KINETICS OF CARBONITRIDE PRECIPITATION
IN MICROALLOYED STEELS

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ABSTRACT

Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) have been used to investigate the morphologies, distributions, compositions, particle size distributions and growth kinetics of niobium carbide and titanium-niobium carbonitride precipitates in steels containing low levels of Ti, Nb, C and N. The microalloyed steels were solution treated at 1390°C for 2 hr and quenched, and then aged at 1000°C and 1100°C for various times.

The precipitates, mostly with spherical shapes for short aging times and polyhedral and cubic shapes for long aging times, were found to be not quite uniform due to preferential sites for heterogeneous nucleation. After rapid growth within the first few minutes, insignificant ripening takes place for precipitation at 1000°C while fast coarsening occurs at 1100°C. During the aging, only complex carbonitride precipitates of the form \((Ti_xNb_{1-x})(C_yN_{1-y})\) were found among the newly nucleated and growing particles. There is a strong size dependence of particle compositions for short aging times. The youngest of these particles, which approach the size of critical nuclei, tend to be Ti-rich. Titanium nitride tends to form at very high temperatures and titanium-niobium carbides go to completion at low temperatures.

A thermodynamic model was applied to the alloy systems to predict the compositions and mole fractions of the complex carbonitrides. The calculated precipitation-time-temperature (PTT) diagrams for carbonitrides exhibit a C shape for all of the steels. A model predicting the growth kinetics of carbonitrides and composition variation within the precipitates for the initial growth stage (before
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CHAPTER I

INTRODUCTION

To meet the ever increasing requirements of higher strength, toughness, ductility and weldability, modern high strength low alloy (HSLA) steels have been developed using the concepts of grain refinement and precipitate strengthening. These are achieved by a fine dispersion of very small and stable carbides, nitrides and carbonitrides. The role of microalloying elements in improving the properties of HSLA steels has been investigated by numerous people [1-5] over the past two decades. The resulting tiny particles greatly refine austenite grains by pinning the grain boundaries during thermomechanical working. The high ratio of grain boundary interface area to grain volume effectively improves the ferrite nucleation kinetics and a fine ferrite grain size is formed on cooling after completion of the $\gamma$ to $\alpha$ transformation. At the same time numerous small particles appear due to the much lower solubility of carbonitride in ferrite than in austenite. Obviously it is necessary to obtain a comprehensive understanding of precipitation behavior in order to control the response of microalloyed steels to thermomechanical processing.

The alloying elements of interest are Group IVA and VA elements, typically niobium, vanadium and titanium, as additives either individually or in combination. A number of authors [6-8] have reviewed the physical and chemical characteristics
of transition metal-interstitial phases. In steels these carbides, nitrides and carbonitrides, so-called interstitial compounds, exist in a NaCl (B1) type structure wherein the metal atoms are close packed with cubic symmetry and carbon/nitrogen atoms are situated in the octahedral interstices surrounded by the metal atoms.

In the recent development of microalloying technology, much attention has been paid to the investigation of the combined effect of several microalloying elements forming a multicomponent precipitate. However, the role of microalloying additions and the optimization of HSLA steel design is complicated by the mutual solubility of carbides and nitrides. Complex carbonitrides of the form, say, \((Ti_x Nb_{1-x})(C_y N_{1-y})^*\) are therefore to be expected when several microalloying elements are added. Thermodynamic structures for the multicomponent phase diagram Fe-\(\Sigma M_1 \Sigma X_j\) of dilute iron alloys containing any number of solutes have been developed by a number of authors for quite general cases [9-15] (here M is the substitutional transition metal Ti, Nb and V; X is the interstitial element C and N). Many experimental studies on complex carbonitride precipitation during various thermomechanical treatments [11-19] have been carried out in the past decade. It has been reported [16] that in \((Ti_x Nb_{1-x})(C_y N_{1-y})\) precipitates internal composition gradients exist and specific patterns of composition are correlated with different morphologies and alloy compositions. However, theoretical understanding of the kinetic process for this kind of compound precipitates is limited. The optimization of microalloying elements demands taking into account not only accurate solubility but also the evolution of microstructure and the entire sequence of precipitation.

* In this thesis, \((Ti_x Nb_{1-x})(C_y N_{1-y})\) is frequently simplified as \((TiNb)(CN)\). The complete formula will be used only in the case when precise knowledge of the compositions of the precipitates is required.
reaction in which the elements are involved.

While multicomponent diffusion theory was developed in the late 1940s and the 1950s [20-22], very few applications to more than three components have been reported. This is due in part to the complications of the theoretical treatment and the difficulty of finding the "ideal" practical case to which the theory can be directly applied. However, we will demonstrate that subject to some reasonable simplifications and machine computation, the multicomponent diffusion theory may be applied to the kinetics of complex carbonitride precipitation in microalloyed steels.

Conventional theories for the precipitation of spherical particles of a second phase in binary alloys [23-25] are shown to be inappropriate when dealing with carbide or nitride species in multicomponent Fe-Mi-Xj alloys. In particular, the application of analytical solutions and the assumption of a constant equilibrium solute concentration at the interface cannot be made. Diffusion in multicomponent system is complicated. In some cases, reasonable simplifications can be found for the microalloyed Fe-Mi-Xj system which makes the problem tractable without making it so idealized that it bears no relation to practice. A number of theoretical treatments and computer simulations [26-29] of the precipitation (or similar dissolution process) of carbides have been offered based on binary diffusion theory without considering the capillarity effect. All of these treat diffusion coefficients as constant and ignore the nonstoichiometry. This is questionable for these particular compounds because of the strong interaction between the substitutional component and interstitial component in austenite solution and the actual large degree of nonstoichiometry. In addition, the surface tension effect can be significant as a result of the typically tiny particle size (5 to 10 nm), which changes the matrix composition at the interface in equilibrium
with precipitates of different size. Although Årgen [30] has recently developed a comprehensive kinetic model of the dissolution of carbides with the application of multicomponent diffusion theory, his method still cannot be directly applied to microalloying systems. Therefore, in the present study a simplified analytic and a finite difference models overcoming all the above drawbacks have been developed to describe the kinetic process of carbonitrides in the initial stage (the rapid growth mainly at the expense of matrix solute). The models proposed have been applied to niobium carbide and Ti-Nb carbonitride, respectively, and have satisfactorily predicted the precipitation behavior of these compounds.

The objectives of this study are to obtain complete experimental kinetic information about the multicomponent carbonitride precipitates in austenite alloyed with titanium and niobium and comparative theoretical predictions with the inclusion of both thermodynamic and kinetic effects. In the present study models have been developed to describe the thermodynamics of complex carbonitride and the kinetic processes of precipitation pertaining to carbonitride in the initial growth stages (before coarsening). The present experimental work has been carried out on the precipitation behavior of carbide and carbonitride particles in microalloyed steels. The alloys, which have compositions similar to those used in industry, have been homogenized at high temperature and quenched, and then heated at 1000°C and 1100°C for the desired times. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were employed to investigate the characteristics and the growth kinetics of NbC and complex \((Ti_xNb_{1-x})(C_yN_{1-y})\) precipitates.
CHAPTER II

LITERATURE REVIEW

2.1 CRYSTAL STRUCTURES AND COMPOSITION OF CARBIDES AND NITRIDES

Transition metal elements in group IVA and VA form interstitial compounds with carbon and/or nitrogen because the small non-metal atom locates at the octahedral void between the metal atoms. Hagg [31] proposed a relationship connecting the structure of interstitial compounds with the radius ratio of the non-metal to metal atoms. If the ratio is less than 0.59, the lattice of the compounds is simple cubic or the hexagonal closed packed structure; if the value of 0.59 is exceeded, a more complex structure forms. These compounds are sometimes referred to as "refractory hard metals" because of their high hardnesses and melting points, and their metallic properties. In the case of carbides and nitrides of Ti, Nb and V, simple cubic structures are formed in practical HSLA steels.

2.1.1 Carbides

F.c.c. carbides of the NaCl type structure are formed with Ti, Zr and Hf, while f.c.c. and h.c.p. carbides are produced with V, Nb and Ta. Ideal stoichiometry is not generally found in the carbides. Almost all [7] of these
compounds are strongly nonstoichiometric resulting from the tolerance of atom vacancies for both metal and non-metal in rather large concentrations. Typically, vacancies are on the non-metal sublattice; but metal vacancies are also evident in nitrides (TiN [32] and NbN [33]). As a result the formula of the form MC_y has been used to symbolize their inexact compositions, where y ≤ 1 is the average atomic ratio of C to M in the compound. The degree of deviation from stoichiometry, i.e., the value of y, depends on the equilibrium C activity.

Group IVA elements only form single carbidés (TiC, ZrC, HfC); on the other hand in Group VA, additionally to VC, NbC and TaC, the lower M_2C carbidés (h.c.p.) also occur. The crystallographic data for carbidés of Ti, Nb and V are listed on Table 2.1.

The most recent and accurate phase diagrams for the Nb-C and Ti-C systems, given by Rudy [35] and predicted by K. Balasubramanian [36], are presented in Fig.2.1 and Fig.2.2. They are characterized by three regions:

i). Solid solubility of C in metal.

ii). Solid solubility (almost nil) of metal in C.

iii). A non-stoichiometric compound MC_y with a considerable solid solution range, i.e. 35-50 at.% C in Nb-C and 33-50 at.% C in Ti-C.

The structures of these carbidés are cubic B1 and are the only carbidés of Nb and Ti precipitating in microalloyed steels. The carbidés NbC_{0.99} and TiC_{0.99} are only in equilibrium with graphite in pure M-C systems; that is when the activity of carbon is unity. This suggests that the cubic carbidés precipitated in HSLA steels will be much more defective due to the much lower carbon activity. Balasubramanian and Kirkaldy [37] have proposed a modified regular solution model to calculate the y in MC_y. The prediction shows that the y value varies from 0.93 to 0.83 for TiC and 0.98 to 0.87 for NbC in the composition range of microalloyed
steels (typically carbon mole fractions of $10^{-4}$ to $10^{-2}$). On the other hand the y value for the vanadium carbide is close to 0.75 in steels [38], consequently, it is often designated to as $V_4C_3$. A hexagonal semi-carbide $Nb_2C$ exists in the Nb-C system whereas this phase does not form in the Ti-C system.

2.1.2 Nitrides

Based on the similarities of electronic structures, atomic radii ($R_N = 0.67$ Å, $R_C = 0.77$ Å) and electronegativities, the nitrides and carbides in transition metals are closely similar to each other as to structures, phase relationships, bonding characteristics, electric and metallic properties, melting points and hardnesses. Table 2.2 lists the nitrides that can be formed with Ti, Nb and V. Although a wide variety of crystal structures are exhibited in the composition range 25-50 at.% N, only cubic nitrides of Ti, Nb and V with the fcc NaCl structures have again been observed in steels.

The lattice parameter of the $MX_y$ compounds vary considerably with composition. The accurate data on the relationships between lattice parameter and non-stoichiometry of NbC are available through a number of sources [43-49]. The lattice dimensions of $NbC_y$ and $TiN_y$ as a function of the degree of its nonstoichiometry are shown in Figs.2.3 and 2.4.

2.1.3 Mixed Carbides and Nitrides or Carbonitrides

Transition metal carbides and nitrides possess a mutual solubility varying widely, depending not only on the isomorphy of the end members, but also on the similarities of chemical and physical properties and relative atomic sizes. NaCl
type carbides of Ti, Nb and V form continuous solid solutions. The normal content of carbon and nitrogen in steels is always associated with cubic carbonitrides having the NaCl type structure. Both the Nb and V carbonitrides are frequently observed in microalloyed steels. Although the NbN particles in the Fe-Nb-N system usually have the h.c.p structure, in the presence of C in Fe-Nb-C-N alloys only Nb(CN) precipitates with a NaCl structure are observed. In this compound, the C and N are randomly mixed on the non-metal sublattice [52]. The same type of structure can be expected for the V(CN) phase. However there are some complications in assessing the existence of Ti carbonitride in microalloyed steels. It has been reported [53] that a nonuniform composition exists in Ti(CN) precipitates - a N rich core with a C rich shell. This may indicate that TiC is nucleated on the existing or an earlier nucleated TiN particle.

2.2 SOLUBILITY OF CARBIDES AND NITRIDES

2.2.1 Thermodynamic Analysis of the Fe-M-X Systems

The thermodynamic conditions which define the character of the two phase region of the constitution diagram are best illustrated with the aid of a ternary free energy diagram as shown in Fig.2.5 (the solid lines). The contact points of the plane tangent to both the austenite and carbide free energy surfaces define one equilibrium tie-line. As this plane rocks over the free energy surfaces the projection of these contact points on the composition plane generates the boundaries and tie-lines of the two phase region. The chemical potentials, or partial molar free energies $G_i$ of each of the three components are given by the intersections of the tangent plane with the three free energy axes and they
therefore automatically generate the equilibrium conditions.

Since cubic transition metal monocarbides and mononitrides are nonstoichiometric compounds they are represented as $MX_y$, where $y$ is the constant average composition of $X$. Now for the Fe-M-X systems the equilibrium between $MX_y$ precipitates and the austenite can be expressed as

$$[M] + y[X] = MX_y$$  \hspace{1cm} (2.1)$$

where $[ ]$ signifies that the component is in the solution of austenite. The free energy of $MX_y$, $\Delta G_{MX_y}$, is then given by

$$\Delta G_M + y \Delta G_X = \Delta G_{MX_y}$$  \hspace{1cm} (2.2a)$$
or

$$\Delta G_M + RT \ln a_M + y(\Delta G_X + RT \ln a_X) = \Delta G_{MX_y}$$  \hspace{1cm} (2.2b)$$

Where $a_i$ is the activity of ith solute in austenite.

Therefore

$$\Delta \Delta G_{MX_y} = RT(\ln a_M + y \ln a_X)$$  \hspace{1cm} (2.3)$$

where $\Delta \Delta G_{MX_y} = \Delta G_{MX_y} - \Delta G_M - y \Delta G_X$ is the free energy of formation of $MX_y$ from $M$ and $X$, with infinite dilution in austenite as the reference state. Assuming ideal or henrian behavior for the solutes in the solution, we obtain

$$\Delta \Delta G_{MX_y} = RT \ln X_M X_X^y$$  \hspace{1cm} (2.4)$$

On the other hand, from $\Delta G^o = \Delta H^o - T\Delta S^o$, where $\Delta H^o$ and $\Delta S^o$ are approximately constant over a certain temperature range, the relationship of the free energy of $MX_y$ formation and temperature can be simplified to the form of
\[ \Delta^o G_{MX_y} = a + bT \]  
where \( a \) and \( b \) are experimentally determined constants corresponding to the entropy and enthalpy of formation of the compound.

We obtain the solubility product \( K_{MX_y} \) in terms of \( \Delta^o G_{MX_y} \) as

\[ K_{MX_y} = \exp \left( \frac{\Delta^o G_{MX_y}}{RT} \right) \] (2.6)

### 2.2.2 Solubility Products of Carbides and Nitrides in Austenite

The solubility product in terms of weight percentages of \( M \) and \( X \) is generally used to represent the solubility of \( MX_y \) carbide and nitride in austenite. The conversion between molar fractions of \( M \) and \( X \) and weight percentages in austenite can be approximately written as follows:

\[ X_M = \frac{1}{100} \frac{[\text{wt.\%}M]}{A_Fe} \frac{A_{Fe}}{A_M} \] (2.7a)

and

\[ X_X = \frac{1}{100} \frac{[\text{wt.\%}X]}{A_{Fe}} \frac{A_{Fe}}{A_X} \] (2.7b)

where \( A_{Fe}, A_M \) and \( A_X \) are the atomic weights of iron, \( M \) and \( X \), respectively. Combining these with Eqs.2.4 and 2.5, the solubility of \( MX_y \) in austenite can be calculated as

\[ \log[\%M][\%X]^Y = A + \frac{B}{T} \] (2.8)

The solution behavior of binary carbides and nitrides in austenite are
reasonably well understood. There have been many experimental determinations of solubility products of carbides and nitrides in steels, especially in iron austenite as presented in Tables 2.3 and 2.4. Almost all the experimenters have analyzed their data on the basis of a solubility product of the form

\[ \log \left[ \frac{\%M}{\%X} \right] = A + \frac{B}{T} \quad (y = 1) \] (2.9)

where \( y \) defines stoichiometry, \( \%M \) and \( \%X \) refer respectively to concentrations of transition metal \( M \), carbon or nitrogen \( X \) in austenite (expressed in weight % or atomic %) and \( A \) and \( B \) are constants determined from experiment.

Indeed most early investigators not only assumed \( y = 1 \), i.e., perfect stoichiometry for the compounds, they also assumed the activity coefficients of \( M \) and \( X \) to be unity. Under these assumptions Eq.(2.9) is used to analyze the solubility product. However, it is well known that transition metal carbides and nitrides in steels are strongly nonstoichiometric. Accordingly, recent investigators [50,52,78] have offered improved solubility relationships which include an assumed constant deviation from stoichiometry. They showed that \( y = 0.87 \) gives a better agreement between correlation of various experimental results.

