec, respectively. This is similar to that of Nb(CN) and V(CN) in deformed materials. AlN precipitation was most rapid for Al-rich, non-stoichiometric compositions, and this was rationalized on the basis of a reaction controlled by aluminum diffusion. It was also found that dynamically coarsened AlN has a higher particle diameter than dynamically coarsened Nb(CN) [180].

Another difficulty in the identification of Nb(CN) is the complex nature of the precipitates in HSLA steels. Houghton et al. [181] have noted the chemically heterogeneous nature of these precipitates. Steep chemical concentration gradients of niobium and titanium in one particle were shown, which is surprising, since the particles are only a few hundred atomic diameters in size. This was interpreted as being due to the precipitation and growth of one species on another. Emenike and Billington [182, 183] studied line pipe steels containing various levels of Nb-Ti-Al-V and analyzed the chemical compositions in particles using EDX spectra. They observed that the size of a precipitate is an important factor in determining the complexity of the chemical composition. They noted that large amounts of Ti and Al were included in coarse niobium particles, and that fine spherical particles exhibited a unique Nb concentration. The amount of Al in coarse precipitates almost reached 40-50 weight pct from their quantitative analyses. This amount increased with increasing particle size and was generally accompanied by a change in shape from a spheroid to a plate. The addition of Ti to a steel decreased the amount of Al in the precipitates because titanium takes up the nitrogen in the form of TiN, limiting the level of N that can react with the Al. In this case, the titanium concentration increased to levels as high as 25 weight pct of the precipitates.

AlN can often be distinguished from Nb(CN) by its morphology, which resembles thin plates, needles or rods, and its relatively large size [184]. The chemical analysis facilities of a TEM can confirm the compositions of particles. In this study almost all the particles were not compositionally complex, but were, instead, dominated by one particular element. The exception was the presence of Nb-Ti precipitates, as was reported by Houghton et al. [181].

Figure 5.13 shows typical shapes of the precipitates frequently found in this investigation. The particles which are spherical and very large are MnS; the plate-like precipitate is AlN. Several other small particles, which are almost spherical in shape, were identified as Nb-rich particles and can be presumed to be Nb(CN) precipitates. Analyses of the chemical composition by EDX spectra are also shown in Fig. 5.13.

#### V.3.2. Morphologies of Nb Precipitates

#### V.3.2.1. Undissolved precipitates

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Undissolved precipitates do not influence the structure and properties of a material because of their large size. Increasing amounts of precipitates can be dissolved at higher reheating temperatures.

In this experiment,  $1150^{\circ}$ C was employed as a dissolution temperature because the precipitate is expected to dissolve at about  $1050-1070^{\circ}$ C (Table 2.1). The holding time at this temperature was 30min. Nevertheless, several undissolved particles were observed in specimens quenched after reheating, as shown in Fig. 5.14 (a). The average size of the undissolved particles is about 160nm after measuring 25 particles. The main composition was Nb, as shown in Fig. 5.14 (b); however, several particles exhibited a strong Ti peak, as in Fig. 5.14 (c).



Fig. 5.13 Typical shape of various precipitates observed in TEM analysis: (a) is the micrograph and (b), (c) and (d) are the chemical analyses of each particle shown in (a).



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Fig. 5.13 Typical shape of various precipitates observed in TEM analysis: (a) is the micrograph and (b), (c) and (d) are the chemical analysis results of each particle shown in (a).



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Fig. 5.14 (a) Undissolved particles found in quenched specimen.



Fig. 5.14 (b) and (c) X-ray spectrum of particles shown in (a) displaying strong (b) Nb, and (c) Nb-Ti peaks.

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#### V.3.2.2. Network of precipitates

The precipitation of Nb(CN) is heterogeneous in nature, i.e. it usually occurs in conjunction with crystal defects. The frequently observed chain-like and cell-like distribution of Nb(CN) precipitates is due to precipitation on such defects. In general, precipitates are therefore not distributed at random, but are concentrated in certain areas, forming a network. Hansen et al. [97] showed a band of Nb(CN) precipitation in proeutectoid ferrite, which was the prior austenite grain boundary, and cell-like precipitation along the prior austenite substructure. It also has been reported that planar arrays of precipitates are formed during phase transformation [97, 185], this being interphase precipitation parallel to the  $\gamma/\alpha$  interface.

Figure 5.15 shows the chain-like distribution of Nb(CN) particles. Precipitates are frequently observed along certain lines, and the line on which precipitates are formed is generally thought to be a sub-boundary, where dislocations are tangled. From the network of precipitates, the boundary of the substructure of austenite can be roughly estimated.

#### V.3.3. Evolution of Precipitation During Continuous Cooling.

Typical TEM micrographs of specimens during continuous cooling testing are shown in Fig. 5.16. Particles smaller than 3 nm can be detected in these carbon extraction replicas (Fig. 5.17). The quench temperature is shown at the top of the micrographs. When the specimen is cooling down from a high temperature at a slow cooling rate, precipitates will be formed during cooling. The size of the precipitates increases when the quenching temperature is low because the time to grow particles during cooling has increased.

It can be observed that the size of precipitate is small when the cooling rate is fast. At higher cooling rates, precipitation starts at lower temperatures because of a higher degree of supercooling. Thus, small nuclei are formed because of the increased driving force for nucleation at that temperature. The growth of nuclei is also restricted because of the low temperature, which further restricts the size of particles formed at higher cooling rates.



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Fig. 5.15 Chain-like distribution of Nb(CN) precipitates.







Fig. 5.16 (b) Carbon extraction replicas showing the progress of Nb(CN) precipitation ( cooling rate ; 0.2°C/sec ).



Fig. 5.16 (c) Carbon extraction replicas showing the progress of Nb(CN) precipitation ( cooling rate ; 0.5°C/sec ).



Fig. 5.16 (d) Carbon extraction replicas showing the progress of Nb(CN) precipitation ( cooling rate ; 1.5°C/sec ).



Fig. 5.17 Small precipitates of Nb(CN) ( cooling rate ; 1.5°C/sec, quench temp. ; 895°C ).

#### V.3.4. Particle Size Distribution

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The most important parameters generated by a quantitative analysis of second phase particles are the volume fraction and mean particle size. However, the accuracy of volume fraction information determined by extraction replicas is somewhat compromised because the extraction efficiency of each carbon replica varies. On the other hand, the quantitative information concerning particle size is more precise.

Particle size distributions are shown in Fig. 5.18. The mean particle diameters and the corresponding standard deviations were measured on replicas and are therefore surface (2-dimensional) quantities. The volume (3-dimensional) mean particle sizes and standard deviations were obtained using the equations developed by Ashby and Ebeling [95]:

$$\overline{d}_{v} = \frac{\overline{d}_{s}}{1 + \left(\frac{SD_{(s)}}{\overline{d}_{s}}\right)^{2}}$$

$$SD_{(v)} = \frac{S.D_{(s)}}{1 + \left(\frac{S.D_{(s)}}{\overline{d}_{s}}\right)^{2}}$$
(5.5)

Here d and S.D. refer to the mean particle diameter and standard deviation, and subscripts s and v refer to surface and volume, respectively. The values of  $d_s$ , S.D.(s),  $d_v$  and S.D.(v), corresponding to the precipitates observed in the quenched specimens, are listed in Table 5.6.

The particle size  $(\log(\tilde{d}_v))$  is plotted against log scale time in Fig. 5.19. In the case of isothermal holding, this plot would exhibit linearity because particle growth is diffusion controlled. During continuous cooling, in contrast to isothermal holding, particle growth is non-linear with log time.

From the measured mean particle diameter, the simple relationship  $y = ax^b + c$  was formulated, where x and y are the particle diameter and time



Fig. 5.18 (a) Particle size distribution of Nb(CN) precipitates ( cooling rate; 0.1°C/sec ).



Fig. 5.18 (b) Particle size distribution of Nb(CN) precipitates ( cooling rate ; 0.2°C/sec ).

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Fig. 5.18 (c) Particle size distribution of Nb(CN) precipitates ( cooling rate ; 0.5"C/sec ).



Fig. 5.18 (d) Particle size distribution of Nb(CN) precipitates ( cooling rate ; 1.5°C/sec ).

| Cooling rate | Quenching<br>Temp. ("C) | Surface F            | Properties           | Volume Properties    |                      |  |
|--------------|-------------------------|----------------------|----------------------|----------------------|----------------------|--|
| (°C/sec)     |                         | đ,                   | S.D.(5)              | $d_v$                | S.D. <sub>(v)</sub>  |  |
|              | 960<br>940              | 17.1                 | 10.6                 | 12.5                 | 7.6                  |  |
| 0.1          | 940<br>930              | 28.7<br>32.4         | 15.6<br>16.7         | $\frac{22.2}{25.6}$  | 12.0<br>13.4         |  |
|              | 890<br>800              | 39.7<br>41.6         | 17.6<br>16.6         | 33.2<br>35.8         | 14.7 $14.3$          |  |
|              | 950<br>930              | 14.2<br>22.4         | 9.3<br>14.8          | 9.9<br>15.5          | 6.5<br>10.3          |  |
| 0.2          | 900<br>860<br>800       | 29.2<br>32.2<br>33.7 | 18.3<br>17.7<br>17.3 | 20.9<br>24.8<br>26.7 | 13.1<br>13.6<br>13.7 |  |
| 0.5          | 935<br>905<br>800       | 10.9<br>18.8<br>27.6 | 7.5<br>12.5<br>15.8  | 7.4<br>13.0<br>20.8  | 5.1<br>8.7<br>11.9   |  |
| 1.5          | 895<br>800              | 11.3<br>19.5         | 8.0<br>14.0          | 7.5<br>12.9          | 5.3<br>9.2           |  |

Table 5.6.The measured mean diameters and standard<br/>deviations of surface and volume properties.

respectively, and a, b and c are constants. The incubation time was then calculated by setting x=0. The experimental times were then modified by subtracting the incubation time from the total time, and the evolution of particle size are replotted as log(d) versus log(t) scale, which allows a more direct comparison of the growth of the particles to be made (Fig. 5.20).

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Time, s

Fig. 5.19 Dependence of mean particle diameter  $(\bar{d}_v)$  on time during cooling.



Time, s

Fig. 5.20 Dependence of mean particle size  $(\bar{d}_v)$  on precipitation time. Times were modified by subtracting the incubation time from total time.

# CHAPTER VI DISCUSSION

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## VI.1. TEMPERATURE DEPENDENCE OF THERMO-DYNAMIC PARAMETERS

Several thermodynamic variables, such as soluble concentration of precipitating elements, composition of precipitates, chemical driving force for precipitation etc., can be determined using the model proposed in chapter III. In this section, the calculated results are presented, and compared with experimental results to determine the accuracy of the present model. For the purposes of the comparison, the results of four different Nb steels taken from the literature are used. The chemical compositions of these steels along with that used in the current work are shown in Table 6.1.

|         | Nb    |       | С     |       | N      |        | rof  |
|---------|-------|-------|-------|-------|--------|--------|------|
|         | wt%   | at%   | wt%   | at%   | wt%    | at%    | 101. |
| Steel 1 | 0.040 | 0.024 | 0.067 | 0.306 | 0.0060 | 0.0235 | *    |
| Steel 2 | 0.065 | 0.039 | 0.180 | 0.832 | 0.0036 | 0.0143 | 186  |
| Steel 3 | 0.197 | 0.118 | 0.029 | 0.135 | 0.0116 | 0.0480 | 187  |
| Steel 4 | 0.531 | 0.319 | 0.081 | 0.376 | 0.0024 | 0.0080 | 187  |
| Steel 5 | 0.957 | 0.575 | 0.102 | 0.474 | 0.0183 | 0.0717 | 187  |

Table 6.1Chemical compositions of precipitating elements for the<br/>steels used in the calculations.

\* Used in this experiment.

#### VI.1.1. Variation of Soluble Concentration of Nb, C and N

As already observed in eqn.(3.23), the soluble concentrations of the precipitate forming elements are expected to depend directly on the mole fractions of the precipitates, and on the overall concentrations of these elements in the steels. The soluble concentrations of Nb, C and N have been calculated in the temperature range 800-1200°C and are shown in Fig. 6.1. The soluble concentrations increase as the temperature increases, but the rate of increase is not the same for each steel because of the differing proportions of precipitating elements. Note, for example, in Fig. 6.1 (a), that despite the higher overall concentration of Nb in steel 2 compared to steel 1, the soluble concentration of Nb in steel 2 is generally lower than that of steel 1. This can be attributed to the higher level of interstitial atoms in steel 2, which can combine with Nb atoms and cause precipitation The atomic ratios between the interstitial atoms (C+N) and Nb are 13.7 and 21.7 in steels 1 and 2, respectively.

In general, low C steels (low atomic ratio of C to Nb) show a somewhat higher dependence of soluble concentration of carbon on temperature (Fig. 6.1 (b)). This is because the ratio of the amount of carbon combined in the carbonitride to the total amount is larger compared to the high carbon steels. The high nitrogen containing grade, steel 3, shows a rather rapid change of soluble content of nitrogen with temperature (Fig. 6.1 (c)). This can be attributed to a higher nitrogen content in the precipitates, which causes the nitrogen concentration to change drastically as the precipitate dissolves. This result can be related to the lower y value (the proportion of NbC in the Nb(CN)) of steel 3, as will be seen in the next section. The predicted soluble concentrations are in reasonable agreement with the experimental data (Table 6.2). The experimentally determined nitrogen concentrations in steel 5 are different from the calculated ones. The reason is not obvious.

#### VI.1.2. Amount of Precipitation and Composition

The volume fraction of precipitate increases as the temperature decreases and as the concentrations of the precipitating elements increase (Fig. 6.2). The temperature at which the amount of precipitate is zero is the



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Fig. 6.1 (a) Temperature dependence of soluble concentrations of (a) niobium, (b) carbon and (c) nitrogen.



Fig. 6.1 (b) Temperature dependence of soluble concentrations of (a) niobium, (b) carbon and (c) nitrogen.



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Fig. 6.1 (c) Temperature dependence of soluble concentrations of (a) niobium, (b) carbon and (c) nitrogen.

|         | Temp. | Nb(at%)   |          | C (at%)   |          | N (at%)   |          |
|---------|-------|-----------|----------|-----------|----------|-----------|----------|
|         | (°C)  | Predicted | Observed | Predicted | Observed | Predicted | Observed |
| Steel 2 | 950   | 0.0035    | 0.0024   | 0.804     | 0.804    | 0.0119    | 0.0091   |
|         | 1050  | 0 0095    | 0.0066   | 0.809     | 0.804    | 0.0125    | 0.0099   |
|         | 1100  | 0.0147    | 0.0119   | 0.813     | 0.809    | 0.0128    | 0.0107   |
|         | 1150  | 0.0222    | 0.0203   | 0.819     | 0.818    | 0.0133    | 0.0115   |
| Steel 3 | 1000  | 0.0197    | 0.0090   | 0.086     | 0.083    | 0.0116    | 0.0108   |
|         | 1100  | 0.0425    | 0.0310   | 0.100     | 0.098    | 0.0177    | 0.0163   |
|         | 1200  | 0.0768    | 0.0576   | 0.118     | 0.116    | 0.0293    | 0.0260   |
| Steel 4 | 1000  | 0.0226    | 0.0114   | 0.126     | 0.130    | 0.0007    | 0.0028   |
|         | 1100  | 0.0507    | 0.0522   | 0.150     | 0.181    | 0.0010    | 0.0068   |
|         | 1200  | 0.0960    | 0.0901   | 0.189     | 0.209    | 0.0015    | 0.0092   |
| Steel 5 | 1000  | 0.0323    | 0.0216   | 0.072     | 0.068    | 0.0023    | 0.0052   |
|         | 1100  | 0.0642    | 0.0715   | 0.098     | 0.121    | 0.0037    | 0.0012   |
|         | 1200  | 0.1111    | 0.1260   | 0.136     | 0.167    | 0.0061    | 0.0004   |

Table 6.2Comparison of the calculated chemical compositions of the precipitating<br/>elements with the experimental ones.