2.2.3 Effects of Curvature

The influence of curvature on the interface equilibrium composition is significant for tiny particles as illustrated in Fig.2.5 (the dashed lines), especially in the initial stage of precipitation. Based on the consideration of the Gibbs-Thompson effect for a binary system, the composition in the matrix at the spherical precipitate and matrix interface, \( ^{\text{C}}_1 \), varies with particle radius, \( r \), as
\[ r C_i = C_i^\infty \exp\left( \frac{2 \sigma V_p}{RT \tau X_p} \right) \]  

(2.10)

where \( C_i^\infty \) is the composition in the matrix at a planar precipitate/matrix interface, \( \tau \) is the specific interfacial free energy of the precipitate/matrix interface, \( V_p \) is the molar volume of precipitate and \( X_p \) is the mole fraction of solute in the precipitate.

Applying the above equation to the solubility product in a ternary solution [79], one obtains approximately,

\[ X_M^e X_X^e = K_{MX}^r = K_{MX} \exp\left( \frac{4 \sigma V_p}{RT \tau X_p} \right) \]  

(2.11)

where \( X_p = 1 \), since MX may be considered as a pure component with respect to Fe, \( X_M^e \) and \( X_X^e \) are compositions of M and X in austenite at equilibrium with the precipitates, \( K_{MX} \) is the solubility product for a planar precipitate/matrix interface, \( \sigma \) refers to interfacial energy between carbide and austenite and \( V_p \) is the molar volume of carbide (the factor 4 in stead of 2 is resulting from the definition of \( V_p \)). For small values of the exponent

\[ K_{MX}^r \approx K_{MX}\left(1 + \frac{4 \sigma V_p}{RT \tau} \right) \]  

(2.12)

Taking the following typical values: \( \sigma = 0.3 \text{ J/m}^2 \), \( V_p = 7 \times 10^{-6} \text{ m}^3 \), \( R = 8.31 \text{ J/mol/K} \) and \( T = 1273 \text{ K} \) gives

\[ \frac{K_{MX}^r}{K_{MX}} \approx 1 + \frac{1}{r(\text{nm})} \]  

(2.13)
with a typical average \( r \sim 10 \text{ nm} \) for MX particles in steels \( K_{\text{MX}}^r / K_{\text{MX}} \sim 1.1 \). It can thus be seen that quite significant solubility product changes can arise for tiny particles in microalloyed steels.

2.2.4 Effects of Nonstoichiometry and Solute Interaction

In the above methodology the assumptions of both ideal behavior for M and X in austenite and a constant \( y \) value are questionable. Titanium and niobium are very strong carbide and nitride forming elements, hence they interact very strongly in austenite. This can result in increased solubility at higher carbon content, as observed by Balasubramanian [37] and Ohtani and Nishizawa [80]. Furthermore, the value of \( y \) also varies as a function of temperature and composition. Accordingly the solute interactions in austenite and the nonstoichiometry of the interstitial compounds should be taken in account for a rigorous thermodynamic analysis of the MX/austenite equilibrium. According to the Wagner formalism [81-84], the variation of chemical potentials of M and X in the Fe-M-X austenite can be expressed as:

\[
\bar{G}^Y_M = RT \ln a^Y_M = RT \ln X^Y_M + RT (\ln \gamma^0_M + \varepsilon^M_{MX} + \varepsilon^X_{MX}) \tag{2.14a}
\]

\[
\bar{G}^Y_X = RT \ln a^Y_X = RT \ln X^Y_X + RT (\ln \gamma^0_X + \varepsilon^X_{MX} + \varepsilon^M_{MX}) \tag{2.14b}
\]

where the \( X^Y_i \) and \( \gamma^0_i \) refer to the concentrations and Henry's law coefficient of the \( i \)th solute in austenite, respectively. The \( \varepsilon^i_i \) and \( \varepsilon^j_i \) are the self and cross interaction parameters of M and X solutes. Pure metals (bcc Ti and bcc Nb) are chosen as standard states.

For the Fe-M-C system, expressions relating chemical potentials of the metal and interstitial components in the compound as functions of composition and
temperature were obtained by Balasubramanian and Kirkaldy [37] using a sublattice regular solution model. The results are stated below:

\[
\bar{G}^{\text{MC}}_M = RT\ln a^{\text{MC}}_M = A_0 + A_2 y^2 + A_3 y^3 + RT\ln(1-y) \tag{2.15a}
\]

\[
\bar{G}^{\text{MC}}_C = RT\ln a^{\text{MC}}_C = B_0 + B_1 y + B_2 y^2 + RT\ln[y/(1-y)] \tag{2.15b}
\]

where \(y\), as defined before, represents the C to M ratio, and the A and B parameters are functions of temperature.

The austenite-metal carbide equilibrium are determined by the condition of equality of chemical potentials, i.e.

\[
\bar{G}^\gamma_M = \bar{G}^{\text{MC}}_M \tag{2.16a}
\]

\[
\bar{G}^\gamma_C = \bar{G}^{\text{MC}}_C \tag{2.16b}
\]

Fig.2.6 shows the calculated solubility curves of NbC in Fe-Nb-C austenite at 1273K and 1473K due to the aforementioned authors. In order to delineate the effects due to the solute interactions and nonstoichiometry of carbides, the following three cases have been considered: case (i) the carbide is stoichiometric and there are no solute interactions in austenite; case (ii) the carbide is stoichiometric and there are solute interactions in austenite; case (iii) the carbide is nonstoichiometric and there are solute interactions in austenite.

As can be seen in case (ii) and (iii), the solubility curve can be divided into three regions correspond roughly to the three areas marked by the two minima. In region A with high C and low Nb and region C with low C and high Nb, the phase boundary is significantly curved inwards due to the strong solute interactions which result in the increase of the carbide solubility. It should be noted that the
microalloyed cast irons fall in region A. By contrast, in region B with both low C and Nb for all three cases, the boundary line is nearly straight since the effects of solute interactions are negligible due to the low content of solutes. Such straight lines can be described using the mass action law represented by Eq.2.8 by choosing proper constant values of y. This means that the influence of the solute interaction and of the nonstoichiometry of carbide on the linearity of the phase boundary can be ignored in region B. It is worth noting that the concentrations of microalloyed steels are generally located within this region; hence the conventional formulas of carbide solubility can be applied to microalloyed austenite.

The above considerations of the effects due to nonstoichiometry and solute interactions on the austenite-carbide equilibrium can be extended in principle to the austenite-nitride equilibrium. Due to the much lower solubility of nitride the amount of nitrogen dissolved in steel is very small and the nitrides are very close to stoichiometry in the steel. Therefore, the mass action law is adequate to the description of the solubility of the nitrides in austenite (i.e. straight lines as in Fig.2.6).

2.2.5 Effects of Other Alloying Elements

Other alloying elements such as Mn, Ni, Cr and Si commonly exist in microalloyed steels and they either do not dissolve in the carbide and nitride particles or form their own compounds with the C and N in austenite. Although the solute interactions between these elements and the interstitials are relatively weak with respect to Ti, Nb and V, their effects on the solubility can still be significant due to their high concentrations (generally up to 1 or 2 wt.%). Koyama
et al [85,86] have experimentally determined the effects of Mn, Ni, Si, and Cr on the solubility for niobium carbide and \(\varepsilon\)-niobium nitride in austenite. Theoretically, these elements may modify the precipitation of carbonitrides only by changing the activities of C, N, Ti and Nb in austenite (and ferrite). Their influence is thus readily incorporated into the solubility model by using the appropriate Wangner interaction parameters [87]. In the past decade, some effort has been expended to quantify such alloying effects on the solubility of NbC, NbN and TiC by thermodynamic methods [52,88,89]. According to Sharma et al [52], the effect of other elements, \(K\) (\(K = 1, 2, \ldots\)), on the activities of the metal \(M\) and interstitial \(X\) in the Fe-M-X-K systems can be expressed as

\[
\ln a_M^Y = [\ln a_M^Y]_{K=0} + \sum e_{M}^{K}X_K^Y
\]

\[
\ln a_X^Y = [\ln a_X^Y]_{K=0} + \sum e_{X}^{K}X_K^Y
\]

(2.17a)

(2.17b)

where the first term in each equation represents the activity of the \(i\)th (\(i = M\) or \(X\)) microalloying element in the absence of other alloying addition \(K\), \(X_K^Y\) is the mole fraction of the \(K\) element and \(e_{i}^{K}\) is the Wagner interaction parameter between \(i\) and \(K\). Accordingly in the presence of the other alloying the effective solubility product of the MX compound in austenite can be changed to [52],

\[
\log[\%M][\%X]^Y = [\log[\%M][\%X]^Y]_{K=0} - (e_{M}^{K} + y e_{X}^{K})[\%K] \frac{A_{Fe}}{230.3A_{K}}
\]

(2.18)

where \(A_{Fe}\) and \(A_{K}\) are the atomic weight of Fe and \(K\), respectively, and the concentration [\(\%K\)] is also in weight percent. Thus, if the Wagner interaction parameters \(e_{i}^{K}\) are known for each \(K\) element, the solubility of the MX interstitial compound in the presence of the \(K\) elements can be evaluated by using the above modified expression for the solubility product. The interaction parameters \(e_{C}^{K}\) in
austenite are fairly reliable, the $\varepsilon^K$ are less accurately known, while the values of $\varepsilon^K_{\text{Nb}}$ were inferred indirectly by Sharma et al [52] from experimental solubility data for NbC and NbN in austenite [85,86]. Estimates for $\varepsilon^K_{\text{T}_1}$ and $\varepsilon^K_v$ are unfortunately not available in the literature at this juncture. Some selected Wagner interaction parameters of alloying elements are given in Table 2.5.

2.2.6 Thermodynamic Analysis of the Fe-M-C-N the Systems

Due to the mutual solubility of carbides and nitrides, the precipitates in the Fe-M-C-N systems can be expressed as $M(C_yN_{1-y})$. According to the ideal solution model for Fe-Nb-C-N system proposed by Hudd et al [96] it is assumed that one mole of $M(C_yN_{1-y})$ can be considered as an ideal mixing of $x$ mole of MC and $(1-x)$ mole of MN, where the titanium and niobium randomly substitute for each other. This gives

$$yMC + (1-y)MN = M(C_yN_{1-y}) \quad (2.19)$$

The total free energy of the compound is then given by

$$G_{M(C_yN_{1-y})} = y\bar{G}_{MC}^P + (1-y)\bar{G}_{MN}^P \quad (2.20)$$

where $\bar{G}_{MC}^P$ and $\bar{G}_{MN}^P$ are the partial mole free energies of MC and MN in the $M(C_yN_{1-y})$ particle solution. According to the ideal solution assumption, the partial molar free energies are now given by

$$\bar{G}_{MC}^P = G^o_{MC} + RT\ln y \quad (2.21a)$$

$$\bar{G}_{MN}^P = G^o_{MN} + RT\ln(1-y) \quad (2.21b)$$

The equilibrium between austenite and carbides can be written as

$$\bar{G}_{MC} = \bar{G}_M^\gamma + \bar{G}_C^\gamma \quad (2.22a)$$
\[ \bar{G}_{MN} = \bar{G}^Y_M + \bar{G}^Y_N \] 

(2.22b)

where \( \bar{G}^Y_i \) are the partial molar free energies of each element in austenite. Thus the equilibrium between austenite and \( M(C_{yN_{1-y}}) \) can be given by the following

\[ RT \ln [a_M a_C] = \Delta G^0_{MC} + RT \ln [y] \] 

(2.23a)

\[ RT \ln [a_M a_N] = \Delta G^0_{MN} + RT \ln [1-y] \] 

(2.23b)

or

\[ a_M a_C = yK_{MC} \] 

(2.23c)

\[ a_M a_C = (1-y)K_{MN} \] 

(2.23d)

where the \( \Delta G^0_{MX} \) refer to the free energies of formation of the respective binary compounds from austenite. The mass balance equations need to be considered to complete the equilibrium picture.

2.3 FORMAL THEORY OF DIFFUSION

The study of phase transformations concerns those mechanisms by which a system attempts to reach a certain state and how long it takes. The rate of a heterogeneous solid-state reaction can be controlled by several different mechanisms such as volume diffusion, grain boundary diffusion or interface reaction. The fundamental process that controls the rate at which many transformations occur is the diffusion of atoms. The trend of diffusion in an isobaric and isothermal system is always so as to produce a decrease in the Gibbs free energy of the system. In many practical cases it is found that the kinetics of
transformation is controlled by volume diffusion of the different solute components. To understand the kinetics of carbonitrides precipitation in isothermal multicomponent phase transformations, it is necessary to review multicomponent diffusion theory.

2.3.1 Phenomenological Diffusion Theory

It is more difficult to deal with multicomponent diffusion with a moving boundary than with the single phase problem or with a stationary boundary. The many variables involved complicate the precipitation kinetics to an extent that analytic mathematical solutions are highly unlikely. Thus the only feasible method of theoretical prediction of precipitation behavior in microalloyed steels is numerical integration using a computer. The numerical treatment of diffusion controlled phase transformation in alloys involves the simultaneous solution of a set of diffusional, equilibrium, nonstoichiometric and mass balance equations. These equations are non-linear and transcendental, and iterative methods must therefore be used.

The formal basis for diffusion theory was established in 1855 by Fick [97]; that is a linear relationship between the diffusive flux, J, and the concentration gradient \( \nabla C \), of the form

\[
J = -D \nabla C
\]

(2.24)

where \( D \) is known as the diffusivity or the diffusion coefficient (a function of temperature and concentration) and has unit \([m^2/s]\). The unit for \( J \) is \([\text{mass}/m^2s]\) and for \( \nabla C \) \([\text{mass}/m^4]\), where the unit of mass can be in terms of atoms, moles, kg, etc., as long it is the same for \( J \) and \( C \). Combining Eq.(2.24) with the mass balance
\[ \text{div } J = -\frac{\partial C}{\partial t} \]  

(2.25)

gives the time-dependent diffusion equation, i.e., Fick's second law

\[ \frac{\partial C}{\partial t} = \nabla (D \nabla C) \]  

(2.26)

Irreversible phenomena of multicomponent diffusion are described by phenomenological equations outlined completely by Onsager [20] in 1945-1946. This work followed directly from his earlier and much celebrated papers [98] on "Reciprocal Relations in Irreversible Processes".

In ternary or higher-order systems, the flux of each of the i components can be expressed by phenomenological relations of the general type

\[ J_i = \sum_{k=1}^{n} L'_{ik} X_k \quad (i = 1, 2, \ldots, n) \]  

(2.27)

where the \( X_k \) are thermodynamic forces, \( J_i \) are the fluxes caused by the forces, and the \( L'_{ik} \) are phenomenological coefficients (or Onsager coefficients). In a volume-fixed reference frame, it can be assumed that the concentration differences are small, or molar volumes are sufficiently constant that the variation in the total volume during diffusion can be neglected. The fluxes may then be simply measured relative to the walls of the sample. The volume-fixed reference frame is defined by the condition

\[ \sum_{i=1}^{n} \bar{V} J_i = 0 \]  

(2.28)

where \( J_i \) is the diffusive flux of ith element and the \( \bar{V}_i \) are the partial molar volumes (assumed constant). Therefore the flux of component n (which commonly stands for solvent, i.e., Fe in this study) can be regarded as a dependent
variable. In the above simplified case the general phenomenological equations of the fluxes of component \( i \) in an \( n \)-component system are then given by \([20, 99, 100]\)

\[
J_i = \sum_{k=1}^{n-1} L_{ik} X_k \quad (i = 1, 2, ..., n-1) \tag{2.29}
\]

The \( X_k \) are expressed in terms of the chemical potentials \( \mu_k \) as

\[
X_k = - \nabla(\mu_k - \frac{V_k}{V_n} \mu_n) \tag{2.30}
\]

where the \( V_k \) are partial molar volumes (assumed constant).

As a consequence of Onsager's reciprocity theorem, the matrix \([L_{ik}]\) is symmetric, viz.,

\[
L_{ik} = L_{ki} \tag{2.31}
\]

Eq.(2.29) states that any flux is caused by a linear contribution from all of the independent forces. From this relation it may be inferred that in multicomponent diffusion the flux of each component is a linear function of all the independent concentration gradients. Therefore, Eq.(2.29) can be transformed to the following expression in three dimensions

\[
J_i = - \sum_{k=1}^{n-1} D_{ik} \nabla C_k \quad (i = 1, 2, ..., n-1) \tag{2.32}
\]

where the \( D_{ik} \) are the diffusion coefficients, and the \( C_k \) are concentrations. The off-diagonal diffusion coefficients \( D_{ik} \) (\( i \neq k \)) specify the diffusivity of one component on the concentration gradient of the other component. The diffusion coefficient matrix \([D_{ik}]\) is the product of the symmetric mobility matrix and the thermodynamic matrix:
\[ [D_{ik}] = [L_{ij}][\mu_{jk}] \quad (2.33) \]

where
\[ \mu_{jk} = \sigma(\mu_i - \mu_n)/\beta C_k = \mu_{kj} \quad (2.34) \]

The Second Law of Thermodynamics and thermodynamic stability of a solution require that the matrices \([L_{ik}]\) and \([\mu_{ik}]\), respectively, be positive definite [100].