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solution temperature. Precipitation begins at higher temperatures with increasing Nb concentrations. The rate of increase in the volume fraction of precipitate is rather unique and depends on the Nb content.

There is a dependence of precipitate composition on temperature, shown in Fig. 6.3, because, at a certain temperature, the free energy change of the formation of NbN is greater than that of NbC. The y value (the proportion of niobium carbide in niobium carbonitride) decreases as the temperature increases. This value can also be related to the chemical compositions of the precipitating elements, i.e. the value increases when the ratio of C/(C+N)increases. However, steel 4 shows a higher y value than steel 2, despite having the same value of C/(C + N) ratio, and steel 5 shows a higher y value than steel 1, despite the lower C/(C+N) ratio. These observations can be attributed to the ratio of the total interstitial (C+N) atoms to Nb atoms because a higher level of nitrogen is advantageous in the formation of stable NbN at high temperatures. For example, the atomic ratio of (C+N)/Nb in steel 1 is approximately 14, in spite of the almost stoichiometric composition in steel 5. Therefore, the excess nitrogen in steel 1 can form NbN more easily at high temperatures, and thus lower the y value. The predicted y values compare well with the experimental ones, as shown in Table 6.3.

#### VI.1.3. Chemical Driving Force and Free Energy of Formation

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The calculated driving forces for the precipitation of Nb(CN) increase monotonically when the temperature is decreased, as displayed in Fig. 6.4. As expected, the steels with higher concentrations of precipitating elements exhibit higher driving forces and result in higher nucleation rates for precipitation. The free energy of formation ( $\Delta G^*$ ) of Nb(CN) in austenite is also calculated (Fig. 6.5) and is shown to increase rapidly as the temperature is increased. Thus, as the temperature increases, the critical size of nucleus also increases. Therefore the reaction kinetics depend on the variation of  $\Delta G^*$ . In contrast, at lower temperatures,  $\Delta G^*$  decreases and the critical radius of nucleus decreases. In this case, the variation of  $\Delta G^*$  no longer strongly influences nucleation. Instead, the temperature dependence of the diffusivity of the solute atoms is found to be the rate controlling factor.

|         | Temp.<br>(°C)               | Predicted                            | Observed                             | Difference*<br>(%)           |
|---------|-----------------------------|--------------------------------------|--------------------------------------|------------------------------|
| Steel 2 | 950<br>1050<br>1100<br>1150 | 0.92<br>0.93<br>0.93<br>0.93<br>0.93 | 0.83<br>0.83<br>0.83<br>0.83<br>0.83 | 10.8<br>12.0<br>12.0<br>12.0 |
| Steel 3 | 1000                        | 0.57                                 | 0.59                                 | -3.4                         |
|         | 1100                        | 0.54                                 | 0.54                                 | 0.0                          |
|         | 1200                        | 0.48                                 | 0.49                                 | -2.0                         |
| Steel 4 | 1000                        | 0.97                                 | 0.92                                 | 5.4                          |
|         | 1100                        | 0.97                                 | 0.92                                 | 5.4                          |
|         | 1200                        | 0.97                                 | 0.92                                 | 5.4                          |
| Steel 5 | 1000                        | 0.85                                 | 0.86                                 | -1.2                         |
|         | 1100                        | 0.85                                 | 0.83                                 | 2.4                          |
|         | 1200                        | 0.84                                 | 0.81                                 | 3.7                          |

**Table 6.3Comparison of predicted and observed y values.** 

\*Negative means predicted value is smaller than the observed one.



Fig. 6.2 Temperature dependence of the amount of niobium carbonitride precipitated.



Fig. 6.3 Temperature dependence of precipitate composition (the ratio of niobium carbide to niobium carbonitride).

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Fig. 6.4 Temperature dependence of the chemical free energy.



Fig. 6.5 Temperature dependence of the free energy of formation of Nb(CN) in austenite.
# VI.2. PARTICLE EVOLUTION DURING CONTINUOUS COOLING

In industrial practice, most of the precipitation takes place during continuous cooling of the alloy and therefore occurs over a range of temperatures. Under these conditions, a broader range of sizes and distributions may arise, as compared to the isothermal case. Consequently, in this section, particle growth during cooling is analyzed.

#### VI.2.1. Particle Growth During Continuous Cooling

The theory of the growth of spherical precipitates from a solid solution during isothermal holding leads to a square root dependence of time on particle diameter, as was shown in eqn. (3.46). Several experimental results [65, 168, 169] have confirmed this derivation. Experimentally, the coarsening stages also exhibit a power law relationship, although the values of the power differ from that of the growth stage [64, 132-134, 136]. However, a consistent power law dependence is not maintained during continuous cooling. As was shown in Figs. 5.19 and 5.20, the plots of log(t) vs. log(d) during continuous cooling are not linear.

During continuous cooling, the cooling curve can be divided into small isothermal steps and the increase in particle diameter with time is assumed to be the sum of several isothermal steps. Suppose the specimen is cooled down from  $T_1$  to  $T_1$  during time interval  $t_1$  (Fig. 6.6), the particle which was nucleated at time t=0 initially grows following the growth curve at  $T_1$  during incremental time  $t_1$ . It subsequently follows the growth curve at  $T_2$  during incremental time ( $t_2$ - $t_1$ ), and so on. Thus the particle evolution during cooling can be represented as the solid line in Fig. 6.6. The increase in particle diameter during cooling is then calculated as:

$$d = \Delta d_1 + \Delta d_2 + \Delta d_3 + \dots + \Delta d_n \tag{6.1}$$

where  $\Delta d_i = d_i \cdot d_{i-1}$ . The increase in particle diameter with time during each isothermal hold can be interpreted in terms of the diffusion controlled growth theory proposed by Zener [188], i.e.:

$$d = \alpha \sqrt{Dt} \tag{6.2}$$

Here a is the growth coefficient which depends on the concentration, D is the diffusivity and t is the reaction time. Since the diffusivity of the substitutional element Nb is significantly lower than that of either interstitial C or N, it is assumed that the growth rate of Nb(CN) is controlled by the diffusion of Nb In this case, following Zener, the growth coefficient a can be written as:

$$a = 2\left(\frac{2(X_{Nb}^{o} - X_{Vb}^{o})}{(C_{p} - X_{Nb}^{e})}\right)^{1/2}$$
(6.3)

Here,  $X_{Nb}^{\circ}$  is the concentration of Nb in the steel and  $X_{Nb}^{\circ}$  is the equilibrium soluble concentration of the element in austenite.  $C_p$  is the concentration of Nb in the Nb(CN) precipitates. The above expression for the growth coefficient was calculated for the one-dimensional growth of a plate shaped particle. The coefficient for the three-dimensional case was derived in Chapter III (eqn. 3.45). In either case, each isothermal step in eqn. (6.1) is expressed as.

$$\Delta d_{1} = \alpha_{1} D_{1}^{1/2} t_{1}^{1/2}$$

$$\Delta d_{2} = \alpha_{2} D_{2}^{1/2} (t_{2}^{1/2} - t_{1}^{1/2})$$

$$\Delta d_{3} = \alpha_{3} D_{3}^{1/2} (t_{3}^{1/2} - t_{2}^{1/2})$$
(6.4)

and

$$\Delta d_{i} = \alpha_{i} D_{i}^{1/2} (t_{i}^{1/2} - t_{i-1}^{1/2})$$

Here  $a_i$  and  $D_i$  are the growth coefficient and diffusivity at the i-th isothermal step at temperature  $T_i$ .



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Fig. 6.6 The evolution of particle diameter during continuous cooling. Broken lines show isothermal behaviour.