By combining Eq.(2.32) with the corresponding mass balances, one obtains
\[ \frac{\partial C_i}{\partial t} + \text{div} J_i = 0 \quad (2.35a) \]

one obtains the set of \(n-1\) simultaneous diffusion equations
\[ \frac{\partial C_i}{\partial t} = \sum_{k=1}^{n-1} \nabla D_{ik} \nabla C_k \quad (2.35b) \]

These are the generalization of Fick's second law. Many problems involving the diffusion process can reduced to finding solutions of the differential Eq.(2.35b) by applying appropriate boundary conditions.

2.3.2 Application of the Multicomponent Diffusion Formalism to Dilute Ternary Systems

For a dilute ternary system in which the relative changes in concentrations are small, the diffusion coefficients may be deemed independent of concentration and Eq.(2.29) may be applied to fluxes measured with respect to a fixed solvent lattice; i.e., lattice parameter changes and the shift of the Matano interface are neglected and Eq.(2.35) reduce to
\[
\frac{\partial C_x}{\partial t} = D_{xx} \nabla^2 C_x + D_{xm} \nabla^2 C_m \quad (2.36a)
\]
and
\[
\frac{\partial C_m}{\partial t} = D_{mx} \nabla^2 C_x + D_{mm} \nabla^2 C_m \quad (2.36b)
\]
or for a one-dimensional system
\[
\frac{\partial C_x}{\partial t} = D_{xx} \frac{\partial^2 C_x}{\partial x^2} + D_{xm} \frac{\partial^2 C_m}{\partial x^2} \quad (2.37a)
\]
and
\[
\frac{\partial C_m}{\partial t} = D_{mx} \frac{\partial^2 C_x}{\partial x^2} + D_{mm} \frac{\partial^2 C_m}{\partial x^2} \quad (2.37b)
\]
where the off-diagonal diffusion coefficients \(D_{xm}\) and \(D_{mx}\) specify the diffusivity of one component on the concentration gradient of the other component. One seeks solutions to this set of equations as linear superpositions of the form [20,101,102]
\[
C_i = a_{i0} + \sum_{k=1}^{2} a_{i,k} C^k \quad (2.38)
\]
where the \(C^k\) are solutions of the binary type diffusion equation. Parametric solutions of Eq.(2.38) were first obtained by Fujita and Gosting [102] in terms of the parameter
\[
\beta = \frac{x}{2t^{1/2}} \quad (2.39)
\]
applicable to the following initial and boundary conditions for an infinite diffusion couple.

Initial conditions:
\[ C_X = C_{X0}, \quad C_M = C_{M0} \quad \text{for } x > 0, \quad t = 0 \quad (2.40a) \]

\[ C_X = C_{X1}, \quad C_M = C_{M1} \quad \text{for } x < 0, \quad t = 0 \quad (2.40b) \]

Boundary conditions:

\[ C_X = C_{X0}, \quad C_M = C_{M0} \quad \text{for } x \to +\infty, \quad t = t \quad (2.41a) \]

\[ C_X = C_{X1}, \quad C_M = C_{M1} \quad \text{for } x \to -\infty, \quad t = t \quad (2.41b) \]

The solutions are of the form

\[ C_X = C_{X1} + a \text{erf}(\sqrt{t} \beta) + b \text{erf}(\sqrt{Q} \beta) \quad (2.42a) \]

\[ C_M = C_{M1} + d \text{erf}(\sqrt{t} \beta) + e \text{erf}(\sqrt{Q} \beta) \quad (2.42b) \]

where \( a, b, d \) and \( e \) depend on the boundary conditions and the diffusion coefficients and \( p \) and \( q \) depend on the diffusion coefficients only.

Purdy et al [103] offered the first quantitative application of Onsager's multicomponent diffusion theory to the prediction of a phase transformation rate. This pertained to the isothermal transformation of the \( \gamma \) (fcc) to the \( \alpha \) (bcc) in a dilute carbon-manganese alloy with iron (i.e., steel). It was demonstrated that the addition of manganese reduces the transformation rate of the first order reaction for two reasons (the so-called hardenability effect). In the first instance Mn is a \( \gamma \) (austenite) stabilizer (as is carbon) and therefore for a given temperature the supersaturation is reduced by the manganese addition. Secondly, Mn and C are attractive in the Fe lattice (C tends to diffuse up a Mn gradient), so in the present reaction where Mn and C are both rejected by the product \( \alpha \)-phase, fast-diffusing C is attracted against the flow and thus a further resistance to
transformation is made evident. These effects are represented analytically within the theory presented by Purdy et al [103] and confirmed by experiment.

The two effects are illustrated comparatively (in Fig.2.7) in terms of a normalized rate parameter \( \beta_1 \) for a high supersaturation alloy of 0.2 wt% C and 1.5 wt% Mn as a function of temperature. As can be seen the constitutional retardation effect is about a factor of five while the diffusional effect is a factor of two to three. Despite the diluteness of the alloy the diffusional cross-effect is highly significant.

2.3.3 Concentration Dependence of Off-Diagonal Diffusion Coefficients

In the above, it has been assumed that all the diffusion coefficients are constant. Such an approximation may be poor for dilute multicomponent systems containing strong carbide-forming alloying elements (V, Nb, Ti), where it is known that the off-diagonal diffusion coefficients are linear functions of composition.

The concentration dependence of the diffusion coefficients for both interstitial and substitutional solutes in dilute ternary solutions has been investigated in detail [104]. It was demonstrated that the on-diagonal D's, \( D_{xx} \) and \( D_{MM'} \), are slowly varying functions of concentrations, and that off-diagonal D's, \( D_{XM} \) and \( D_{MX} \) are approximately proportional to \( C_C \) and \( C_{M'} \) respectively. Accordingly, for dilute solutions the use of average on-diagonal D's will give good approximations but average off-diagonal D's may not.

The ternary Fe-M-X austenite has one interstitial component X and one substitutional component M, so one can assume that \( \bar{V}_M = \bar{V}_F \), \( \bar{V}_X = 0 \). Also due to diluteness we can approximate that \( L_{XM} = 0 \) [105], one then obtains
\[
\begin{align*}
\frac{D_{XM}}{D_{XX}} &= \frac{\partial \mu_X}{\partial X_M} = \frac{\varepsilon^M_X X_X}{1 + \varepsilon^M_X X_X} \\
\frac{D_{MX}}{D_{MM}} &= \frac{\varepsilon^M_M + L_{MX} L_{MM} X_M}{1 + \varepsilon^M_M X_M}
\end{align*}
\] (2.43a, 2.43b)

where the \( \varepsilon^j_i \) are the constant Wagner interaction parameters and the \( L_{ij} \) are the Onsager coefficients. For very dilute ternary systems, \( X_X, X_M \ll 1 \), these reduce further to

\[
\begin{align*}
\frac{D_{XM}}{D_{XX}} &= \varepsilon^M_X X_X \\
\frac{D_{MX}}{D_{MM}} &= \varepsilon^M_M X_M
\end{align*}
\] (2.44a, 2.44b)

and in this simplified case, Eqs.(2.37) remain non-linear. The fact that \( D_{XX} \gg D_{MM} \) assures that the effect of \( D_{MX} \) on the concentration profile of component M can be neglected, and the fact that \( \partial X_M / \partial x \) will be much greater than \( \partial X_X / \partial x \) reinforces this approximation. Thus the Eqs.(2.37a,b) become

\[
\begin{align*}
\frac{\partial C_X}{\partial t} &= D_{XX} \left( \frac{\partial^2 C_X}{\partial x^2} + \varepsilon^M_X X_X \frac{\partial^2 C_X}{\partial x^2} \right) \\
\frac{\partial C_M}{\partial t} &= D_{MM} \frac{\partial^2 C_M}{\partial x^2}
\end{align*}
\] (2.45a, 2.45b)

and the fluxes of the components are
\[ J_x = - D_{xx} \frac{\partial C}{\partial x} + D_x X \frac{\partial C}{\partial x} \]  \hspace{1cm} (2.46a)

and

\[ J_M = - D_{MM} \frac{\partial C}{\partial x} \]  \hspace{1cm} (2.46b)

### 2.3.4 Diffusion in Spherical Coordinates

The diffusion equation for a binary system in terms of spherical coordinates \( r, \theta \) and \( \phi \) is obtained by writing

\[ x = r \sin\theta \cos\phi \]  \hspace{1cm} (2.47a)
\[ y = r \sin\theta \sin\phi \]  \hspace{1cm} (2.47b)
\[ z = r \cos\theta \]  \hspace{1cm} (2.47c)

Thus

\[ \frac{\partial C}{\partial t} = \frac{1}{r^2} \left\{ \frac{\partial}{\partial r} \left[ r^2 \frac{\partial C}{\partial r} \right] + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left[ \sin\theta \frac{\partial C}{\partial \theta} \right] \frac{D}{\sin^2\theta} \frac{\partial^2 C}{\partial \phi^2} \right\} \]  \hspace{1cm} (2.48)

If it is restricted to the case in which the diffusion is radial, the diffusion equation for a constant diffusion coefficient takes the form

\[ \frac{\partial C}{\partial t} = D \left\{ \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right\} \]  \hspace{1cm} (2.49)

On substituting

\[ u = C r \]  \hspace{1cm} (2.50)

Eq.(2.49) becomes
\[
\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial r^2} 
\]  
(2.51)

Since this is the equation for linear flow in one dimension, the solutions of many problems in spherical radial flow can be deduced immediately from those of the corresponding linear problem.

For the quasi steady state, Eq.(2.49) takes the form of

\[
\nabla^2 C = 0 
\]  
(2.52a)

i.e.

\[
\left\{ \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right\} = 0 
\]  
(2.52b)

The radial solution is

\[
C = A + \frac{B}{r} 
\]  
(2.53)

where \(A\) and \(B\) are constants determined by initial and boundary conditions. This Laplacian solution will prove to be valid at low supersaturations.

For a fixed spherical boundary with radius of \(\phi\) in an infinite medium and the following initial and boundary conditions,

\[
C(r, t) = C_0, \quad r \to \infty, \text{ or } r > \phi, \quad t = 0 
\]  
(2.54a)

\[
C(r, t) = C_s, \quad r = \phi, \quad t > 0 
\]  
(2.54b)

where \(C_0\) is the composition at infinity and \(C_s\) at the particle/matrix interface, the radial solution [106] is expressed as

\[
\frac{C_0 - C}{C_0 - C_s} = \frac{\varphi}{r} \text{erf}\left[ \frac{r - \varphi}{2[Dt]^{1/2}} \right] 
\]  
(2.55)
CHAPTER III

EXPERIMENTAL PROCEDURES AND TECHNIQUES

3.1 INTRODUCTION

The present experimental investigation of carbonitride precipitation processes in austenite was carried out using four niobium or niobium and titanium bearing microalloyed steels which were prepared in the laboratory. A variety of experimental techniques was employed for preparation, treatment and analysis of specimens and characterization of carbonitride precipitates. These techniques include electric arc melting, annealing and homogenization, chemical analysis, optical microscopy, X-ray diffraction and analytical electron microscopy.

3.2 PROCESSING OF SAMPLES

3.2.1 Fabrication of Alloys

The high purity electrolytic iron lump (99.98%), niobium wire (99.5%), titanium wire (99.96%) of about 0.25 mm in diameter and graphite rod (99.99%) used in this study were supplied by Alfa Products, Danvers, Mass., USA. Before melting, the iron lump was cleaned in dilute hydrochloric acid to remove any trace of surface oxides and then rinsed in acetone and methanol to remove other possible
contaminants. The alloy without nitrogen was prepared by melting mixtures of iron, niobium, titanium and graphite in an electric arc furnace with a non-consumable tungsten electrode in an ultrapure argon atmosphere. They were cast into a horizontal mold machined in the water-cooled copper hearth. They were remelted at least four times and inverted during each melting to promote homogeneity of the components. The total weight of each batch was approximately 50 g. For preparation of the alloys with high nitrogen content, the furnace bell was first evacuated and backfilled with ultrapure nitrogen, and re-evacuated down to roughly 200 to 1000 millitorr, depending upon the desired nitrogen levels, and then refilled with argon. Nitrogen was dissolved into the liquid iron from the gas mixture.

The internal stresses which have been introduced during the casting can lead to the fracture of the ingot during rolling. In order to relieve such stresses, the circular ingot in cross section of ~35 mm diameter and ~8 mm thick was annealed at 1000°C for two hours in evacuated and sealed quartz capsules with a one fourth atmosphere of argon and then cold rolled to 4.5 mm thick slabs which were ready for chemical analysis using emission spectroscopic techniques.

### 3.2.2 Chemical Analysis

Accurate chemical analysis of the alloy is essential to obtain the necessary thermodynamic and kinetic quantities for prediction of the precipitation processes. The chemical analyses were performed on the rolled base ingot on at least three spots on both sides using inductive coupled argon plasma (ICAP) emission spectroscopy. No significant differences of compositions between all spots were observed for any element. Separate nitrogen and oxygen analysis were carried out by combustion method using a LECO simultaneous oxygen/nitrogen analyzer with a
dedicated computer. The carbon content was determined by the direct microcombustion method. Five samples, each of about one gram were employed for N and C analysis. The base chemical compositions of the alloys studied are given in Table 3.1, which are the average of five to eight measurements. The impurities present in a typical alloy are listed in Table 3.2.

3.2.3 Heat Treatment

After chemical analysis the rolled slabs were cut into 4.5 mm cubes, followed by the heat treatment illustrated in the flow chart of Fig.3.1. In order to dissolve all of the carbides particles and as much as possible of the nitrides the small cubic specimens were given a solution treatment at 1390°C for four hours for steels 1 and 2 with high Nb (and Ti) levels, and two hours for steels 3 and 4. According to the solubility product data in Table 2.3 the equilibrium solution temperatures of Nb and Ti carbides in austenite were less than 1300°C and the time for complete dissolution of carbide particles is estimated to be less than 1 minute. Consequently such a high temperature and long time adopted were sufficient for elimination of the micro-inhomogeneities. The samples were encapsulated in quartz tubes which were back-filled with 100 mmHg of argon to prevent oxidation. At the end of homogenization treatment, the capsules were quickly taken out and smashed, and the specimens were swiftly plunged into a agitated iced brine. This rapid quenching was to ensure that the quenching product would be martensite with a high density of defects (dislocations) which serve as the main nucleation sites. They were then reencapsulated and up-quenched to the desired temperatures, and held for various times. At the end of each aging period the specimens were immediately quenched to prevent further precipitation during cooling.
For heating times of less than 10 minutes, specimens sized from 0.5 mm to 2 mm in thickness were up-quenched by suspension within a composite salt bath to reduce the heat transfer time. Temperature in the bath was monitored with a thermocouple protected in a one-end-sealed mullite tube. K-60 composite salt (rough molten temperature range 990 - 1300°C) was supplied by Park Chemicals. The metal crucible was placed in a vertical electrical furnace.

Another treatment was explored for application to the precipitation transformation. In this approach, the specimens were rapidly transferred to a furnace preheated to the aging temperature after the solution treatment. This rapid process was achieved by combining two horizontal cylindrical furnaces end to end and sliding the capsules from one hot zone to the other and holding at 1000°C for various times. These specimens always had a clean surface at the end of heat treatment. They were then ground to a depth of one mm on one side of the outer surface to eliminate the risk of contamination. The horizontal Lindberg furnace (Model 54233 with SiC heating elements) was employed in the present study. Its hot zone was over 8 cm long and the quartz capsules were 6-8 cm long. During the isothermal transformation, the furnace temperature was periodically monitored with a R-type (Pt/Pt-13% Rh) thermocouple that was placed in contact with the capsule in the tube and was controlled to within ± 5°C of the desired temperature.

3.3 PREPARATION OF SPECIMENS FOR ELECTRON MICROSCOPY

3.3.1 Preparation of Specimens for Optical Microscopy and SEM

After solution treatment the general microstructures of some quenched specimens were examined under conventional light microscopy and scanning electron
microscopy (SEM). The cubic specimens were mounted using cold setting epoxy resin and hardener. They were ground through 220, 320, 400 and 600 mesh SiC abrasive papers using water as lubricant. They were then polished on napless cloths impregnated with 6 μm, and finally 1 μm diamond paste using kerosene as the lubricant. After thoroughly washing with petroleum ether and methanol, the specimens were etched in 3 v/o nital (3 volume percentage of nitric acid - 70% HNO₃ in methanol) for 10 to 20 s and then were ready for microscopic examination.

3.3.2 Preparation of Carbon Extraction Replicas

Almost all of the delicate microscopic studies were performed using carbon extraction replicas. To be able make accurate microanalysis it is desirable that the carbonitride particles are separated from the matrix, since otherwise the Fe-peaks of the spectra would be extremely large, thereby considerably reducing accuracy of microanalysis for the other elements. The primary advantage of extraction replicas over thin foils is that the matrix around the particles is removed.