Although the growth coefficient is a weak function of temperature, the diffusivity exhibits a very strong dependence on temperature. The calculated results show that, within the experimental temperature range (960-800°C),  $\alpha$  varies by about 20%, but the exponential term in D varies by two orders of magnitude. From eqn. (6.2), the particle growth at any temperature is expressed as:

$$d = \alpha D_o^{1/2} exp\left(-\frac{Q}{2RT}\right) t^{1/2}$$
 (6.5)

where  $D_0$  is the frequency factor. Here,  $\alpha D_0^{1/2}$  is a weak function of temperature, and thus the growth rate is considered to be dependent on temperature exponentially, i.e. display Arrehenius type behaviour. The activation energy for the diffusion of solute atoms and the frequency factor are determined from the experimental observations of the particle size, using:

$$\Delta d^2 = \alpha^2 D_0 exp \left( -\frac{Q}{RT} \right) \Delta t \tag{6.6}$$

where  $\Delta d^2 = d^2 - d_0^2$  and  $\Delta t = t - t_0$ . Here,  $d_0$  is the particle diameter at time  $t_0$ . The calculated diffusivity of Nb using the above equation is shown in Fig. 6.7, along with values from the literature. The result obtained for the diffusivity is:

$$D = 1.49 \exp\left(-\frac{234700}{RT}\right) X 10^{-4} m^{2/\text{sec}}$$
(6.7)

The activation energy obtained by this method is compared with data from other workers in Table 6.4. The activation energy and frequency factor for Nb diffusion in the present experiment is of the same order of magnitude as that reported in other investigations (except for [189]).

Using equations (6.5) and (6.7), particle evolution during a temperature change can be predicted. For example, particle growth during a cooling rate of 0.1°C/sec was calculated for particles with various initial sizes. As shown in Fig. 6.8, the calculated results coincide quite well with the experimental data, the latter of which were taken from Fig. 5.20. The difference between the





| D <sub>o</sub> (m <sup>2</sup> /sec) | Q(kJ/mole) | ref.                |
|--------------------------------------|------------|---------------------|
| 0.66x10-4                            | 264.0      | 123                 |
| 0.83x10 <sup>-4</sup>                | 266.5      | 146                 |
| <b>1.12x1</b> 0-4                    | 283.0      | 169                 |
| 5.30x10-2                            | 343.0      | 189                 |
| 1.49x10-4                            | 234.7      | Present Calculation |

Table 6.4Comparison of activation energy (Q) and<br/>frequency factor  $(D_0)$  for solute diffusion.

predicted and observed values increases because coarsening is involved in the later stages of the experiment. The increase in particle size at different cooling rates is also shown in Fig. 6.9 in terms of cooling times (a) and temperatures (b). As expected, the growth rate is lower when the cooling rate is higher.

#### VI.2.2. Determination of P<sub>s</sub> and P<sub>f</sub> Times

It has been observed [161] that mean diameters of 5nm and 10nm are associated with 1% volume fraction of Nb precipitates for the isothermal conditions of 900°C and 1000°C, respectively. Thus, when the mean particle diameter is 5nm, the volume fraction is very low, and it can be considered as corresponding to the precipitation start time.

In Figs. 5.19 and 5.20, the experimental mean particle size increase is not linear, which confirms that there is no power law dependence of particle diameter with time during continuous cooling. The basic formula which describes the increase of particle diameter is expressed as  $d = Ct^{1/2}$  where C is  $aD^{1/2}$ . During cooling, C varies with temperature via the exponential term in the expression for the diffusivity. In Fig. 6.10, the calculated values of lnC are



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Fig. 6.8 The increase of particle diameter with cooling time (cooling rate; 0.1°C/sec).

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Fig. 6.9 (b) The increase of particle diameter according to cooling temperature.

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plotted against 1/T for the case of  $0.1^{\circ}$ C/sec cooling. This diagram shows an almost linear relationship between the two parameters within the temperature range 960-800°C. In general, lnC drops rapidly when the particle coarsening stage begins, because the particle coarsening rate is much lower than growth. For instance, during particle coarsening, the radius depends on  $t^n$  (n = >3) when the process is controlled by the diffusion of solute atoms Therefore, at the P<sub>f</sub> temperature, the slope of the relationship ln(C) vs. 1/T will deviate from linearity (Figs. 6.11 (a) and (b)).

Using the experimental data,  $P_f$  times were determined for cooling rates of 0.1°C/sec and 0.2°C/sec. The  $P_s$  time was taken from Fig. 5.19, by assuming that the precipitate size at  $P_s$  is 5 nm, and the  $P_f$  time was determined from Fig. 6.11. The values so determined are superimposed on the calculated C' P diagrams (Fig. 6.12) and correlate closely with the predicted CCP curves for each cooling rate.



Fig. 6.10 The variation of lnC with inverse temperature.



Fig. 6.11 The variation of lnC with inverse temperature: (a) 0.1°C/sec; (b) 0.2°C/sec; (c) 0.5°C/sec; (d) 1.5°C/sec.



Fig. 6.11 The variation of lnC with inverse temperature: (a) 0.1°C/sec; (b) 0.2°C/sec; (c) 0.5°C/sec; (d) 1.5°C/sec.

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Fig. 6.12 Comparison of observed  $P_s$  and  $P_f$  times with predicted CCP diagrams.

#### VI.3. STRESS RELAXATION AFTER DEFORMATION

In this section, stress relaxation mechanisms are discussed for each region of the stress-time curve (region I, region II and region III in Fig. 5.3). The correlation between the stress relaxation behaviour and the occurrence of precipitation is interpreted, based on a consideration of thermally activated dislocation movement. The stress directed diffusion of vacancies (diffusion creep) and grain boundary sliding are not considered in this analysis, because plastic flow associated with these mechanisms is significant only at very high temperatures (close to the melting point) and very low stresses [190].

#### VI.3.1. Stress Relaxation Behaviour Before Precipitation

As was pointed out by Langdon [191], the high temperature properties of crystalline materials depend critically upon the glide and climb of dislocations. The time dependence of stress relaxation is associated with the moving dislocation overcoming localized barriers. The resistance of crystals to plastic deformation is determined by the critical resolved shear stress that is required for dislocation glide to take place. If no obstacles are present in the material, the dislocations can move under infinitesimally small stresses. The obstacles to dislocation motion are associated with either long range or short range stress fields. The long range obstacles, such as dislocations on parallel slip planes and large second phase particles, are not influenced by thermal fluctuations, and they are termed athermal obstacles. Since thermal fluctuations can assist the applied stress in overcoming short range obstacles, such barriers are termed thermal obstacles. Some common thermal obstacles are the Peierls-Nabarro stress, forest dislocations, the motion of jogs in screw dislocations, cross slip and the climb of dislocations [192].

Sherby et al. [193, 194] demonstrated that the activation energy for high temperature deformation and self diffusion are the same for an appreciable number (more than 25) of metals, as shown in Fig. 6.13. This implies that the rate controlling mechanism of hot deformation is the diffusion of atoms. Conrad [192] showed that the rate controlling mechanisms in fcc

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metals for high temperature deformation are the non-conservative motion of jogs and dislocation climb. Weertman [195] developed a creep rate equation based on dislocation climb which led to a power law dependence on stress:

$$\dot{\varepsilon} = C \left( \frac{\sigma^{\alpha}}{kT} \right) \exp(-\frac{Q}{kT})$$
(6.8)

where C and a are constants ( $\alpha \sim 3$  to 4), Q is the activation energy for diffusion and  $\sigma$  is the applied stress. However, the equation does not apply well for materials with low stacking fault energies. In these materials, a dislocation splits up easily into partial dislocations with a stacking fault between them, making dislocation climb difficult [196].

Liu [65] assumed that the rate controlling step is only governed by the motion of jogged screw dislocations. The plastic strain rate can then be related to the structure and dislocation movement as follows:

$$\dot{\varepsilon} = \frac{b^2 \upsilon Z}{h \,\overline{M}} \, \exp(-\frac{\Delta G_o}{k \,T}) \, \exp(\frac{b \, A^* \, \iota^*}{k \,T}) \tag{6.9}$$

where b is the Burgers vector, u is approximately the Debye frequency, Z is the coordination number, h is the height of jogs,  $\overline{M}$  is the average Taylor factor,  $\Delta G_0$  is the free energy of formation of a vacancy, A<sup>\*</sup> is the average area swept out by the dislocation following each successful fluctuation (activation area), and  $\tau^*$  is the effective shear stress.

Since stress relaxation before precipitation can be described by eqn. (4.3), the strain rate during stress relaxation can be expressed as:

$$\dot{\varepsilon} = \frac{S'\alpha}{E} \exp(-\frac{\sigma_o}{S'}) \exp(\frac{\sigma}{S'})$$
(6.10)

Comparison of the above two equations shows clearly that the strain rate is exponentially dependent on the stress. This demonstrates that the rate controlling mechanism in the absence of precipitation during stress relaxation



Creep Activation Energy (MJ/mole)

Fig. 6.13 Correlation between the activation energy for creep and the activation energy for self diffusion [194].

\* -2 can be interpreted as the thermally activated movement of jogged screw dislocations.

In the present stress relaxation tests, jogs can be created as a result of encounters between moving dislocations during pre-deformation. Jogs in edge dislocations do not restrain the motion of the dislocation because they lie in the slip plane. But jogs in screw dislocations are edge dislocations which are out of the slip plane. Thus if the screw dislocation is forced to move, such jogs must move from one slip plane to another by non-conservative motion. After prestraining, the dislocations are apt to move continuously in the direction of the effective stress by converting the elastic strain into plastic strain. However, jogs on screw dislocations, which were formed during prestraining, act as barriers to dislocation movement, but can be overcome by thermal fluctuations.

#### V.3.2. Stress Relaxation Behaviour After Precipitation

Precipitates strengthen the material via interactions between dislocations and precipitates. The degree of strengthening depends on precipitate strength, size, spacing and volume fraction. In the literature, three key types of interactions between particles and dislocations have been considered: i) long range interactions; ii) dislocations cutting through the particles in the sup plane; and iii) dislocations circumventing particles in the slip plane.

The most important of the long range interactions was treated in the theory by Mott and Nabarro [197]. They estimated that the extent of the shear stress produced by precipitates was dependent only on the misfit dilatation. The critical shear stress was thus expressed as:

$$\mathbf{r}_{c} = E \, \varepsilon_{m} \, f_{v} \tag{6.11}$$

where  $\varepsilon_{\rm m}$  is the misfit parameter and was given as a function of the lattice parameters,  $(a_{\rm Nb(CN)}-a_{\rm Fe})/a_{\rm Fe}$ , and  $f_v$  is the volume fraction of precipitates. Thus the critical shear stress is independent of the size and spacing, and depends only on the precipitate volume fraction. However, in practice, there is little probability that the critical shear stress will be controlled only by the magnitude of  $\varepsilon_m$  and  $f_v$  [198]. This is because the short range interaction between dislocations and particles is the more important factor.

When the precipitates are impenetrable to the dislocations, moving dislocations circumvent the particles, leaving dislocation loops around them The shear stress necessary to bend a dislocation between particles (Orowan stress) is:

$$v_{\alpha} = 0.8 \frac{\mu b}{\lambda} \tag{6.12}$$

where  $\lambda$  is the interparticle spacing,  $\mu$  is the shear modulus and b is the Burger's vector.

Two main particle hardening mechanisms are considered here, coherency hardening and elastic modulus hardening. For the precipitation of Nb(CN) in austenite, these two mechanisms are expected to be the strongest ones, because both the lattice parameter and the elastic modulus are significantly different between the precipitates and the austenite matrix. The stress associated with the coherency hardening mechanism is given by [199]:

$$\tau_{ch} = 3 \,\mu_M \,\varepsilon_m^{3/2} \,\left(\frac{df_v}{2b}\right)^{1/2} \tag{6.13}$$

where d is the diameter of the particle, and  $\mu_M$  is the shear modulus of the matrix. Knowles and Kelly [200] derived the stress which is associated with elastic modulus hardening:

$$\iota_m = \frac{\Delta \mu}{4\pi^2} \left(\frac{3\,\Delta \mu}{\mu_M}\right)^{1/2} \left\{ 0.8 - 0.13\,\ln(\frac{d}{2b}) \right\}^{1/2} \left(\frac{df_v}{2b}\right)^{1/2}$$
(6.14)

where  $\Delta \mu$  is the difference between the shear modulus of the matrix and that of the precipitates. The critical shear stresses of each hardening mechanism were calculated using the following parameters.

| $\lambda = 0.5 (\pi/6/f_v)^{1/2} d$                 | [201]      |
|-----------------------------------------------------|------------|
| $\mu_{\rm M} = 8.1\{1-0.91({\rm T}-300)/1810\}X104$ | [202]      |
| $\mu_{\rm p} = 1.34\{1.0, 18(T.309)/3886\}X105$     | [169, 202] |
| $T = 1173^{\circ}K$                                 |            |
| $a_{\rm Nb(CN)} = 4.445 \text{\AA}$                 |            |
| $a_{Fe} = 3.54$ Å                                   |            |
| b = 2.58Å                                           |            |
| $f_v = 0.1 \times 10^{-6}$                          |            |

The calculation results for three critical shear stresses are exhibited in Fig. 6.14 (a). As can be seen in the figure,  $\tau_{ch}$  and  $\tau_{m}$  increase with the particle diameter, which explains the behaviour of underaged precipitates. The Orowan stress, by contrast, decreases as the diameter of precipitates increases because it is mainly dependent on  $\lambda$  for a fixed precipitate volume fraction. It should be noted that cutting the particle is only possible when the particle is very small. The critical diameter of a precipitate below which it can be cut by a dislocation is about 1.5-3 nm, which indicates that the precipitates will tend not to be cut. Thus the main hardening mechanism of Nb(CN) precipitates is the Orowan stress. Coherency hardening does not change significantly with temperature. However, the shear stress associated with elastic modulus hardening increases as the temperature increases (Fig. 6.14 (b)). This phenomenon is mainly attributed to the dependence of  $\Delta \mu$  (= $\mu_{\rm p}$ - $\mu_{\rm M}$ ) on temperature. Since the rate of decrease of  $\mu_M$  with increasing temperature is larger than that of  $\mu_{\rm p}$ ,  $\Delta\mu$  increases at higher temperatures. If elastic modulus hardening is the main mechanism for precipitation strengthening, then the Orowan mechanism is more dominant at higher temperatures.

Another possible explanation for the effect of precipitates was proposed by Liu [65] on the basis of a dynamic interaction between dislocations and growing particles. The lattice mismatch between Nb(CN) particles and austenite is almost 25%, thus it is difficult for these to nucleate and grow coherently in the matrix. As was mentioned earlier, Nb(CN) precipitation occurs mainly on lattice defects, such as dislocations and dislocation substructures, which often leads to chain like precipitation (Fig. 5.15). The precipitates tend to nucleate on segments of dislocations, pinning their

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Particle Diameter (Å)



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Particle Diameter (Å)

Fig. 6.14 (b)

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The temperature dependence of modulus hardening (temperature intervals are 100°C from 800 to 1200°C).

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movement. Another phenomenon of dynamic interaction is the absorption of vacancies during particle growth because of the difference of lattice parameter between Nb(CN) and austenite. The dislocations are attracted by the growing particles since the former are good sources (as well as sinks) of vacancies. As a result of vacancy absorption by a growing particle, edge dislocations climb down and contact the surface of the particle, and are finally pinned by the stress field around the particle. Therefore the mobile dislocations will become pinned either by the precipitates which are nucleated directly on them, or by being attracted to growing particles because of vacancy absorption.

#### V.1.3. Stress Relaxation During Particle Coarsening

A two phase microstructure is almost always unstable because the total interfacial free energy is invariably not a minimum. Therefore a high density of small precipitates will tend to coarsen into a lower density of larger particles with a smaller total interfacial area. In the coarsening stage, the volume fraction of the precipitates is constant, and the number of particles decreases because larger particles grow continuously at the expense of redissolving finer precipitates.

During the coarsening stage, dislocations are unpinned from the precipitates which are being redissolved and vacancies are emitted during the dissolution of the fine particles. These extra vacancies help the edge dislocations to unpin from precipitates by accelerating dislocation climb. The diminishing particle diameter makes dislocation removal by climb easier. Once the dislocations have escaped from the particles, the force required to move them is smaller than previously until other obstacles are encountered.

Another mechanism is that the shear stress required to move dislocations around particles (Orowan stress) becomes lower because the interspacing of particles increases as a result of the re-dissolution of small ones. The above mechanisms lead to a rapid increase in dislocation mobility and a decrease in the shear stress required for dislocation movement.