There are a number of different methods [107-109] to make carbon extraction replicas. The basic mechanism is illustrated schematically in Fig.3.2. The direct carbon extraction replicas were produced by the following process in this study. Specimens were polished by the above-mentioned metallographic polishing technique down to a quarter micron diamond paste prior to etching, followed by ultrasonic cleaning. Then the specimens were ultrasonically agitated in distilled water, washed in ethanol and dried in a stream of clean compressed air. Finally they were very lightly etched with 2 v/o nital for a few seconds. A high vacuum coating unit Micro-BA3 (Balzers) was used to evaporate a thin carbon film (20-30 nm) onto the
etched specimens. The film was scored into squares with size 2x2 mm² whilst it was still on the specimens, followed by immersion in 8 v/o nital in order to strip the replicas off. The thin replicas often curl up on a liquid surface and also break easily when being taken directly from the etching solution to distilled water. This is due to the shock of the large interfacial tension difference between the nital and water. To prevent this, they were usually straightened by transferring them to a series of solutions of the appropriate surface tension; water-methanol mixtures of 70% and 30% are the easiest and most suitable solutions. Then the floating replicas were caught on 200-mesh aluminum grids, after which they were rinsed in distilled water and dried. Fresh solutions were used at each step in the replicating process so as to prevent the possibility of cross contamination. The replicas were stored in a desiccator kept under vacuum.

In order to obtain accurate Ti:N ratios from the EDX spectra, extreme care must be taken to make the thinnest possible carbon replicas so as to minimize the effect of C on N peaks since C and N peaks in EDX are close to each other. The carbon replica is so thin that the possibility to pick up them without breaking down is less than 50%.

To minimize the potential contamination of the replica, they were treated with freon steam for about 15 minutes prior to microanalysis. This treatment was conducted as follows. The replica was put into a copper mesh basket which was hung onto the stopper of a flask with a round bottom. The flask was heated on a pad heater (Glas-col Series O mantles). By adjusting the power supply, the heating temperature is controlled to around 35°C to vaporize the freon. The vaporized freon was condensed on the replica as a cleaning agent. This procedure reduced potential contaminants so that prolonged imaging at a magnification of 10x10⁶ (~10 min) induced no visible contamination. The use of Al grids rather than Cu grids was
adopted to reduce spurious X-ray fluorescence from the grids and improve spatial resolution of X-ray microanalysis.

3.3.3 Preparation of Thin Foils

For checking the efficiency of carbon extraction replication and retention of the particle distribution, thin-foil microscopic specimens were employed based on a process [110,111] which has four distinct steps:

1. Machining.

A slice of sample approximately 0.3-0.4 mm in thickness was cut from the starting sample with cross section 4.5x12 mm$^2$ by using a low speed silicon carbide blade. At this stage the most important thing is to obtain a uniform specimen thickness.

2. Preliminary (Chemical) Thinning.

For thinning a mixture of 100 ml of hydrogen peroxide (30 to 35%), 30 ml of distilled water, and 10 ml of hydrofluoric acid (48%) was prepared and this was placed in a polyethylene beaker cooled by a circulating water bath. The specimen was gripped with a Teflon-coated tweezer, dipped in the mixture and removed at regular intervals to check the thickness with a micrometer. The final thickness after these steps should be around 50 to 75 μm.

3. Final (Electrolytic) Thinning

This stage was achieved with double-sided jet polishing equipment as shown in Fig.3.3. The electrolyte used for the final thinning comprises 500 ml of glacial
acetic acid (>99.7%) and 100 grams of sodium chromate (anhydrous). The electrolysis was performed at 17°C and 38 V (4.5 mA) until a tiny perforation in the center occurs, surrounded by a reasonably large thinned area with 50-100 nm thickness.

4. Washing.

The perforated specimens together with the holder must be rinsed twice in glacial acetic acid, then twice in methanol, followed by rinsing three more times in methanol after removing the holder. The specimen is stored briefly on filter paper and then as soon as possible put into the electron microscope so as to minimize the chance of oxidation and contamination in air.

3.3.4 Preparation of Ti-Nb Thin Foil Standard

Accurate microanalysis in the AEM using EDX spectrum is generally conducted by the use of experimentally determined sensitivity factors for the required elements. Thus in order to obtain reliable quantitative information on the Ti and Nb contents of the carbonitride precipitates a Ti and Nb alloy thin foil standard was prepared to determine the instrumental response under conditions identical to those used throughout this investigation.

The alloy of the Ti-Nb standard was made using the aforementioned arc melting technique. The composition of the standard was 46.03% Ti - 53.97% Nb in weight percentage. The comparison of total weight of the materials both before and after melting indicated that the relative compositional error for the standard is less than 0.05%. The Ti-Nb ingot was cold rolled to thin sheet with thickness of ~75 μm. Then a 3 mm-disc was punched out from the sheet. A Gatan Dimple Grinder (Model 656) was use to dig a ~40 μm deep dimple centered on the disc. Then the
perforation of the dimpled disc was achieved with a Gatan Dual Ion Mill 600 using argon ions under a gun voltage of 6 kV and gun current of 0.5 mA.

3.3.5 Preparation of Carbon Holey Replicas of a TiN Standard

Windowless EDX technique offers the simpler and faster route to semi-quantitative compositional information on a fine scale for light elements and EELS method appears to offer an excellent technique for the quantitative analysis of light elements such as C, N and O that may be present in the precipitates. For the same purpose as the Ti and Nb alloy standard, a TiN standard was applied to determine the proportionality constant of Ti to N for both EDX and EELS.

TiN* powder standard with particles ranging from ~20 to 80 nm was obtained from the National Research Institute for the Study of Metals (NRIM), Japan. A very small amount of the fine powder was put into high purity methanol in a dish. The solution was stirred by a glass rod for a couple of minutes to obtain a clear and transparent suspension. The carbon holey replica on a copper grid was then dipped into the solution for a couple of seconds, and taken out and dried on a filter paper.

3.4 ELECTRON MICROSCOPIC METHODS

One of most useful functions of electron microscopy is the identification and microanalysis of the phases in a sample. This is particularly important in the

* The fine TiN powder was collected from the exhaust fumes of arc welding of pure Ti in a N₂ arc.
case of very tiny particles such as in microalloyed steels. When a high energy electron beam strikes an electron transparent specimen in the electron microscope many signals [112], some of which are characteristic, are generated in the specimen as shown in Fig.3.4. Useful information can then be obtained by processing the different signals.

3.4.1 Scanning Electron Microscopy -- SEM

In addition to conventional optical microscopy, the SEM (Philips 515) was used to examine the microstructures of quenched specimens and produce high resolution photographs. The X-ray energy dispersive spectra were obtained using a Lithium drifted silicon detector (Kevex-ray 2002) in the SEM to ensure macrohomogeneity on both surfaces and inside the Ti-Nb alloy standard.

3.4.2 Transmission Electron Microscopy -- TEM

The conventional transmission electron microscope (Philips CM12) was used to examine the precipitate morphologies, distributions and sizes as well as to perform selected area diffraction (SAD) and convergent beam diffraction (CBD). Since the particles were usually very fine (1 to 100 nm), they were separated from the iron-rich matrix by using carbon extraction replicas. The efficiency of replication was checked by means of the thin foil technique.

3.4.3 Scanning Transmission Electron Microscopy -- STEM

The modern analytical electron microscopy (AEM) based on STEM has the
ability to generate localized, fine scale, quantitative chemical and structural information while simultaneously retaining the high resolution imaging properties. It is the only technique for the quantitative microanalysis of very fine carbonitride precipitates in microalloyed steels.

In order to identify the precipitates, microanalysis and microdiffraction were performed with a vacuum generator HB5-dedicated STEM equipped with a Tracor Northern TN 200/4000 EDS (energy dispersive spectrum) X-ray system, whose high resolution allows the quantitative microanalysis of isolated particles down to ~1.5 nm, and image resolution down to nearly 1 nm by using a high brightness field emission gun. The high vacuum conditions (routinely less than 5x10^{-9} torr) minimize contamination build-up on the analyzed region. The replica was mounted in a double tilt goniometer. The specimen holder is made of beryllium and all microscope components in the vicinity of the sample consist of low atomic number material in order to minimize instrumental effects and the continuum background. The Al grids were always presented on the exit side of the replicas and microanalysis was conducted only near the center of each grid square so as to minimize the contribution of the grid bars to the continuum radiation.

There was in general no problem of image drift on the screen except for the analysis of the smallest particles (~2 nm) where long count times were required. In this case, microdiffraction from the particle was used to "track" the smallest precipitates by minor adjustments to the probe centering knobs so as to keep a nearly constant intensity of the diffraction spots during the EDX acquisition period.

X-ray composition analysis employs a windowless solid state detector for detection of elements as light as carbon. The absolute accuracy of EDS-X-ray techniques was found by the use of thin film standards to be better than ±5%. The
minimum detectable mass in this microanalytical configuration was about $10^{-20}$ gram which corresponds to approximately 100 atoms of microalloying elements.

3.5 QUANTITATIVE MICROANALYSIS

3.5.1 Energy Dispersive X-Ray Spectrometry -- EDX

The unique capabilities of dedicated STEM microscopy allow the quantitative microanalysis of isolated particles down to $\sim$1.5 nm using a 1 nm probe size. Once the energy dispersive X-ray spectrometry has been obtained, the procedure for quantification is straightforward. The relative simplicity of the quantification process is a major advantage of X-ray microanalysis. Quantitative microanalysis can easily be performed using the Cliff-Lorimer k factor [112] which is suitable for thin foils, including extraction replicas. On the adoption of the thin film criterion, it gives

$$\frac{C_A}{C_B} = K_{AB} \frac{I_A}{I_B}$$  \hspace{1cm} (3.1)

where $C_A$ and $C_B$ are the weight percentage of element A and B in the analyzed volume, $I_A$ and $I_B$ the intensities of characteristic X-ray peaks of A and B in the analyzed volume after subtracting the background and using the same window, and $k_{AB}$ is an appropriate sensitivity factor (often termed the Cliff-Lorimer factor). This factor is independent of particle compositions and size, varying only with acceleration voltage kV. The major difficulty with this technique is that for accurate analysis the $k_{AB}$ factor must be measured experimentally using a standard having a known composition. The k factor can be calculated theoretically [113], but
this may not provide sufficient accuracy for quantification. In this work a thin foil standard of niobium and titanium alloy was employed to determine the \( k_{\text{Tinb}} \) factor and to enable a high degree of accuracy in microanalysis of precipitate compositions.

During X-ray data acquisition the counting rates vary from 500 to 1500 CFS (counts per second) with the particle size range from 1.5 nm to 10 nm, and therefore the live time of 200 s was selected for particles less than 4 nm and 100 s for particles larger than 4 nm. The entire calculation of the carbonitride compositions can be made directly from recorded spectra and be executed by a computer.

Because particles of different size show significant concentration variations in steels 3 and 4, the composition of the precipitates as a function of their sizes was determined using the EDX-microanalysis technique as described above. The analysis was usually followed by a photographic exposure and subsequent measurement of the individual particles sizes on the STEM micrographs. For long aging specimens some large long carbonitride particles showed internal concentration variations. The profiles of these variations were computed in the form of \( C_{\text{Ti}}/(C_{\text{Ti}} + C_{\text{Nb}}) \).

### 3.5.2 Electron Energy Loss Spectrum -- EELS

The analysis of the energy distribution of electrons which have interacted with a target is referred to as electron energy loss spectroscopy (EELS). When passing through the extremely thin specimen, the electrons interact inelastically with the atoms of the specimen. Ionization of inner shells give rise to discontinuities in the EELS and these are characteristic of the element. The most
common EELS technique is the detection of electrons that have lost energy by ionization of individual atoms in the specimen. As shown in Fig.3.5, pertaining to the principal layout of a typical magnetic spectrometer, the spectrometry is performed by a magnetic prism spectrometer positioned beneath the final viewing screen of the AEM which deflects the electrons entering it according to their energy and sequentially displays the spectrum over the slit and photon multiplier. It is able to detect a relatively wide range of energy losses (~0-2keV) to reasonable resolutions ≤5eV at incident voltages of ~ 100 kV with collection angles from ~1 mrad to larger than 20 mrad.

EELS technique can quantitatively determine the concentration of light elements (specifically N, O and C). It is not plagued by some of the difficulties associated with EDX; for example beam broadening, fluorescence and peak overlapping. The limitations of this technique are that the particles for analysis cannot exceed 100 nm in thickness and that the ideal particle morphology is a thin plate. In combination with the windowless EDX discussed above, it provides a means of direct detection of all elements except H, with good spatial resolution and accuracy.

The light element quantification process from energy loss spectra can be done by exact analogy with the EDX microanalysis, i.e., the ratio method as following

\[
\frac{C_A}{C_B} = K_{AB} \frac{I_A}{I_B}
\]

(3.2)

but here \(C_A\) and \(C_B\) are the atomic fraction of element A and B, \(I_A\) and \(I_B\) the integral of the characteristic peaks and \(k_{AB}\) is the proportionality constant (EELS k factor). This factor \(k_{TIN}\) relating relative intensity to concentration was
determined using a TiN standard.

The atomic ratios of titanium to nitrogen were determined from EELS spectra obtained from precipitates suitable to EEL analysis, 20 - 50 nm in this study. The procedure was carried out at 120 kV in the TEM mode using a Phillips EM400T TEM/STEM equipped with a Gatan 607 electron energy loss spectrometer. The selected particles were chosen by working in the image (M) mode, using the shadow image at a focused probe size of ~30 nm; then, by switching to the diffraction mode, the energy loss spectra were acquired with a focused beam diffraction pattern on the screen. For all the measurements the incidence angles and collection angle of 2 and 5.9 mrad, respectively, were adopted. The data were analyzed using an energy integration window of 40 eV to avoid the N-K/Ti-L edge overlap. Rather than using the usual procedure of working with partial cross-sections to obtain the ratios of the elements, we obtained the EELS $k_{\text{TiN}}$ factor for Ti-L and N-K edges from the TiN standard for the experimental conditions described. The Ti to N ratios can be obtained by the k-factor proportionality method.

As carbon replicas were used to extract Ti-Nb carbonitrides in microalloyed steels, only N (and O) could be reliably detected.

### 3.5.3 Electron Diffraction

#### A Microdiffraction

The concept of microdiffraction can be broadly defined as the acquisition of electron diffraction information from regions $< \sim 0.5 \ \mu \text{m}$ in diameter, which is the spatial limit of selected area diffraction (SAD) patterns.

Diffraction has a dual purpose: to identify and characterize all Ti, Nb, C
and N bearing particles with the NaCl structure and to determine an accurate lattice parameter of niobium carbide particles. A microdiffraction technique was necessarily adopted to track extremely small particles (nearly 2 nm) during X-ray data acquisition since combined thermal and electronic drift cannot be completely compensated at ultra-high magnifications of $10^6$.

For the determination of precise NbC$_y$ lattice parameters an internal calibration standard of evaporated gold was used, the gold was evaporated as islands onto selected extraction replicas. Particles adjacent to the gold islands were chosen for microdiffraction. The diffraction patterns were indexed by comparing angles and length ratios with the standard patterns for the f.c.c. crystal structure. In principle the lattice parameter could be determined using the following relation

$$R_{xd} = \lambda x L$$

(3.3)

where $R$ is the distance between the central spot and diffraction spot, $\lambda$ is the electron wave length, $L$ is the camera constant and $d$ is the interplanar spacing. However, the diffraction patterns were compared with the standard gold diffraction pattern obtained so as to eliminate the $\lambda$ and $L$. Without the requirement of absolute calibration of the microscope the parameters were then directly calculated using the following expression

$$R_{gold} \times d_{gold} = R \times d_p$$

(3.4)

where the subscript $p$ stands for precipitates. Once the lattice parameter of interstitial phase NbC$_y$ is obtained, the nonstoichiometry coefficient, $y$, of NbC$_y$ can be deduced from the experimentally determined lattice parameter vs. $y$ diagram. In practice the method is limited by the precision with which $a_{NbC_y}$ can be measured.
by electron microdiffraction. An absolute accuracy of better than ±0.5% was possible using this technique.

B Convergent Beam Diffraction

Convergent beam diffraction (CBD) technique can be applied to make quick and routine identification of phases without elaborate analysis or calculation. Once appropriate standards have been established, the convergent beam patterns can be readily recognized to give immediate identification of the phase under observation. It differs from the other methods in that the specimen is illuminated with a convergent beam of electrons instead of a parallel beam. The unavoidable limitation of the technique is that the use of fine detail in CBD patterns for phase identification relies essentially upon the existence of perfect regions larger than the probe diameter in use (usually >50 nm).

3.6 X-RAY DIFFRACTION -- XRD METHOD

The X-ray diffraction method was used to obtain an accurate lattice parameter for the TiN standard. The diffraction angle is given by the Bragg law

$$2d_{hkl} \sin \theta = \lambda$$  \hspace{1cm} (4.5)

where $d_{hkl}$ is the interplanar spacing of \{(hkl)\} plane family, $\theta$ is the Bragg diffraction angle and $\lambda$ is the X-ray wavelength.

X-ray diffraction was performed using a Nicolet X-ray powder diffractometer. Only Cu-K$_{\alpha}$ radiation with a wavelength of 1.5405 Å was involved in the diffraction. The sample was run at 50 kV and 20 mA with a scanning speed of
~2°/min. The calculation of the lattice parameter was made directly from a recorded spectrum and executed by a computer. The accuracy of this measurement was expected to be about 0.0001 Å, this being adequate for identification of the nonstoichiometry of TiN compound.