## CHAPTER VII CONCLUSIONS

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In the present investigation, the precipitation behaviour of Nb(CN) during continuous cooling was studied in terms of the precipitation start ( $P_s$ ) and finish ( $P_f$ ) times. Using the CCP model, precipitation behaviour can be predicted under conditions that are closer to those of industry. The precipitation of Nb(CN) during isothermal holding was studied by means of the stress relaxation method. The  $P_s$  times during isothermal holding were calculated from the PTT data using the Liu and Jonas model, and the  $P_f$  times were predicted using a newly proposed  $P_f$  model. The CCP behaviour was then calculated from the predicted PTT curves using the additivity rule. The calculated CCP behaviour was compared to the  $P_s$  and  $P_f$  times obtained from an analysis of the evolution of particle size during continuous cooling tests performed by hot deformation dilatometry. As a result of this research, the following conclusions are drawn:

- 1. A model for predicting the precipitation finish time during isothermal holding was developed, based on reaction kinetics and the classical nucleation and growth theory. The time exponent and rate constant for the kinetic rule were formulated for the cases of growth only, and for nucleation and growth. In the latter case, the rate of nucleation was taken to be constant during the whole reaction process. This model leads to predictions which are in good agreement with the experimental data.
- 2. A three-dimensional diffusion controlled growth model of the spherical particle was derived. The growth coefficient evaluated from this relationship is smaller than that for the one-dimensional case.
- 3. A CCP model was proposed to describe precipitation behaviour during continuous cooling. The calculated CCP diagrams are shifted to the right and are lower, compared to the PTT diagrams, because nucleation and growth of the precipitate are suppressed during cooling. This effect is more prominent at higher cooling rates.

- 4. The additivity rule, in conjunction with isothermal data, can be used to predict precipitation start and finish times during continuous cooling with reasonable accuracy.
- 5. The thermodynamic parameters of soluble concentration of precipitating elements, mole fraction of precipitates, composition of precipitates, driving force and free energy of formation can be calculated as a continuous function of temperature using the present model. As the temperature increases, the soluble concentrations of precipitates are elements are increased and the mole fractions of precipitates are decreased. The ratio of NbC to Nb(CN) increases as the temperature is decreased. The driving force for precipitation decreases and free energy of formation for critical size nuclei increases rapidly as the temperature is increased.
- 6. The stress relaxation behaviour prior to precipitation shows an exponential dependence of the applied stress on strain rate. The possible rate controlling mechanism for this stage is the thermally activated movement of jogged screw dislocations. The strain rate of stress relaxation is rapidly decreased during precipitation because the materials are strengthened by dispersion hardening. The mobile dislocations are pinned either by the precipitates which nucleate directly on them, or via attraction to growing particles because of vacancy absorption during precipitation. At the coarsening stage, the strain rate increases once more because of the increase in dislocation mobility by unpinning from the redissolving particles.
- 7. A model for particle growth during continuous cooling was derived by considering the temperature dependence of the growth coefficient during diffusion controlled particle growth. The experimental particle size evolution during cooling can well be described using this model.
- 8. The activation energy and frequency factor obtained from the particle size evolution data are 234.7 kJ/mole and 1.49x10 4 m<sup>2</sup>/sec, respectively.

## STATEMENT OF ORIGINALITY AND CON-TRIBUTION TO KNOWLEDGE

The present study includes the following original contributions:

- 1. A prediction model for the finish time of Nb(CN) precipitation during isothermal holding was developed. Two boundary conditions, growth only and nucleation and growth, were used to derive the time exponent and rate constant for the prediction model.
- 2. A three-dimensional growth coefficient for particle growth was derived. This approximation affords a more accurate estimation of the growth of spherical particles when the reaction is controlled by the diffusion of solute atoms.
- 3. Continuous-cooling-precipitation (CCP) diagrams have been introduced to display precipitation behaviour during continuous cooling. A method of deriving the CCP behaviour from isothermal PTT data was developed using the additivity rule. This method was confirmed as a good approximation for such predictions. The present model more closely predicts the precipitation behaviour during industrial processing.
- 4. A model for particle growth during continuous cooling was proposed based on the temperature dependence of the growth coefficient during diffusion controlled particle growth. Using this model, the particle size evolution can be predicted at any cooling rate.

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| *<br>*<br>*                                                                 | IMPLICIT REAL*8 (A-H,L-Z)<br>REAL*8 PS(10), STEMP(10), PF(10), FTEMP(10), RTRMS(10).<br>RTRMF(10),NPS(50), NPF(50), NEWT(50), FNPF(50), XCON(500),<br>YCON(500), FVALUE(500), FUNKN(10), FTMP(10), FUNK(10),<br>TINV(10), LNDD(10) |  |
|-----------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|
|                                                                             | COMMON /AREA1/A,B,TEMP,MNB,MC,MN<br>COMMON /AREA2/MFNB,CP<br>DATA PI/3.141592654D0/                                                                                                                                                |  |
|                                                                             | OPEN (5,FILE = 'NCCPINP',STATUS = 'OLD')<br>OPEN (6,FILE = 'NCCPOUT',STATUS = 'NEW')                                                                                                                                               |  |
| ****************** CONSTANTS VALUES ************************************    |                                                                                                                                                                                                                                    |  |
|                                                                             | SCNST = 0.0 FCNST = 0.0 A = 1./1.87 B = 0.87/1.87 R = 8.31434 Q = 234700. FF = 1.49 CP = 1./1.87                                                                                                                                   |  |
|                                                                             | BOLTZ = 1.38062*(10.**(-23))<br>NO = 6.02*(10.**23)<br>VOL1 = (4.445*(10.**(-10)))**3<br>VOL2 = (4.445*(10.**(-8)))**3<br>XSI = 0.42<br>GAMMA = 0.5<br>GELAST = 0.0                                                                |  |
| **************************************                                      |                                                                                                                                                                                                                                    |  |
| 100                                                                         | READ (5,100) 1PT,WNB,WC,WN,WMN<br>FORMAT(I2,4(F6.4))                                                                                                                                                                               |  |
| ******** TRANSFORM WEIGHT % TO ATOMIC % *********************************** |                                                                                                                                                                                                                                    |  |
|                                                                             | WFE = 100-WNB-WC-WN-WMN<br>ANB = WNB/92.91D0<br>AC = WC/12.01D0<br>AN = WN/14.01D0<br>AMN = WMN/54.94D0<br>AFE = (100.D0-WNB-WC-WN-WMN)/55.85D0<br>ATOT = ANB + AC + AN + AMN + AFE                                                |  |
|                                                                             | MNB = ANB/ATOT $MC = AC/ATOT$ $MN = AN/ATOT$ $MMN = AMN/ATOT$ $MFE = AFE/ATOT$                                                                                                                                                     |  |

DO 50 KDATA = 1, IPT READ (5,200) PS(KDATA), PF(KDATA), FTEMP(KDATA) STEMP(KDATA) = FTEMP(KDATA)FORMAT(F6.1,F6.1,F6.1)200TMEX = 4.07/(DLOG(PF(KDATA))-DLOG(PS(KDATA)))RTCN = DEXP((-2.97\*DLOG(PF(KDATA))-1.10\*DLOG(PS(KDATA)))/(DLOG(PF(KDATA))-DLOG(PS(KDATA))))  $(\omega)$ WRITE (\*,\*) 'mean n value', TMEX, 'mean k value', RTCN \*\*\*\*\*\*\*\*\*\*\*\* CALCULATION OF NBC FRACTION IN NBCN (YVALUE) AND EQULIBRIUM SOLUTE CONCENTRATION CALL PPT(FTEMP(KDATA), XRES, YRES, FTNV1) SNB1 = (MNB-XRES\*A)/(1.-XRES)300 SC1 = (MC-YRES\*XRES\*B)/(1.-XRES)SN1 = (MN - (1 - YRES) \* XRES \* B)/(1 - XRES)\*\*\*\*\*\*\*\* CALCULATION OF CHEMICAL FREE ENERGY \*\*\*\*\*\*\*\*\*\*\*\* TERM = DLOG(SNB1/MNB) + YRES\*DLOG(SC1/MC) + (1.-YRES)\*DLOG(SN1/MN) (a) GCHEM = 4.\*R\*STEMP(KDATA)/NO/VOL1\*TERM \*\*\*\*\*\* CALCULATION OF CRITICAL FREE ENERGY, GSTAR \*\*\*\*\*\* GSTAR = 16.\*PI\*((XSI\*GAMMA)\*\*3)/(3.\*((GCHEM + GELAST)\*\*2))RTRMS(KDATA) = DEXP(Q/R/STEMP(KDATA))\*DEXP(GSTAR/BOLTZ/STEMP(KDATA))/SNB1 (a) SUNKN = PS(KDATA)/RTRMS(KDATA)SCNST=SCNST+SUNKN RTRMF(KDATA) = DEXP(-2.5\*Q/R/FTEMP(KDATA))\*\* DEXP(-GSTAR/BOLTZ/FTEMP(KDATA)) CNST1 = (16.\*1.4142\*PL/15.)\*(1./VOL2)\*(FF\*\*(2.5))CNST2 = CNST1\*SNB1MFNB = MNBCALL CONC(SNB1, PRM1) FUNKN(KDATA) = RTCN/CNST2/PRM1/RTRMF(KDATA) FCNST = FCNST + FUNKN(KDATA)WRITE (\*,\*) 'SUNKN, FUNKN ', SUNKN, FUNKN(KDATA) 50 CONTINUE