3.7 PARTICLE SIZE ANALYSIS

Precipitate sizes were measured from high resolution TEM bright field images for long time aged specimens and from STEM dark field images for short aging times. However, the recording of particle sizes for the 1 s and 2.5 s aging samples was carried out directly on the STEM dark field screen thus avoiding micrography which is subject to vibration, drift and sometimes contamination at the highest magnification of 10x10⁶. Even so there exists a large residual error in this measurement due to the limitations of equipment and our inability to detect nuclei with sizes less than 1 nm.

The average of maximum and minimum observed linear dimensions of each particle was taken as the measure of its size. The particle size distributions, arithmetic means, standard deviations have been deduced for a given aging time from size measurements on typically 200-250 (about 100 particles for 1 s and 2.5 s aging) particles. Meanwhile these particles were classified and used for constructing histograms of different class-width.
CHAPTER IV

EXPERIMENTAL RESULTS

Within the objectives of the investigation, the experimental results to be presented in this chapter all deal with the various aspects of carbonitride precipitates in the microalloyed steels.

4.1 OPTICAL MICROSCOPY AND SEM

In examining the experimental results, it is useful to consider first the quenched structures observed under the optical microscope and SEM. This is necessary to verify the formation of nearly 100% lath martensite and to trace possible very coarse carbonitride particles that may be not picked up by the carbon replicas.

Optical metallography was used to reveal the general features of the microstructure. SEM was also applied as a supplementary means to reveal more detail. Both the optical microscope and SEM show no signs of any large carbonitride precipitates (> 1 μm). Fig.4.1 shows the perfect lath martensite microstructures of alloys quenched after solution treatment. This structure has a relatively uniform very high density of dislocations which serves to provide nucleation sites for precipitates.

For the alternative treatment wherein the samples were transferred from a
solution treatment directly to the aging temperature (1000°C) and held from 5 minutes to 15 minutes in a two zone furnace, high magnification electron microscopic study shows no newly formed particles in austenite in accord with expectations. This is reasonable since after the high temperature homogenization the microstructure and compositions of alloy become much more uniform and the defects (especially dislocations) which are the favored nucleation sites become depleted and nucleation inhibition is encountered. Accordingly, the rest of our work is focused on the alloys that were homogenized, quenched and aged, further justification for this choice lying in the fact that high defect (mainly dislocation) densities are characteristic of steels during thermomechanical processing.

4.2 ELECTRON MICROSCOPES -- TEM AND STEM

In order to investigate the details of the microstructural observations, a combination of bright field and dark field micrographs from TEM and STEM (for short time heating specimens) was utilized for high resolution mapping of precipitates, particle distributions, their location and their morphologies.

4.2.1 Undissolved Particles

After the 1390°C solution treatment some of the quenched specimens were checked for undissolved particles. High magnification electron microscopic images showed no undissolved NbC particles in steel 1 as well as no evidence of newly formed precipitate during quenching for all of the steels. However, quite a few
remaining cubic particles were found in steels 3 and 4 as shown in Fig.4.2.a. These cuboids are spaced far apart and randomly distributed. On the other hand no undissolved particles were found in steel 2, which was the much more dilute in N, although a very small amount was thermodynamically expected (see §5.4.2.2). This discrepancy can be understood within the uncertainty of the solubility data, and the possible insufficiency of area examined. Fig.4.2.b shows the EDX spectrum from the undissolved particles, and the sharp nitrogen peak can be seen clearly together with a very large Ti peak and a very small Nb peak. Therefore the undissolved cuboids are close to the composition TiN.

4.2.2 NbC Precipitate Morphologies

Figs.4.3 to 4.4 show the typically fine dispersion of precipitates resulting from the shortly aged Fe-Nb-C alloy (steel 1) at 1000°C and 1100°C, respectively, for various times. The fine dispersion of niobium carbide precipitates nucleates and grows in the surrounding austenite matrix during aging. Fig.4.5 demonstrates the course of coarsening of NbC particles in steel 1. Concerning the morphologies of newly formed precipitates visible in replicas, only two typical shapes were found: spherical and polyhedral (mostly hexagonal and cuboidal). Almost all of the carbides have a spherical shape typical of those observed in specimens aged less than one minute as shown in Figs.4.3.a-b and Figs.4.4.a-b, while the shapes of some particles begin to change to polyhedral for longer heating times.

Although no detailed assessment of the relationship between size and morphology of precipitates was undertaken in this study, the results do indicate that the morphology is roughly related to particle size. Small carbide nuclei,
diameter < 7 nm, when visible, look fairly spherical suggesting that nuclei are incoherent with the matrix and therewith the growth is mainly diffusion controlled. Large size particles appear as polyhedral or cuboidal shapes (Figs.4.3.d-f, Figs.4.4.c-d and Figs.4.5.a-b). This change of morphology may result from interface instability [114] featured by the formation of polyhedral facets on spherical nuclei when the particle diameter exceeds a critical value (roughly 7 nm). In this stage the very slow growth rate could be associated with the sluggish interface reaction as a consequence of epitaxy. It was very interesting to find that after the NbC particle size increases beyond about 40 nm at 1100°C the shape of particles changed back to spherical. This begins to happen after aging for about 5 to 10 hr at 1100°C. Fig.4.4.e (10 hr at 1100°C) shows some particles already reverted into spheres and others being smoothed at the edges of the polyhedrons. In Fig.4.4.f and 4.5.c (100 and 200 hr at 1100°C) only spherical particles are left. In contrast, Figs.4.5.a and b (100 and 200 hr at 1000°C) illustrate unchanged polyhedral shapes with clear and sharp edges.

4.2.3 (TiNb)(CN) Precipitate Morphologies

The TEM and STEM micrographs are presented in Figs.4.6 to 4.15 to illustrate the growth and coarsening of the (TiNb)(CN) particles in steels 2 to 4. Figs.4.6-7, 4.10-11 and 4.13-14 show the course of development of the typically very fine dispersion of carbonitride precipitates appearing in the aged Fe-Ti-Nb-C-N alloys (steels 2 to 4) at 1000°C and 1100°C, respectively, for short holding times (≤ 60 s). During this period of time, the complex carbonitrides grow at the expense of matrix solutes. Figs.4.8-9, 4.12 and 4.15 show the gradual coarsening of carbonitride precipitates in steels 2 to 4 at 1000°C and 1100°C,
respectively, for the longer heating times (60 s to 100 hr). It can be seen from Fig.4.6 to 4.15 that very fine particles are visible in each steel almost immediately after up-quenching. The minimum distinguishable diameter of particles was nearly 1 nm as shown in Fig.4.13.a (on the STEM screen the spherical particles were clearer and more perfect). It is difficult to obtain satisfactory photos at these high magnification levels \( (10\times10^6) \) due to the narrow range of adjustable camera parameters. Moreover drifting and vibration effects become severe at these high magnification levels.

The precipitates visible in the replicas reveal three shapes: spherical, polyhedral (mostly hexagonal) and cuboidal. Insofar as could be ascertained, nearly all of the newly formed particles for short aging times \( (< 60 \text{ s}) \) approach sphericity, while some particles begin to change to polyhedrons for longer holding times. The sphericity for younger particles suggests that the growth of carbonitrides at the expense of matrix solutes is mainly diffusion controlled and this statement is the basis for the kinetic modelling of particle growth developed in a later chapter.

Figs.4.6 to 4.15 also indicate that newly formed precipitate nuclei have appeared at 1 s for 1100°C and this aging time is extended to 2.5 s for 1000°C in steel 4. These are evidently upper limits on the incubation times. Such short incubation times (compared with other treatments and predictions [115,116]) is presumably a consequence of the very high supersaturation which results in a very large driving force for the nucleation of precipitates. Besides, high dislocation densities can accelerate nucleation by short circuit solute diffusion. A high density of quenched-in vacancies can also assist nucleation by increasing diffusion rates, and by relieving misfit energies.

During long holding times for steels 2 and 3 at 1100°C, almost all of
particles have ripened to a perfectly spherical shape as shown in Fig.4.9.d and 4.12.e. On the other hand, for prolonged aging of steel 4 the early formed spherical and polyhedral particles were slowly converted to the faceted cuboidal morphology as shown in Fig.4.15. At 1100°C for 10 hr about half of (TiNb)(CN) particles has transformed to cuboids with smooth edges (Fig.4.15.e) and for 100 hr most of particles are cuboids, with few remaining spherical and polyhedral particles (Fig.4.15.f). The number of these cuboids is much greater than the undissolved cuboids. However, at 1000°C for 100 hr, only about half of particles are cuboids (Fig.4.15.c) whose number is also much greater than the undissolved cuboids and the rest of them are spheroids or polyhedrons.

These observations in steel 4 suggest that diffusion of Ti and Nb in the particles and matrix occurred. This transformation may be accomplished by dissolution and reprecipitation or an in-situ diffusional exchange within the particles. The diffusion coefficients of Ti and Nb in carbides are collected in Table 4.1. There is no diffusion data for carbides at temperatures below 1450°C, but if the high temperature data for NbC, TiC and (TiNb)C in the literature are extrapolated to the experimental temperature range 1000-1400°C, calculation shows that the rates of diffusion of Ti and Nb are extremely slow. On the other hand the C and N diffusion is several orders of magnitude faster, so that these elements should readily attain uniform activities throughout the particles and matrix.

4.2.4 Precipitate Distributions

In order to investigate large areas relatively low magnification micrographs were produced as in Fig.4.16 so as to illustrate the distributions of newly formed fine particles. In most cases the distribution of particles is nearly
random, which can be attributed to the relatively uniform high density of dislocations in the quenched specimens.

However, there are a few regions which have a low density of precipitates, and some areas are almost completely free of precipitates, possibly due to retained austenite or to the areas between the martensite laths which have a much lower dislocation density. Some of the precipitates appear to form linear arrays (e.g. Fig.4.16.a) and some are situated in clusters, likely resulting from overetching and settling (e.g. Fig.4.10.e and Fig.4.16.b). It is interesting that some particles in steel 4 at 940°C are distributed in the form of bands as shown in Fig.4.16.c which probably reveals the directions (or the domains) of martensite laths, and this is not common at higher holding temperatures. There seems to be no preferential presence of the fine precipitates on primary grain boundaries. Quite a few flat precipitates were found for long aging times (in Fig.4.4.d) which might have been formed at primary austenite grain boundaries which serve as fast paths for solutes during coarsening. A few abnormally large particles (in Fig.4.4.e) appeared and these were excluded from the estimation of average particle size due to their small number and obvious deviation from the normal case. It is worth mentioning that the extracted particles have tended in a few cases to agglomerate (see Fig.4.3.b), so that the micrographs may not be truly representative of the particle dispersions in some cases.

Comparison of Fig.4.3.d (from a replica) with Fig.4.3.e (from a thin foil) shows that extraction by carbon replica is usually effective so an accurate size distribution can be obtained. It seems that the particle density and distribution are only weakly affected by the etching technique. The main disadvantage of the replica technique lies in the difficulty of obtaining crystallographic information relating the matrix and particles. On the other hand, the thin foil specimens
produce low contrast and reduce the resolution due to strain fields around precipitates. This is illustrated by the fact that in Fig.4.3.d all the particles have less angular edges than those in Fig.4.3.e.

4.3 IDENTIFICATION OF PRECIPITATES

Small NbC and (TiNb)(CN) particles (usually less than 10 nm) are common constituents of microalloyed steels. However, they are difficult to be conclusively identified by STEM microanalysis and are impossible to be quantitatively analyzed when embedded in a conventional thin foil suitable for TEM due to the strong contribution from the surrounding matrix to the emitted X-ray spectrum. When extracted on a carbon replica, the total mass of microalloying element in a single particle is extremely low (about $10^{-19}$ gram). As a result, the x-ray count rate from a focused electron beam is often too low for microanalysis using a conventional W filament or LaB$_6$ sources in the TEM. However, microanalysis can be performed with the high brightness field emission gun in STEM. Identification of carbides and complex carbonitrides was made by STEM-EDX microanalysis of the particles and by electron diffraction.

4.3.1 Energy Dispersive X-Ray Spectrometry -- EDX

Figs.4.17 to 19 show the Energy Dispersive X-Ray spectra (EDX) from various precipitates in four steels. The EDX spectrum from steel 1 (Fig.4.17.a) is taken close to the Al bar of the grid; the first peak is the C peak contributed from the thick carbon replica and the C in a large NbC particle. The following two peaks (O and Al) come from the Al bar of the grid. The 4th peak is Nb L$_{\alpha}$ from the NbC
particle. For steels 2 to 4 (Figs. 4.17.b and 4.18), Ti-K$_{\alpha}$ and Ti-K$_{\beta}$ peaks appeared. It can be seen from these EDX spectra that the intensity ratios of Ti and Nb peaks (reflected by the high ratios) are directly correlated to the ratios of Ti and Nb compositions in the steels; that is an increase of Ti/Nb ratios in particles with increasing Ti/Nb ratios in the steels 2 to 4. Normally no Fe or other residual elements were detected inside the precipitates analyzed. However, in a few cases for very fine particles (~ 3 nm) in shortly aged samples the appearance of weak Fe peaks was encountered. The parts of the replica where this was an evident problem were not used in the microanalysis to avoid possible contamination of replicas.

A simple method was employed to distinguish the newly formed carbonitrides from the undissolved particles in steels 3 and 4. It is based on the observation that the undissolved TiN particles existing in austenite have a typically more angular and well defined cubic shape, as shown in Figs. 4.2.a and 4.19.a and also these particles are much larger than those precipitated during the aging. An example is given in Fig. 4.19.a, showing the morphology and size differences between the two kinds of particles. It can be seen that the central large undissolved cubic particle is surrounded by the newly formed very fine particles. The corresponding X-ray spectrum from the cuboid is shown Fig. 4.19.b, revealing the presence of very strong Ti peaks for cubic particles as well as N. On the other hand the EDX spectrum from a surrounding newly formed fine particle shows that the Nb peak is almost as high as the Ti peak in Fig. 4.19.c. The EDX analysis procedure was also tried on larger spherical particles (~ 20 nm) for the shortly aged specimens. In a few cases N was detected in particles having this morphology; however for aging to 100 h, clear and sharp N peaks appeared in all EDX spectra from both spherical and cubic particles in steel 4.

The undissolved cubic particles were identified as (Ti$_{0.91}$Nb$_{0.09}$)(C$_{0.1}$N$_{0.9}$)
in steel 3 and as \((\text{Ti}_{0.95}\text{Nb}_{0.05})\text{(C}_{0.05}\text{N}_{0.95})\). The later reported theoretically predicted equilibrium compositions for carbonitride precipitates at the solution temperature 1390°C are \((\text{Ti}_{0.90}\text{Nb}_{0.10})\text{(C}_{0.07}\text{N}_{0.93})\) in steel 3 and \((\text{Ti}_{0.97}\text{Nb}_{0.03})\text{(C}_{0.02}\text{N}_{0.98})\) in steel 4, which shows very good agreement with the measured values.

4.3.2 Electron Diffraction

STEM microdiffraction was applied to determine the NbC lattice parameters. The focused electron beam with a size of 1 nm was directed to individual extracted particles. The STEM microdiffraction patterns from the extracted NbC particles and the gold standard are shown in Fig.4.20. In Fig.4.20.a the weak micro-diffraction spots generated from the middle particle in Fig.4.4.a are immersed in the amorphous carbon ring. The lattice parameter of NbC_y determined from the best patterns obtained (in Fig.4.20.c) with reference to the gold pattern (in Fig.4.20.b) is 4.46 ± 0.02 Å, which corresponds approximately to the C/Nb atomic ratio 0.85 (Fig.2.3) which is very similar to that reported in previous studies [54,122,123].

Combining with the conventional selected area diffraction (SAD) method, the convergent beam diffraction (CBD) technique has been applied to make fast and routine identifications of large particles. The diffraction patterns from the given particle can be fitted to the fcc crystal structure of MX after comparison with standards [124]. The SAD and the CBD patterns from TiN and (TiNb5)(CN) in steel 3 are shown in Fig.4.21. The CBD pattern in Fig.4.21.c has a [112] axis. We obtained no acceptable CBD patterns with detailed line features in the zero-order disc so as to enable the determination of more accurate lattice parameters. This was due to smallness of the particles and their spherical shape.
4.4 PRECIPITATE SIZE ANALYSIS

4.4.1 NbC Precipitates

The carbides increase their size monotonously with time; the micrographs (Figs.4.3 to 4.5) indicate that niobium carbides grow quite rapidly to a size of about 7 nm within the first few minutes. The further growth (coarsening) is extremely slow (at 1100°C, within 5 hr) which evidently results from a sluggish interfacial reaction. This is to be associated with the change of precipitate shape from spherical to polyhedral. Also, as expected, the growth rate is faster at 1100°C than at 1000°C. More importantly, the particles coarsened very significantly at 1100°C after aging over 10 hr whereas at 1000°C little coarsening occurred in times up to 200 hr. The average particle size has reached ~290 nm at 1100°C for 200 hr but the average value is only ~16.4 nm at 1000°C for the same holding time. We would like to emphasize that fast ripening of NbC particles at 1100°C is also associated with the spherical shape and the sluggish growth at 1000°C with the polyhedral shape. The growth characteristics of NbC particles formed during aging in steel 1 is summarized in Tables 4.2 and 4.3.

One of the objectives of the present work has been to obtain statistics on particle size dispersions for various aging times, and several examples of these measurements are to be presented in this section. The data from this analysis is very useful in determining the potential retardation of grain growth and recrystallization during controlled rolling.

Particle size histograms and the cumulative size distributions were obtained for various aging times (in Figs.4.22 and 4.23). Unfortunately, data were insufficient to determine particle size distributions for aging over 10 hr at
1100°C. The form of the particle size distributions (normalized) at 1000°C is essentially independent of time, in agreement with the original Lifshitz-Wagner theory [125,126]. However the 'cut-off' particle size is approximately 2.3 times the mean size, larger than that predicted for interface reaction controlled coarsening, being 2 times the mean particle size [126]. At the shorter aging times the deviation from the theoretically predicted size distribution is small, but increases with aging time.

It should be noted that the size distributions, as well as the mean values and standard errors of the distributions shown in later figures, are based on measurements made on replicas. Such surface magnitudes can be converted to the desired volume quantities by the following equations given by Ashby and Ebeling [127]

\[ \overline{d}_v = \frac{\overline{d}}{1+(S \cdot D_s / \overline{d}_s)^2} \]  

(4.1) and

\[ S.D.(v) = \frac{S \cdot D_s}{1+(S \cdot D_s / \overline{d}_s)^2} \]  

(4.2)

where the subscripts s and v refer to the surface and volume, respectively, and \( \overline{d} \) and S.D. refer to the mean particle diameter and standard deviation. The values of the surface and volume mean particle sizes for each distribution measurement expressed in Figs.4.22 and 4.23 are also listed in Tables 4.2 and 4.3.

4.4.2 (TiNb)(CN) Precipitates

Fig.4.24 shows the particle size distributions for various short aging times at 1000°C and 1100°C in steel 4. The particle size trends as a function of
aging time indicate that the distribution shifts to the right very rapidly (within 10 s) and then changes very slowly as it widens. The carbonitrides apparently increase their average sizes in a monotone way with aging time, growing quite rapidly to an average size of about 5 nm within 30 s with further growth (coarsening) being slow. The similar trends (but faster growth rates) have been observed in steels 2 and 3 for short aging times.

For long aging times, the coarsening of particles occurred. There is insufficient data collected to give particle size distributions for long aging times due to the dramatic decrease of particle numbers per photo (containing only about 5 large particles). This point is made to emphasize some of the difficulties that are encountered in obtaining statistically significant data from long aged samples. The behaviour of carbonitride particle ripening in steels 2 and 3 are quite similar as can be seen in Figs.4.8-9 and 4.12. Because of the spherical shape the particle coarsening rate in steels 2 and 3 is greater than in steel 1 at 1000°C. Indeed for up to 100 hr (24 hr for steel 3) at 1000°C, the size increase is very significant, approaching an average value of ~27 nm. The growth is much more pronounced at 1100°C than at 1000°C, but much less than in steel 1 at this temperature. The particle sizes reached an average of ~180 nm in steel 2 and 100 nm in steel 3 at 1100°C. This fast coarsening is also associated with a perfect spherical shape as observed with NbC in steel 1 (Figs.4.5 and 4.12).

The coarsening behaviour of carbonitride particles in steel 4 is substantially different from those in the first three steels. It is unexpectedly found that the sizes of (TiNb)(CN) particles in steel 4 at 1000°C and 1100°C is not very much different for long aging times as indicated in Fig.4.15.c and f. In spite of the semi-cubic shape the average particle size (~30 nm) in steel 4 at 1000°C for 100 hr is larger than in steels 1 to 3. On the other hand, the growth rate of
carbonitride particles at 1100°C is extremely sluggish as compared with steels 1 to 3. The particle size reached an average ~ 35 nm up to 100 hr aging. It should be emphasized that such slow growth is associated with the cubic shape which results in a very sluggish interfacial reaction.

4.5 QUANTITATIVE MICROANALYSIS OF COMPLEX CARBONITRIDES

4.5.1 Determination of the K Factor of EDX

The method of the quantification of X-ray data was detailed in §3.5.1 (i.e. the proportionality method, $C_{Ti}/C_{Nb} = k_{TiNb} I_{Ti}/I_{Nb}$). In this work thin foil standards of niobium and titanium alloy were employed to determine the k factor and to enable a high degree of accuracy in microanalysis of precipitate compositions. The determined k factors for Ti-Nb and Ti-N are summarized in Table 4.4. The relative intensities of the Ti-K$_{\alpha}$ and Nb-L$_{\alpha}$ peaks were used after background subtraction to find the Ti:Nb ratios. The average value of $k_{TiNb}$ for Ti-K$_{\alpha}$ and Nb-L$_{\alpha}$ was determined to be 0.56 ± 0.025 and this compares favorably with both the theoretical value of 0.58 [128] and the value of 0.53 ± 0.03 determined experimentally by previous workers on the McMaster STEM [129]. The value (0.53) was obtained using a multilayered film of Ti and Nb, in which a Ti layer was first evaporated on to an amorphous carbon substrate and then a Nb layer was sputtered on top of the Ti. When the error in the experimental value of $k_{TiNb}$ is considered, the accuracy of energy dispersive X-ray spectrometry (EDX) technique for the Ti:Nb ratio in a single particle can be better than 5%.

In the present experimental conditions the effects of absorption can be neglected. This conclusion is supported by a simple calculation [128] showing that
the thin film approximation is likely to break down at a thickness larger than \( \sim 134 \) nm, compared to less than 100 nm for a thickness of the measured area in a Ti-Nb thin film. EDX analysis from SEM, TEM and STEM shows that the Ti-Nb alloy has an uniform composition at both the micro scale and macro scale.

4.5.2 Determination of the K Factor of EELS

The quantification of EELS data was also performed using the k proportionality factor, that is, \( C_\text{Ti}/C_N = k_{\text{TiN}} I_\text{Ti}/I_N \). In this study a TiN powder standard was used to determine the k factor and to enable a high degree of accuracy in microanalysis of Ti:N ratios.

Fig.4.25.a shows a TEM micrograph of the TiN standard particles on the C-holey replica. In order to avoid the effect of carbon replica only the particles lying over the hole were used for the EELS and EDX analysis. The X-ray diffraction method was used to obtain an accurate lattice parameter for the TiN powder standard which was in turn adopted to determinate the k factors of both EELS and EDX. Fig.4.25.b shows the X-ray diffraction spectrum from the TiN powder. The computer analysis of the spectra gave the average value of 4.4202 Å from five runs as the lattice parameter of the TiN standard. Therefore, the standard has the form of TiN\(_{0.98}\) (see Fig.2.4).

The average value of \( k_{\text{TiN}} \) for EDX from the Ti-K\(_\alpha\) and the N peaks was determined to be 0.123 \( \pm \) 0.017. No comparison value has been found in the literature. The average value of \( k_{\text{TiN}} \) for EELS from Ti-L and N-K peaks was determined to be 0.286 \( \pm \) 0.026 and this compares favorably with the value of 0.295 determined experimentally by previous workers on the CANMET TEM [130]. When the error in the experimental value of \( k_{\text{TiN}} \) is considered, the relative accuracy of
energy dispersive X-ray spectrometry (EDX) technique for the Ti:N ratio in a single particle can be about 14%, and the accuracy of the electron energy loss spectrometry method (EELS) is about 10%.

Fig. 4.26 illustrates the typical EEL and EDX spectra obtained from the TiN standard particles and carbonitride particles in steel 4; all the particles analyzed contained both N and Ti, and no Nb was visible. There is no C peaks in the EEL spectra from the TiN standard particles (Fig. 4.26.a), but the C peaks appeared in the EEL spectra from the precipitates (Fig. 4.26.d) because of the use of carbon replicas.

4.5.3 Compositions of the Complex Carbonitride Particles

A microanalysis for Ti, Nb and N was performed for various samples and precipitate morphologies. In the previous section it has been shown that the newly formed precipitates in steel 1 are pure NbC, and the particles of the other three steels are essentially of the quaternary composition \((\text{Ti}_x\text{Nb}_{1-x})_1\text{N}_{1-y}\)\). These particles were sufficiently thin that the Cliff-Lorimer k factor approach can be used directly to quantify their composition. The k factors were determined in this study for this kind of microalloyed steels. Particle compositions were measured using the EDX and EELS microanalysis and plotted as a function of particle size in steels 2 to 4 at different aging temperatures. Not every aged specimen was studied by EDX, but sufficient data were obtained to establish clear trends. In most treatments the precipitates are too small to carry out EELS and EDX for Ti:N ratios. Therefore, for short aging times, EDX was used to obtain only Ti:N ratios; while for longer aging times both EDX and EELS were applied to obtain Ti:N ratios. According to the definition of \(x\) and \(y\) in the \((\text{Ti}_x\text{Nb}_{1-x})_1\text{N}_{1-y}\), we have the
following:

\[ \frac{x}{(1-x)} = \frac{C_{Ti}}{C_{Nb}} \]  \hspace{1cm} (4.3a)

\[ \frac{x}{(1-y)} = \frac{C_{Ti}}{C_{N}} \]  \hspace{1cm} (4.3b)

Note that here \( C_i \) are in atomic fractions. In principle, having accurate values of \( \frac{C_{Ti}}{C_{Nb}} \) from the analysis of the EDX data and \( \frac{C_{Ti}}{C_{N}} \) from the analysis of the EELS and EDX data, the particle compositions, \( x \) and \( y \) can be determined from the above two equations.

Steel 2

Fig.4.27 shows the (TiNb)(CN) particle compositions measured in steel 2 as a function of particle size. The scatter of the compositions of individual particles with different sizes is very small. The compositions for aging 5 s seems to be slightly higher than that for 20 s at 1100°C (one is \( \sim 0.58 \) and the other is \( \sim 0.54 \)), while the compositions for 60 s and 10 hr at 1000°C are the same at around 0.62. Since steel 2 has the least N level, the precipitates is actually close to the composition (TiNb)C. Thus the variation of particle composition of Ti-Nb carbide for different sizes and aging times is very small.

Steel 3

In Fig.4.28 and 4.29 it is seen that the compositions of the particles in steel 3 are quite scattered for different sized particles through various holding times, whereas this scatter decreases with increasing particle size for aging 1 and 5 s at 1000°C. The large scatter may result from the large differences of the solubility product of TiN from those of the other binary compounds since later
predictions in Ch.5 illustrate that there is higher proportion of TiN in the particles in steels 3. Although the scatter is fairly large, a particle size dependence of composition is apparent. Fig.4.28 indicates that the youngest smaller particles have a higher average Ti content ($x \sim 0.4$) than the larger ones ($x \sim 0.2$) for aging 1 s and 5 s; and it also shows that the differences in compositions between the smaller precipitates and the larger ones has almost vanished for the longer holding times (10 s to 24 hr in Figs.4.28 and 4.29.a). The same but weaker trend is observed for aging at 1100°C for 1 s in steels 3 (Fig.4.29.b), but not in steel 2.

Steel 4

Figs.4.30 to 4.31 show the carbonitride particle compositions in steel 4 as a function of particle size for short holding times at 1000°C and 1100°C. It can be seen that the compositional scatter of different sized carbonitrides in steel 4 is the highest in the three steels due to the highest proportion of TiN in the carbonitride. The strong particle size dependence of composition extends at least to 60 s at 1000°C. It is obvious that the smaller the particles, the higher the Ti content (from about 0.6 to 0.95 in a particle size range of 10 to 1.5 nm). Fig.4.30 indicates the same trend for aging 1 s and 5 s at 1100°C, but not for aging 10 s. Fig.4.32 shows the particle compositions for various aging times at 940°C and 1200°C. An even stronger size dependence of particle compositions is observed for aging 30 s and 60 s at 940°C; the particle compositions change from about 0.75 to 0.45 in the size range of 2 to 10 nm. On the other hand in Fig.4.32.b, it can be seen that particle compositions appear to be fairly independent of the particle size for aging 30 s at 1200°C with $x$ values of about 0.95 to 0.7 in the size range of 2 to 10 nm.
A comparison of Figs.4.30 to 4.32 suggests that the higher is the aging temperature the higher is the Ti content in the carbonitrides of steel 4, as predicted later in Ch.5. All of these figures demonstrate that the lower is the aging temperature, the stronger is the dependence of carbonitride compositions on particle size, and in turn this indicates that the diffusivities of Ti and Nb in carbonitrides are extremely small at aging temperatures 940°C to 1200°C. The microanalysis of the carbonitrides in steels 3 and 4 indicates that the youngest smaller particles have a higher average Ti content than the larger ones for short aging times and this can be considered to be a true and significant result since the theoretical model in Ch.6 also suggests it.

Steel 4 for Aging 100 hr

EDX and EELS were also applied to analyze particles in steel 4 at 1000°C and 1100°C for aging 100 hr. Fig.4.33 shows the particle compositions (both x and y) as a function of particle size, and this figure demonstrates no evident size dependence of particle compositions for such long aging times. The transition of morphologies from spheres to cuboids take place for steel 4 during long holding times. At 1100°C for 100 hr almost all of the particles are cuboids. However, at 1000°C for 100 hr, only about half of the particles are cuboids or ellipsoids. In this case there is a considerably larger scatter, particularly for the y values, and this is associated with the coexistence of two distinct morphologies of particles, one, Ti-rich, which usually displays a cuboidal morphology and the other, less Ti-rich, with a spheroidal morphology. However, almost all of the spherical precipitates, like the cuboids, show clear N peaks in their EDX spectra. These observations suggest that diffusion of Ti and Nb in the particles and matrix has occurred over such a long aging time. At 1100°C, overall equilibrium may be
approached, but not for 1000°C since cubic and spherical particles exist with apparently different compositions. For 1000°C the average x value for spherical particles is 0.85 and y is 0.43, while for cubic particles the average x value is 0.94 and y is 0.16 which implies that there is more C than in the undissolved particles at 1390°C.

Concerning undissolved cuboid interiors, microanalysis of some large cubic particles like the one in Fig.4.2.a shows that concentrations are fairly homogeneous. However, for cuboids in steel 4 at 1000°C and at 1100°C held for 100 hr, the concentration variations through the particles have been observed and this is more evident for plate-like particles (Fig.4.34.a). It appears that there are an increasing number of plate-like particles in steel 4 after aging for 100 hr at 1100°C. Composition gradients are always observed to some extent inside these precipitates and are not monotonic in most cases. A typical concentration profile for a plate-like carbonitride is shown in Fig.4.34.b. Ti is strongly enriched at the center and less enriched on both ends. It has been reported [17,19,131] that Nb enriched caps nucleate and grow on pre-existing TiN, which may indicate that the two ends grew upon the undissolved cuboids over a very long coarsening time.
CHAPTER V

THERMODYNAMICS OF
THE COMPLEX CARBONITRIDES

In this chapter thermodynamic models relevant to the description of the complex interstitial compounds like \((\text{Ti}_x\text{Nb}_{1-x})\text{C}\) and \((\text{Ti}_x\text{Nb}_{1-x})(\text{C}_y\text{N}_{1-y})\) in dilute quaternary and pentenary austenites will be outlined. The primary purposes of the thermodynamic analysis are

a) To calculate the effective contents of Ti, Nb, C and N available for the formation of the complex precipitates during aging.

b) To calculate the equilibrium compositions and mole fractions of these precipitates at a given temperature, and for the residual solutes in the matrix.

c) To estimate the chemical driving forces for precipitate nucleation.

The sublattice-regular solution model proposed by Hillert and Staffansson [132] is modified and applied to the description of the thermodynamics of the complex carbonitride of Ti and Nb.