> SCONST = SCNST/IPT FCONST = FCNST/IPT WRITE (\*,\*) 'SCONST,FCONST ',SCONST,FCONST

CALL DDDT(IPT,FTEMP,FUNKN,RT1,R'T2)

```
TTP = 1063
DO 53 ICH = 1,30
TTR = TTP + ICH*10
CHDD = DEXP(RT1*(1./TTR) + RT2)
WRITE (*,*) 'TEMP,DISL. DENSITY',TTR,CHDD
53 CONTINUE
```

\*\*\*\*\*\*\* CALCULATION OF PF AT TEST TEMP. RANGE \*\*\*\*\*\*\*\*\*\*\*\*\*\*\*

TEST = 1063. ITEM = 31 ICRI = 0 MPPT = 0.95

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DO 800 ITST = 1,ITEM TEST = TEST + 10. NEWT(ITST) = TEST CALL PPT(TEST,XVAL,YVAL,FTNV2) WRITE (\*,\*) 'XVAL, YVAL,FTN VALUE ',XVAL,YVAL,FTNV2

SNB2=(MNB-XVAL\*A)/(1.-XVAL) SC2=(MC-XVAL\*YVAL\*B)/(1.-XVAL) SN2=(MN-XVAL\*(1.-YVAL)\*B)/(1.-XVAL) FCTRM=DLOG(SNB2/MNB)+YVAL\*DLOG(SC2/MC)+

\* (1.-YVAL)\*DLOG(SN2/MN) FECHEM = (4.\*R\*TEST/NO/VOL1)\*FCTRM FESTAR = 16.\*PI\*((XSI\*GAMMA)\*\*3)/(3.\*(FECHEM + GELAST)\*\*2) RSDS = DEXP(Q/R/TEST)\*DEXP(FESTAR/BOLTZ/TEST)/SNB2 NPS(ITST) = SCONST\*RSDS

$$\begin{split} &RSDF = DEXP(-2.5*Q/R/TEST)*DEXP(-FESTAR/BOLTZ/TEST)*SNB2\\ &CALL CONC(SNB2,PRM2)\\ &FCONST = DEXP(RT1*(1./TEST) + RT2)\\ &FNPF(ITST) = (DLOG(1./(1.-MPPT))/FCONST/CNST1/PRM2/RSDF)\\ &**(1./TMEX)\\ &NPF(ITST) = FNPF(ITST) + NPS(ITST) \end{split}$$

TMPRT = TEST-273. ICRI = ICRI + 1 IF (ICRI.LE.10) GO TO 398 IF (NPS(ITST).GT.1.0D + 20) THEN HTEMP = NEWT(ITST) JCOND = 10 ENDIF WRITE (\*,\*) 'HIGH TEMP',HTEMP

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    398 WRITE (6,450) FNPF(ITST),NPS(ITST),NPF(ITST),TMPRT
    450 FORMAT (4(D15.6))
IF (JCOND.EQ.10) GO TO 217
WRITE (*,*) ITST
    800 CONTINUE
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| 217        | CTEMP = 1073.<br>KSOLU = IDINT(6770./(2.26-DLOG10(WNB*(WC + 12.*WN/14.))) + 1)<br>TSOLU = FLOAT(KSOLU)<br>BTEMP = TSOLU-CTEMP<br>KRANGE = IDINT(BTEMP + 1)                                                                                                                  |
|------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 368<br>101 | DO 101 KK = 1,KRANGE<br>TCRIT = TSOLU-(KK-1)<br>RTEMP = TCRIT-273.<br>IF (TCRIT.GT.HTEMP) GO TO 101<br>CALL PPT(TCRIT,XCON(KK),YCON(KK),FVALUE(KK))<br>WRITE (6,368) RTEMP,XCON(KK),YCON(KK),FVALUE(KK)<br>FORMAT (F10.1,3D16.6)<br>WRITE(*,*) KK,' OF ',KRANGE<br>CONTINUE |
|            | DO 111 I=1,61<br>CR1=-2.0+0.05*(I-1)<br>CLRT=10.**CR1<br>SUM1=0.0<br>SUM2=0.0<br>TIMC1=0.0<br>TIMC2=0.0<br>ICOND=0<br>KCOND=0<br>DTIME=1./CLRT                                                                                                                              |
|            | DO 900 K1=1,KRANGE<br>TIMC1 = TIMC1 + DTIME<br>TIMC2 = TIMC2 + DTIME<br>DTEMP = TSOLU-(K1-1.)<br>IF (DTEMP.GT.HTEMP) GO TO 900                                                                                                                                              |
|            | SNB3 = (MNB-XCON(K1)*A)/(1XCON(K1))<br>SC3 = (MC-XCON(K1)*YCON(K1)*B)/(1XCON(K1))<br>SN3 = (MN-XCON(K1)*(1YCON(K1))*B)/(1XCON(K1))                                                                                                                                          |
| *          | CFAC = DLOG(SNB3/MNB) + YCON(K1)*DLOG(SC3/MC) + (1YCON(K1))*DLOG(SN3/MN) $CHEM = (4.*R*DTEMP/NO/VOL1)*CFAC$ $STAR = 16.*PI*((XSI*GAMMA)**3)/(3.*(CHEM + GELAST)**2)$                                                                                                        |
| *          | SRIGHT=DEXP(Q/R/DTEMP)*DEXP(STAR/BOLTZ/DTEMP)<br>/SNB3                                                                                                                                                                                                                      |
| *          | FRIGHT = DEXP(-2.5*Q/R/DTEMP)*DEXP(-STAR/BOLTZ<br>/DTEMP)*SNB3<br>CPS = SCONST*SRIGHT                                                                                                                                                                                       |
|            | CALL CONC(SNB3,PRM3)<br>FCONST = DEXP(RT1*(1./DTEMP) + RT2)<br>FCPF = (DLOG(1./(1MPPT))/FCONST/CNST1/PRM3/FRIGHT)                                                                                                                                                           |
| *          | **(1.TMEX)                                                                                                                                                                                                                                                                  |