5.1 THE AUSTENITE - Ti-Nb CARBIDE EQUILIBRIUM

In this sublattice regular solution model the metal atoms occupy one
lattice and the non-metal species occupy the interstitial sublattice. Following the assumption for an ideal solution model for Fe-Nb-C-N system proposed by Hudd et al [96], it is assumed that one mole of $(\text{Ti}_x\text{Nb}_{1-x})\text{C}$ can be considered as mixing of $x$ moles of TiC and $(1-x)$ moles of NbC, where the titanium and niobium randomly substitute for each other. We have

$$x\text{TiC} + (1-x)\text{NbC} = (\text{Ti}_x\text{Nb}_{1-x})\text{C}$$

(5.1)

The total free energy of the ternary compound is then given by

$$G_{\text{Ti}_x\text{Nb}_{1-x}\text{C}} = xG_{\text{TiC}}^p + (1-x)G_{\text{NbC}}^p$$

$$= xG_{\text{TiC}}^o + (1-x)G_{\text{NbC}}^o - T \frac{1}{2}S^m + G^m$$

(5.2)

where the $G_{\text{MC}}^o$ are the molar free energies of the pure binary compounds at the temperature of interest, $1S^m$ is the integral ideal molar entropy of mixing, $E^m$ is the integral excess molar free energy of mixing, and the $G_{\text{MC}}^p$ are the partial mole free energies of TiC and NbC in the $(\text{Ti}_x\text{Nb}_{1-x})\text{C}$ particle solution. If the compound entropy of mixing is assumed to arise due to ideal mixing of the metallic atoms, and the interstitial atoms are taken to be pure, and consequently offering no contribution, then it can be shown that

$$-\frac{1}{R}S^m = x\ln x + (1-x)\ln(1-x)$$

(5.3)

The integral excess molar free energy of mixing is expressed using a regular solution model, allowing for TiC and NbC interaction. The expression is

$$E^m = (1-x)\Omega$$

(5.4)

where $\Omega$ is the empirical regular solution parameter.
According to the regular solution assumption, the partial molar free energies are now given by

\[ \bar{G}_{TiC}^p = G_{TiC}^o + RT\ln x + (1-x)^2\Omega \]  \hspace{1cm} (5.5a)  

\[ \bar{G}_{NbC}^p = G_{NbC}^o + RT\ln(1-x) + x^2\Omega \]  \hspace{1cm} (5.5b)  

The equilibrium between austenite and carbide can be written as

\[ \bar{G}_{TiC} = \bar{G}_{Ti}^Y + \bar{G}_C^Y \]  \hspace{1cm} (5.6a)  

and

\[ \bar{G}_{NbC} = \bar{G}_{Nb}^Y + \bar{G}_C^Y \]  \hspace{1cm} (5.6b)  

where \( \bar{G}_i^Y \) are the partial molar free energies of each element in austenite (i refers to the solutes). At very low alloying contents the austenite matrix will obey Henry’s law. Thus the partial molar free energies of Ti, Nb and C in austenite can be written as

\[ \bar{G}_i^Y = G_i^o + RT\ln[\gamma_i X_i] \]  \hspace{1cm} (5.7a)  

or

\[ \bar{G}_i^Y = G_i^o + RT\ln[X_i] + \Sigma \varepsilon_i^j X_j \]  \hspace{1cm} (5.7b)  

where \( X_i \) is the mole fraction of the ith element in austenite at the precipitate interface at equilibrium with the particle, \( G_i^o \) refers to the infinitely dilute standard state in austenite, \( \gamma_i \) is the Henry’s law coefficient, and the \( \varepsilon_i^j \) are the constant Wagner interaction parameters defined by the linear Taylor expansion of \( \ln\gamma_i \). Since the compositions of microalloyed steels studied are very dilute, the effect of the last terms in Eq.5.7b on the thermodynamics can be neglected but this may not be the case for diffusional kinetics discussed in Ch.6. Thus the
equilibrium Eqs.5.6 can be rewritten as

$$RT\ln[X_{TiC}] = \Delta G_{TiC}^0 + RT\ln[x] + (1-x)^2\Omega$$  \hspace{1cm} (5.8a)

$$RT\ln[X_{NbC}] = \Delta G_{NbC}^0 + RT\ln[1-x] + x^2\Omega$$  \hspace{1cm} (5.8b)

where $\Delta G_{MX}^0$ refer to the free energies of formation of the respective binary compounds from austenite.

The data for $\Omega$ are generally not readily available. Roberts and Sandberg [133] derived a value of -4260 J/mole for TiN-TiC. It is assumed that $\Omega$ for the other possible combinations of compound components in microalloyed steels are of the same order of magnitude.

To complete the picture, the mass balance equations must be included. We can write

$$X_C^o = X_C(1-Z) + \frac{1}{2} Z$$  \hspace{1cm} (5.9a)

$$X_{Ti}^o = X_{Ti}(1-Z) + \frac{x}{2} Z$$  \hspace{1cm} (5.9b)

$$X_{Nb}^o = X_{Nb}(1-Z) + \frac{(1-x)}{2} Z$$  \hspace{1cm} (5.9c)

where the $X_i^o$ refer to the overall (or initial) composition of the steel and $Z$ refers to the equilibrium mole fraction of the carbide. Eqs.5.8 through 5.9 can be solved numerically to determine the austenite/carbide equilibrium.

5.2 THE AUSTENITE - Ti-NB CARBONITRIDE EQUILIBRIUM

Based on the assumption of perfect compound stoichiometry, the Ti-Nb
complex carbonitride may be expressed by the chemical formula \((\text{Ti}_x\text{Nb}_{1-x})(\text{C}_y\text{N}_{1-y})\), where \(0 < x < 1\) and \(0 < y < 1\).

To express the free energy of the \((\text{Ti}_x\text{Nb}_{1-x})(\text{C}_y\text{N}_{1-y})\) phase in terms of the free energies of the binary compounds, it is necessary to define the amount of each individual binary compound in the precipitate. Hillert and Staffansson [132] propose that the molar free energy of the precipitate may be written as

\[
G_{\text{TiN}_x\text{Nb}_{1-x}\text{C}_y\text{N}_{1-y}} = xyG_{\text{TiC}}^0 + (1-x)yG_{\text{NbC}}^0 + (1-x)(1-y)G_{\text{NbN}}^0 \\
+ x(1-y)G_{\text{TiN}}^0 - T \frac{I^m}{R} + E_G^m
\]

(5.10)

where \( I^m \) is the integral ideal molar entropy of mixing, \( E_G^m \) is the integral excess molar free energy of mixing. Although Hillert and Staffansson do not specify explicitly the amount of each binary compound in the precipitate, they imply that the free energy of the precipitate may be represented as though the precipitate is a mixture of

\[
xy = \text{mole fraction of TiC} \\
x(1-y) = \text{mole fraction of TiN} \\
y(1-x) = \text{mole fraction of NbC} \\
(1-x)(1-y) = \text{mole fraction of NbN}
\]

Hillert and Staffansson calculate the ideal entropy of mixing according to Temkin [134] assuming that Nb and Ti, C and N mix independently on two different sublattices in the interstitial compound; thus

\[
-\frac{I^m}{R} = x\ln x + (1-x)\ln(1-x) + y\ln y + (1-y)\ln(1-y)
\]

(5.11)

The integral excess molar free energy of mixing is expressed using a regular solution model, allowing for C-N and Nb-Ti interactions. The expression is
\[ E_G^m = x(1-x)y\Omega_{T1Nb}^C + x(1-x)(1-y)\Omega_{T1Nb}^N + (1-x)y(1-y)\Omega_{CN}^{Nb} + xy(1-y)\Omega_{CN}^{T1} \]  (5.12)

where \( \Omega_{T1Nb}^C, \Omega_{T1Nb}^N, \Omega_{CN}^{Nb} \) and \( \Omega_{CN}^{T1} \) are the four regular solution parameters. The partial molar free energies of the individual compounds in the \((Ti_{1-x}Nb_x)(C_yN_{1-y})\) precipitate solution are given by

\[ \bar{G}_{TC} = G_{TC}^0 + RT\ln(xy) + \Delta G(1-x)(1-y) + E\bar{G}_{TC} \]  (5.13a)

\[ \bar{G}_{NbC} = G_{NbC}^0 + RT\ln((1-x)y) - \Delta G(x)(1-y) + E\bar{G}_{NbC} \]  (5.13b)

\[ \bar{G}_{TIN} = G_{TIN}^0 + RT\ln(x(1-y)) - \Delta G(1-x)(y) + E\bar{G}_{TIN} \]  (5.13c)

\[ \bar{G}_{NbN} = G_{NbN}^0 + RT\ln((1-x)(1-y)) + \Delta G(x)(y) + E\bar{G}_{NbN} \]  (5.13d)

where \( \Delta G \) is defined by

\[ \Delta G = G_{TIN}^0 + G_{NbC}^0 - G_{NbN}^0 - G_{T1C}^0 \]  (5.14a)

or

\[ \Delta G = \Delta G_{TIN}^0 + \Delta G_{NbC}^0 - \Delta G_{NbN}^0 - \Delta G_{T1C}^0 \]  (5.14b)

and the partial excess molar free energies may be written in terms of the regular solution parameters. The complete expressions for the partial excess molar free energies are given by Hillert and Staffansson. Since the regular solution parameters are not well known for this system, it is assumed that \( \Omega_{T1Nb}^C = \Omega_{T1Nb}^N = \Omega_{T1Nb} \) and \( \Omega_{CN}^{Nb} = \Omega_{CN}^{T1} = \Omega_{CN} \). The partial excess molar free energies are then given by

\[ E\bar{G}_{T1C} = (1-x)^2\Omega_{T1Nb} + (1-y)^2\Omega_{CN} \]  (5.15a)
\[ \tilde{E}_{NbC} = x^2 \Omega_{TINb} + (1-y)^2 \Omega_{CN} \]  
(5.15b)

\[ \tilde{E}_{NbN} = x^2 \Omega_{TINb} + y^2 \Omega_{CN} \]  
(5.15c)

\[ \tilde{E}_{TiN} = (1-x)^2 \Omega_{TINb} + y^2 \Omega_{CN} \]  
(5.15d)

It is further assumed that the effect of interstitials on Ti-Nb is negligible; i.e., taking \( \Omega_{TINb} = 0 \), we have

\[ \tilde{E}_{TiC} = \tilde{E}_{NbC} = (1-y)^2 \Omega_{CN} \]  
(5.16a)

\[ \tilde{E}_{NbN} = \tilde{E}_{TiN} = y^2 \Omega_{CN} \]  
(5.16b)

The austenite-carbonitride equilibrium condition is satisfied when the partial molar free energies of each element are equal and this can be identically expressed as

\[ \bar{G}_{TiC} = \bar{G}^Y_{Ti} + \bar{G}^Y_{C} \]  
(5.17a)

\[ \bar{G}_{NbC} = \bar{G}^Y_{Nb} + \bar{G}^Y_{C} \]  
(5.17b)

\[ \bar{G}_{NbN} = \bar{G}^Y_{Nb} + \bar{G}^Y_{N} \]  
(5.17c)

\[ \bar{G}_{TiN} = \bar{G}^Y_{Ti} + \bar{G}^Y_{N} \]  
(5.17d)

where \( \bar{G}_{MX} \) are given by Eqs.(5.13). According to Henry's law, the partial molar free energies of Ti, Nb, C, and N in austenite can be written as

\[ \bar{G}^Y_i = \delta_{i} G^0_i + RT \ln[X_i] \]  
(5.18)

Substituting Eqs.5.13, 5.16 and 5.18 in Eqs.5.17 we obtain the following four
chemical potential equalities in terms of the composition of the two phases:

\[
RT\ln[X_{T1, C}] = \Delta G^o_{T1C} + RT\ln[xy] + \Delta G(1-x)(1-y) + (1-y)^2\Omega_{CN} \quad (5.19a)
\]

\[
RT\ln[X_{Nb, C}] = \Delta G^o_{NbC} + RT\ln[(1-x)y] - \Delta G(x)(1-y) + (1-y)^2\Omega_{CN} \quad (5.19b)
\]

\[
RT\ln[X_{T1, N}] = \Delta G^o_{T1N} + RT\ln[x(1-y)] - \Delta G(1-x)(y) + y^2\Omega_{CN} \quad (5.19c)
\]

\[
RT\ln[X_{Nb, N}] = \Delta G^o_{NbN} + RT\ln[(1-x)(1-y)] + \Delta G(x)(y) + \Omega_{CN} y^2 \quad (5.19d)
\]

Note that when the terms to the right of the \(\Delta G^o_{MX}\)s become zero, the expression corresponds to the binary compound solubility. It can be shown that only three of the equations are independent. For example the addition of Eqs.(5.19a) and (5.19d) equals the sum of the other two equations.

The influence of curvature on the interface composition is significant for the tiny spherical particles that exist in the initial stage of precipitation. Therefore the effect of curvature must be taken into account for the calculation of the chemical potential in the precipitates. Including capillarity for spherical precipitates, the partial molar free energies of the individual binary compounds in the \((Ti_{1-x}Nb_{1-x})(C_{y}\,N_{1-y})\) precipitate solution are rewritten as

\[
\bar{\bar{G}}_{T1C} = G_{T1C}^o + RT\ln[xy] + \Delta G(1-x)(1-y) + \frac{4\sigma V_p}{r} \quad (5.20a)
\]

\[
\bar{\bar{G}}_{NbC} = G_{NbC}^o + RT\ln[(1-x)y] - \Delta G(x)(1-y) + \frac{4\sigma V_p}{r} \quad (5.20b)
\]

\[
\bar{\bar{G}}_{T1N} = G_{T1N}^o + RT\ln[x(1-y)] - \Delta G(1-x)(y) + \frac{4\sigma V_p}{r} \quad (5.20c)
\]

\[
\bar{\bar{G}}_{NbN} = G_{NbN}^o + RT\ln[(1-x)(1-y)] + \Delta G(x)(y) + \frac{4\sigma V_p}{r} \quad (5.20d)
\]

where \(r\) is the average particle radius. Thus the equilibrium between austenite and
a spherical particle can be represented as

\[
RTln[X_{Ti} X_{C}] = \Delta G_{TiC}^0 + RTln[xy] + \Delta G(1-x)(1-y) + \Omega_{CN} \frac{(1-y)^2 + \frac{4\sigma V}{r}} (5.21d)
\]

\[
RTln[X_{Nb} X_{C}] = \Delta G_{NbC}^0 + RTln[(1-x)y] - \Delta G(x)(1-y) + \Omega_{CN} \frac{(1-y)^2 + \frac{4\sigma V}{r}} (5.21d)
\]

\[
RTln[X_{Ti} X_{N}] = \Delta G_{TiN}^0 + RTln[x(1-y)] - \Delta G(1-x)(y) + \Omega_{CN} \frac{y^2 + \frac{4\sigma V}{r}} (5.21d)
\]

\[
RTln[X_{Nb} X_{N}] = \Delta G_{NbN}^0 + RTln[(1-x)(1-y)] + \Delta G(x)(y) + \Omega_{CN} \frac{y^2 + \frac{4\sigma V}{r}} (5.21d)
\]

The mass balance equations can be written as

\[
X^0_C = X_C(1-Z) + \frac{y}{2} Z \tag{5.22a}
\]

\[
X^0_N = X_N(1-Z) + \frac{(1-y)}{2} Z \tag{5.22b}
\]

\[
X^0_{Ti} = X_{Ti}(1-Z) + \frac{x}{2} Z \tag{5.22c}
\]

\[
X^0_{Nb} = X_{Nb}(1-Z) + \frac{(1-x)}{2} Z \tag{5.22d}
\]

Eqs.(5.21) through (5.22) can be solved numerically to determine the austenite-carbonitride equilibrium and this effectively defines the Fe-rich corner of the phase diagram Fe-Ti-Nb-C-N, including tie-lines to the precipitate phase boundary.
5.3 CHEMICAL DRIVING FORCE $\Delta G_v$ FOR NUCLEATION
OF PRECIPITATES

5.3.1 $\Delta G_v$ for Nucleation of Precipitates in Binary Solid Solutions

In this section let us review the classical theory of nucleation of second phase particles in binary solid solutions. Consider a hypothetical binary phase diagram with an exaggeration of the $\alpha$ region as shown in Fig.5.1.a, where B is soluble in $\alpha$-A but A is virtually insoluble in $\beta$-B. If the alloy $X_B^0$ is solution treated at $T_1$ and then cooled rapidly to $T_2$ it will become supersaturated with B and will precipitate $\beta$-B. The chemical driving force, $\Delta G_v$, for nucleation of precipitation is defined as the free energy change upon formation of unit volume of nuclei from the matrix. One should be aware of the difference between the chemical driving force for nucleation and for overall precipitation (i.e. the difference between $\Delta G_n$ and $\Delta G_0$ shown in Fig.5.1.b). At the supercooling temperature the creation of a volume $V$ of precipitate will cause a volume free energy reduction of $V\Delta G_v$, and at the same time an interfacial energy increase of $\Sigma A\sigma$. We assume that the misfit strain energy, $\Delta G_s$, is negligible for an incoherent interface. The total free energy change associated with the nucleation process can then be represented as

$$\Delta G = V\Delta G_v + \Sigma A\sigma$$  \hspace{1cm} (5.23)

If we ignore the variation of $\sigma$ with interface orientation and assume that the nucleus is spherical with a radius of $r$, Eq.(5.23) becomes

$$\Delta G(r) = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \sigma$$  \hspace{1cm} (5.24)

Differentiation of the above equation gives
\[ r^* = -\frac{2\sigma}{\Delta G_v} \]  \hspace{1cm} (5.25)

and

\[ \Delta G^* = \Delta G(r^*) = \frac{16\pi r^{*3}}{3\Delta G_v^2} \]  \hspace{1cm} (5.26)

where \( r^* \) is the critical nucleus size.

Since the critical nucleus size, \( r^* \), is much smaller than the subsequent average partitioned particle size (i.e. just before coarsening), the initial change in matrix composition is negligible after the formation of a critical nucleus in the matrix. Therefore for the purposes of the driving force calculation, the critical nucleus can be defined as that the compositions (chemical potential) of the solutes in the matrix at the matrix/nucleus interface at equilibrium with the necessarily metastable nucleus is equal to the solute compositions (chemical potential) in the initial supersaturated matrix. I.e., with the inclusion of the capillarity effect the chemical potentials of solutes in the critical nuclei are equal in a metastable configuration to the chemical potentials in the initial matrix (see Fig.5.1.b). Thus the critical nuclei with the radius \( r^* \) are unstable with respect to the surrounding supersaturated matrix, so growth can ensue.

Fig.5.1.c shows the variation of the equilibrium composition at the matrix/nucleus interface with nucleus size. It can be seen that when \( r < r^* \), \( \Gamma_{X^0_B}^e > X_B^0 \), the solute B atoms diffuse away from the \( \beta \)-cluster and the \( \beta \)-nucleus shrinks whereas when \( r > r^* \), \( \Gamma_{X^0_B}^e < X_B^0 \) and the atoms move towards the cluster and the nucleus grows. Strictly speaking, the composition \( X \) should replaced by the chemical potential \( \Gamma_B^c \) for the non-henrian cases.