| 537                                    | SFRCTN = DTIME/CPS<br>FFRCTN = DTIME/CPF<br>SUM1 = SUM1 + SFRCTN<br>SUM2 = SUM2 + FFRCTN                         |  |
|----------------------------------------|------------------------------------------------------------------------------------------------------------------|--|
|                                        | IF (ICOND.EQ.10) GO TO 895<br>IF (SUM1.GE.1.) THEN<br>TEME = DTEMP-273.<br>TIME = TIMC1<br>ICOND = $10$<br>ENDIF |  |
| 895                                    | IF (SUM2.GE.1.) THEN<br>TEMF = DTEMP-273.<br>TIMF = TIMC2<br>KCOND = $10$<br>GO TO 910<br>ENDIF                  |  |
| 900                                    | CONTINUE                                                                                                         |  |
| 910                                    | IF (ICOND.EQ.10.AND.KCOND.EQ.10) THEN<br>WRITE (6.980) CLET TIME TEME TIME TEME                                  |  |
| 980                                    | FORMAT (F8.4,2(D15.6,F8.1))<br>ELSELF (ICOND EQ 10 AND KCOND NE 10) THEN                                         |  |
| 981                                    | WRITE (6,981) CLRT,TIME,TEME,SUM2<br>FORMAT (F8.4,D15.6,F8.1,D15.6)<br>ELSE                                      |  |
| 982                                    | WRITE (6,982) CLRT,SUM1,SUM2<br>FORMAT (F8.4,2D15.6)                                                             |  |
| 111                                    | CONTINUE                                                                                                         |  |
| 1000                                   | STOP<br>END                                                                                                      |  |
| ************************************** |                                                                                                                  |  |
|                                        | SUBROUTINE PPT(TP,XOUT,YOUT,RESUL)<br>IMPLICIT REAL*8(A-H,L-Z)<br>COMMON /AREA1/A.B.TEMP.MNB.MC.MN               |  |
| 20                                     | TEMP = TP  LY = 0.01D0  UY = 0.99D0  LX = 0.1D-07  UX = MNB/A-0.1D-07  XR = 0.0D0  YR = 0.0D0  EA = 1000.0D0     |  |
|                                        | DO 1050 J=1,99<br>Y0=LY+(UY-LY)/100.*J<br>UX1=MNB/A                                                              |  |

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UX2 = MC/B/Y0UX3 = MN/B/(1.-Y0)UX = DMIN1(UX1, UX2, UX3) - 0.1D - 07

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- DO 500 I = 1.99X0 = DEXP(DLOG(LX) + (DLOG(UX) - DLOG(LX))/100.\*I)DUM1 = CALC(X0, Y0, RA, RB)\*1.EAB = DABS(RA) + DABS(RB)IF (EAB.LT.EA) THEN EA = EABXR = X0YR = Y0**ENDIF** CONTINUE 500
- **1050 CONTINUE** CALL NEWTON(XR, YR, XOUT, YOUT, RESUL)

RETURN END

SUBROUTINE NEWTON(X,Y,XO,YO,FTN) IMPLICIT REAL\*8(A-H,L-Z) COMMON/AREA1/A,B,TEMP,MNB,MC,MN

UUX1 = MNB/AUUX2 = MC/B/YUUX3 = MN/B/(1.-Y)UUX = DMIN1(UUX1,UUX2,UUX3)-0.1D-10IF (X.GT.UUX) THEN X = UUX**ENDIF** 

DUM2 = CALC(X, Y, OUTA1, OUTA2)F = OUTA1G = OUTA2K = 220 C = 1.-XD=1.-Y

DFDX = (1/(MNB-A\*X))\*(MNB-A)/C + (0.87\*C/(MC-B\*X\*Y))\*(MC-C)B\*Y/C\*\*2.-(2.+57644/TEMP)\*((MNB-A)/C\*\*2)-58523(a)/TEMP\*(MC-B\*Y)/C\*\*2-61220./TEMP\*(MN-B\*D)/C\*\*2 @DFDY = 0.87\*(-B\*X/(MC-B\*X\*Y) + 58523.\*A\*X/TEMP/C + A\*X/C\*(*a*) (-61220./TEMP)-1./Y)DGDX = C/(MC-B\*X\*Y)\*(MC-B\*Y)/C\*\*2+3100./TEMP\*(MC-B\*Y)/C\*\*2-504/TEMP\*(MN-B\*D)/C\*\*2-(MN-B\*D)/(MN-B\*D\*X)/C (a) DGDY = -B\*X/(MC-B\*X\*Y)-(3604./TEMP)\*B\*X/C-B\*X/(MN-B\*D\*X)-1./D-1./Y @XN = (-F\*DGDY + G\*DFDY)/(DFDX\*DGDY-DGDX\*DFDY) + X

UUUX1=MNB/A UUUX2=MC/B/YN UUUX3=MN/B/(1.-YN) UUUX=DMIN1(UUUX1,UUUX2,UUUX3)-0.1D-10 IF (XN.GT.UUUX) THEN XN=UUUX ENDIF

DUM3 = CALC(XN,YN,OUTB1,OUTB2) F = OUTB1 G = OUTB2 FANDG = DABS(F) + DABS(G)IF (DABS(FANDG).LT.1.D-6) GO TO 300 IF (K.GT.30) GO TO 300 X = XN Y = YN K = K + 1GO TO 20

 $\begin{array}{ll} 300 & \text{XO} = \text{XN} \\ & \text{YO} = \text{YN} \\ & \text{FTN} = \text{FANDG} \end{array}$ 

RETURN END

FUNCTION CALC(X,Y,F,G) IMPLICIT REAL\*8(A-H,L-Z) COMMON/AREA1/A,B,TEMP,MNB,MC,MN

F1 = DLOG((MNB-X\*A)/(1.-X)) F2 = 0.87\*DLOG((MC-Y\*X\*B)/(1.-X)) F3 = (MNB-A\*X)/(1.-X)\*(-2.-57644./TEMP) F4 = (MC-B\*X\*Y)/(1.-X)\*(-58523./TEMP) F5 = (MN-B\*(1.-Y)\*X)/(1.-X)\*(-61220./TEMP) F6 = -0.87\*DLOG(Y) + 16454./TEMP + 1.32

G1 = DLOG((MC-X\*Y\*B)/(1.-X)) G2 = ((MC-B\*X\*Y)/(1.-X))\*(3100./TEMP) G3 = ((MN-B\*(1-Y)\*X)/(1.-X))\*(-504./TEMP) G4 = -DLOG((MN-(1.-Y)\*X\*B)/(1.-X)) G5 = DLOG(1.-Y)-DLOG(Y)-2170./TEMP

F = F1 + F2 + F3 + F4 + F5 + F6G = G1 + G2 + G3 + G4 + G5

RETURN END

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SUBROUTINE CONC(SOLNB,PARAM) IMPLICIT REAL\*8(A-H,L-Z) COMMON /AREA2/MFNB,CP

TRM = 3 + 4\*(CP-MFNB)/(MFNB-SOLNB) XB = TRM\*\*(1/3.) XA = XB-0.1

10  $FA = XA^{**3} + XA^{**2} + XA-TRM$   $FB = XB^{**3} + XB^{**2} + XB-TRM$  KSEC = 2  $EKSN = (FA^{*}XB-FB^{*}XA)/(FA-FB)$   $EFN = EKSN^{**3} + EKSN^{**2} + EKSN-TRM$  IF (DABS(EFN).LT.0.1D-09) GO TC 757IF (KSEC.GT.50) GO TO 757

> XA = XB XB = EKSN FA = FB FB = EFN KSEC = KSEC + 1GO TO 10

757 PARAM = ((MFNB-SOLNB)/(EKSN-1)\*\*3/(CP-SOLNB))\*\*(1/2.)

RETURN END

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\*\*\*\*\*\* SUBROUTINE FOR CALCULATION OF THE RELATIONSHIP BETWEEN DISLOCATION DENSITY AND TEMPERATURE \*\*\*\*\*\*

SUBROUTINE DDDT(KPTS,FTMP,FUNK,ROOT1,ROOT2) IMPLICIT REAL\*8(A-H,L-Z) REAL\*8 FTMP(10),FUNK(10),TINV(10),LNDD(10)

DO 55 KD = 1,KPTS TINV(KD) = 1./FTMP(KD) LNDD(KD) = DLOG(FUNK(KD)) CONTINUE

55 CONTIN

PL1 = 0.0PL2 = 0.0PL3 = 0.0PL4 = 0.0

DO 205 ID = 1,KPTS PL1 = PL1 + TINV(ID) PL2 = PL2 + LNDD(ID) PL3 = PL3 + TINV(ID)\*LNDD(ID) PL4 = PL4 + TINV(ID)\*\*2 205 CONTINUE

## $\begin{array}{l} \textbf{ROOT2} = (\textbf{PL2*PL4-PL1*PL3})/(\textbf{KPTS*PL4-PL1**2})\\ \textbf{ROOT1} = (\textbf{PL2-ROOT2*KPTS})/\textbf{PL1} \end{array}$

RETURN END

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