The equilibrium between \( \alpha \) and planar \( \beta \) can be expressed as
[B] = B \hspace{1cm} (5.27)

where [ ] signifies that the component B is in the solution.

For a regular solution in \( \alpha \)

\[
\tilde{G}_B^\alpha = G_B^\alpha + RT\ln X_B + \Omega (1 - X_B)^2
\hspace{1cm} (5.28)
\]

where \( \Omega \) is the regular solution parameter. For equilibrium

\[
G_B^\beta = \tilde{G}_B^\alpha
\hspace{1cm} (5.29)
\]

and

\[
RT\ln X_B = \Delta G_B
\hspace{1cm} (5.30)
\]

where \( \Delta G_B = G_B^\beta - G_B^\alpha - \Omega \) (assuming \( X_B^\alpha << 1 \)). The equilibrium composition with a planar precipitate is

\[
X_B^e = \exp \left( \frac{\Delta G_B}{RT} \right)
\hspace{1cm} (5.31)
\]

Since the first nuclei do not significantly change the \( \alpha \) composition from \( X_B^\alpha \), the free energy released per volume of nuclei formed can be calculated as follows

\[
\Delta G_v = \frac{1}{V_p} (G_B^\beta - \tilde{G}_B^\alpha) = \frac{1}{V_p} (\Delta G_B - RT\ln X_B^\circ) = - \frac{RT}{V_p} \ln \left( \frac{X_B^\circ}{X_B^e} \right)
\hspace{1cm} (5.32)
\]

Then the critical radius is

\[
r^* = - \frac{2\sigma}{\Delta G_v}
\hspace{1cm} (5.33)
\]

However if we consider the equilibrium with a spherical nucleus of radius \( r^* \), we have
\[ r_{G_b}^{*\alpha} = \bar{G}_b \]  

or

\[ r_{G_b}^{*\beta} = G_b^{\beta} + \frac{2\sigma V_p}{r^*} \]  

(5.35)

By rearrangement, we have

\[ RT\ln X_B^o = \Delta G_B + \frac{2\sigma V_p}{r^*} \]  

(5.36)

This gives the same \( r^* \) as obtained from Eq.(5.33)

5.3.2 \( \Delta G_v \) for MX\(_y\) Nucleation in the Fe-M-X Solutions

Now let us consider MX\(_y\) precipitates from supersaturated Fe-M-X matrix \( (y \) is the nonstoichiometric constant). The precipitation reaction can be written as

\[ [M] + y[X] = MX_y \]  

(5.37)

With ideal or Henrian assumptions for the substrate the solubility product of MX\(_y\) is expressed as

\[ K_{MX_y} = \ln[X_M X^V_y] = \exp \left( \frac{\Delta G_{MX_y}^V}{RT} \right) \]  

(5.38)

where \( \Delta G_{MX_y} \) is the free energy of formation of MX\(_y\). Based on the same argument, the chemical driving force for nucleation is

\[ \Delta G_v = \frac{1}{2V_p} \left[ G_{MX_y} - \bar{G}_M^V - y\bar{G}_X^V \right] \]  

(5.39)

i.e.
\[
\Delta G_v = -\frac{RT}{2V_p} \ln \left( \frac{X_M^0 X_X^0}{K_{MX_y}} \right) = -\frac{RT}{2V_p} \ln [k_s]
\]  

(5.40)

where \(k_s\) is referred to as the supersaturation ratio. It should be noted that the factor 2 in the above equation comes from the definition of \(V_p\) for carbides and nitrides. On the other hand, we can consider that the equilibrium between initial matrix and critical spherical nuclei is expressed by

\[
\tilde{G}_M^y + y\tilde{G}_X^y = \Delta G_{MX_y}^0 + \frac{4\sigma V_p}{r^*}
\]

(5.41)

Therefore for ideal or dilute solutions, one obtains

\[
RT(ln X_M^0 + yln X_X^0) = \Delta G_{MX_y}^0 + \frac{4\sigma V_p}{r^*}
\]

(5.42)

\[
r^* = -\frac{4\sigma}{\Delta G_v}
\]

(5.43)

This is equivalent to substituting Eq.(5.40) into Eq.(5.25)

5.3.3 \(\Delta G_v\) for (Ti\(_x\)Nb\(_{1-x}\))C Nucleation in the Fe-Ti-Nb-C Solutions

The total free energy of the ternary compound is given by

\[
G_{Ti_xNb_{1-x}C} = x\tilde{G}_{Ti^0} + (1-x)\tilde{G}_{NbC}^p
\]

(5.44)

For the formation of one molar volume of (Ti\(_x\)Nb\(_{1-x}\))C critical nuclei from the initial matrix, the free energy change is

\[
\Delta G_v = -\frac{1}{2V_p} \left\{ G_{(Ti_xNb_{1-x})_C} - [x\tilde{G}_T^y + (1-x)\tilde{G}_{Nb}^y + \tilde{G}_{C}^y] \right\}
\]
\[ = \frac{1}{2V_p} \left\{ x \left[ \tilde{G}_{\text{Tic}}^p - \tilde{G}_{\text{Ti}}^{\gamma} - \tilde{G}_{\text{C}}^{\gamma} \right] + (1-x) \left[ \tilde{G}_{\text{NbC}}^p - \tilde{G}_{\text{Nb}}^{\gamma} - \tilde{G}_{\text{C}}^{\gamma} \right] \right\} \]

\[ = - \frac{1}{2V_p} \left\{ RT \ln \left[ \frac{X_{\text{Tic}}^0 X_{\text{C}}^0}{K_{\text{Tic}}} \right] + RT(1-x) \ln \left[ \frac{X_{\text{Nb}}^0 X_{\text{C}}^0}{K_{\text{NbC}}} \right] - RT \ln x \right\} - RT(1-x) \ln(1-x) - x(1-x)^2 \Omega - (1-x)x^2 \Omega \]  

(5.45)

For a critical nucleus

\[ \frac{\delta \Delta G}{\delta x} = \frac{\delta \Delta G}{\delta x} = 0 \]  

(5.46)

i.e.

\[ RT \ln \left[ \frac{X_{\text{Tic}}^0 K_{\text{NbC}}}{X_{\text{Nb}}^0 K_{\text{Tic}}} \right] - RT \ln x \left[ \frac{x}{1-x} \right] - (1-2x) \Omega = 0 \]  

(5.47)

For ideal or dilute model, \( \Omega = 0 \) we have

\[ \ln \left[ \frac{X_{\text{Tic}}^0 K_{\text{NbC}}}{X_{\text{Nb}}^0 K_{\text{Tic}}} \right] - \ln x \left[ \frac{x}{1-x} \right] = 0 \]  

(5.48)

or equivalently

\[ x = \frac{X_{\text{Tic}}^0 K_{\text{NbC}}}{X_{\text{Nb}}^0 K_{\text{Tic}}} \]  

(5.49)

and

\[ \frac{\delta \Delta G}{\delta \Gamma} = 0 \]  

(5.50)

Therefore for regular solution, \( r^* \) and the value of \( x \) for a critical nucleus can be obtained by solving Eqs.(5.47) and (5.50).

But if we consider the equilibrium between initial matrix and critical spherical nuclei, we have
\[ RTln[X_{Ti}^{c} X_{C}^{c}] = \Delta G_{TiC}^{o} + RTln[x] + (1-x)^{2} \Omega + \frac{4\sigma V}{^p r^*} \] (5.51a)

and

\[ RTln[X_{Nb}^{c} X_{C}^{c}] = \Delta G_{NbC}^{o} + RTln[1-x] + x^{2} \Omega + \frac{4\sigma V}{^p r^*} \] (5.51b)

With some rearrangement, it can be shown that Eqs.(5.47) and (5.50) and Eqs.(5.51) have identical solutions. It should be noted that the treatment is also applicable to \( M(C_y N_{1-y}) \).

5.3.4 \( \Delta G_{v} \) for \((Ti_x Nb_{1-x})(C_y N_{1-y})\) Nucleation in the Fe-Ti-Nb-C-N Solutions

The precipitation reaction in Fe-Ti-Nb-C-N austenite can be written as

\[ x[Ti] + (1-x)[Nb] + y[C] + (1-y)[N] = (Ti_x Nb_{1-x})(C_y N_{1-y}) \] (5.52)

According to Hillert and Staffansson's regular solution model the total free energy of the \((Ti_x Nb_{1-x})(C_y N_{1-y})\) compound is given by

\[ G_{Ti Nb_{1-x} C_y N_{1-y}} = x\bar{G}_{TiC}^{p} + (1-x)y \bar{G}_{NbC}^{p} + (1-x)(1-y)\bar{G}_{NbN}^{p} + x(1-y)\bar{G}_{TIN}^{p} \] (5.53)

For the formation of one molar volume of the \((Ti_x Nb_{1-x})(C_y N_{1-y})\) critical nuclei, the free energy change is

\[ \Delta G_{v} = \frac{1}{2V_{p}} \left\{ G_{Ti Nb_{1-x} C_y N_{1-y}} - [x\bar{G}_{TiC}^{Y} + (1-x)\bar{G}_{NbC}^{Y} + y\bar{G}_{C}^{Y} + (1-y)\bar{G}_{N}^{Y}] \right\} \]

\[ = \frac{1}{2V_{p}} \left\{ x\bar{G}_{TiC} - \bar{G}_{Ti}^{Y} - \bar{G}_{C}^{Y} + (1-x)y \left( \bar{G}_{NbC} - \bar{G}_{Nb}^{Y} - \bar{G}_{C}^{Y} \right) \right\} \]

\[ + x(1-y) \left( \bar{G}_{TIN} - \bar{G}_{Ti}^{Y} - \bar{G}_{N}^{Y} \right) + (1-x)(1-y) \left( \bar{G}_{NbN} - \bar{G}_{Nb}^{Y} - \bar{G}_{N}^{Y} \right) \] (5.54)
Substituting $G_{mx}^\gamma$ and $G_i^\gamma$ and rearranging gives

$$
\Delta G_v = \frac{1}{2V_p} \left[ \text{RTLn}[X_C^{o}X_{Ti}^{o}] + \Delta G_{T1iC}^{o} + \text{RTLn}[x] + \Delta G(1-x)(1-y) + \Omega(1-y)^2 \right]
+ (1-x)y \left[ - \text{RTLn}[X_C^{o}X_{Nb}^{o}] + \Delta G_{NbC}^{o} + \text{RTLn}[(1-x)y] - \Delta G(x)(1-y) + \Omega(1-y)^2 \right]
+ x(1-y) \left[ - \text{RTLn}[X_N^{o}X_{Ti}^{o}] + \Delta G_{TiN}^{o} + \text{RTLn}[x(1-y)] - \Delta G(1-x)(y) + \Omega y^2 \right]
+ (1-x)(1-y) \left[ - \text{RTLn}[X_N^{o}X_{Nb}^{o}] + \Delta G_{NbN}^{o} + \text{RTLn}[(1-x)(1-y)] + \Delta G(x)(y) + \Omega y^2 \right] \right) \tag{5.55}
$$

For the critical nucleus

$$
\frac{\partial \Delta G}{\partial x} = \frac{\partial \Delta G_y}{\partial x} = 0 \tag{5.56}
$$

whence

$$
\text{RTLn} \left[ \frac{X_{Nb}^{o}}{X_{Ti}^{o}} \right] - y \Delta G + (\Delta G_{TiN}^{o} - \Delta G_{NbN}^{o}) + \text{RTLn} \left[ \frac{x}{1-x} \right] = 0 \tag{5.57}
$$

and

$$
\frac{\partial \Delta G}{\partial y} = \frac{\partial \Delta G_y}{\partial y} = 0 \tag{5.58}
$$

whence

$$
\text{RTLn} \left[ \frac{X_{N}^{o}}{X_{C}^{o}} \right] - x \Delta G + (\Delta G_{NbC}^{o} - \Delta G_{Nbn}^{o}) + \text{RTLn} \left[ \frac{y}{1-y} \right] + (1-2y)\Omega = 0 \tag{5.59}
$$

and

$$
\frac{\partial \Delta G}{\partial r} = 0 \tag{5.60}
$$

If we consider the equilibrium between the initial matrix and spherical nuclei, we have
\[ \text{RTln}[X^c_{C,T1}] = \Delta G^o_{T1C} + \text{RTln}[xy] + \Delta G(1-x)(1-y) + \Omega(1-y)^2 + \frac{4\sigma V_p}{r^*} \]  
(5.61a)

\[ \text{RTln}[X^o_{C,Nb}] = \Delta G^o_{NbC} + \text{RTln}[(1-x)y] - \Delta G(x)(1-y) + \Omega(1-y)^2 + \frac{4\sigma V_p}{r^*} \]  
(5.61b)

\[ \text{RTln}[X^o_{N,Ti}] = \Delta G^o_{TIN} + \text{RTln}[x(1-y)] - \Delta G(1-x)(y) + \Omega y^2 + \frac{4\sigma V_p}{r^*} \]  
(5.61c)

\[ \text{RTln}[X_{N,Nb}] = \Delta G^o_{NbN} + \text{RTln}[(1-x)(1-y)] + \Delta G(x)(y) + \Omega y^2 + \frac{4\sigma V_p}{r^*} \]  
(5.61d)

With some rearrangement, it can be seen that Eqs.(5.57,59,60) and Eqs.(5.61) have identical solutions. Therefore by application of an equilibrium condition between the initial supersaturated matrix and the critical nuclei we can readily calculate the critical size, \( r^* \), and its compositions, \( x \) and \( y \), and then the chemical driving force for nucleation can be inversely obtained by the following equation

\[ \Delta G_v = - \frac{2\sigma}{r^*} \]  
(5.62)

This is the convenient approach for the evaluation of \( \Delta G_v \) for high order (\( \geq 3 \)) multicomponent precipitate nucleation.

This methodology should also be applicable to the nucleation of general second phase precipitation reactions, say, \( (A_x B_y)(C_z D_w) \).

### 5.4 RESULTS OF THE COMPUTATIONS

#### 5.4.1 Computation Method

The seven non-linear simultaneous equations which represent the equilibrium and mass balance pertaining to the austenite - \( (Ti_{x Nb_{1-x}})(C_y N_{1-y}) \) system are summarized as follows:
\[ \text{RTLn}[X_{Ti} \cdot X_{C}] = \Delta G^0_{TiC} + \text{RTLn}[xy] + \Delta G(1-x)(1-y) + (1-y)^2 \Omega_{\text{CN}} \]

\[ \text{RTLn}[X_{Nb} \cdot X_{C}] = \Delta G^0_{NbC} + \text{RTLn}[(1-x)y] - \Delta G(x)(1-y) + (1-y)^2 \Omega_{\text{CN}} \]

\[ \text{RTLn}[X_{Ti} \cdot X_{N}] = \Delta G^0_{TiN} + \text{RTLn}[x(1-y)] - \Delta G(1-x)(y) + y^2 \Omega_{\text{CN}} \]

\[ X_C^o = X_C(1-Z) + \frac{y}{2} Z \]
\[ X_N^o = X_N(1-Z) + \frac{1-y}{2} Z \]
\[ X_{Ti}^o = X_{n}(1-Z) + \frac{x}{2} Z \]
\[ X_{Nb}^o = X_{Nb}(1-Z) + \frac{1-x}{2} Z \]

Numerical method must be used to solve the nonlinear system and we chose the Newton-Raphson technique. The method of steepest descent has also been incorporated. Considerable care in the choice of the numerical method and initial guesses was required in the search for real positive roots to ensure convergence. Only one self-consistent set of solution parameters was found to simultaneously satisfy the thermodynamic equilibrium and mass balance relations for a given temperature and alloy composition. I.e., the concentrations of Ti, Nb, C and N dissolved in the austenite and the equilibrium mole fractions of \((Ti_xNb_{1-x})(C_yN_{1-y})\), as well as the carbonitride composition in terms of \(x\) and \(y\) were determined simultaneously. In this manner a series of unique solutions to the simultaneous equation set was generated as temperature and composition were varied systematically. The same approach is applicable to (TiNb)C and the calculation of driving forces.

The adopted solubility data expressed in the form of free energies of
formation of TiC, NbC, TiN and NbN in austenite are summarized in Table 5.1. As already noted, the regular solution parameters $\Omega$ have not been previously determined for C-N mixing in the Ti-Nb-C-N system. The value $\Omega = -4260\text{J/mole}$ deduced for C-N mixing in the Ti-C-N system has been adopted following Roberts and Sandberg [133] on the grounds that the C and N mixing should have a similar sub-lattice chemical effect in the carbonitrides. The general outcome is not very sensitive to this assumption for our conditions.

5.4.2 Computation Results

In this section we illustrate the evolution of mole fractions and compositions of complex carbonitrides and matrix compositions with temperature. These quantities are reassessed using the concept of effective compositions for the newly-formed carbonitride precipitates during thermomechanical processing, and compared with the experimental results obtained in this study. The chemical driving forces for nucleation and the critical nucleus size and compositions are also calculated based on the effective compositions.

5.4.2.1 Mole Fraction of NbC Precipitates and Matrix Compositions

Fig. 5.2 shows the mole fraction of NbC precipitates and Nb and C compositions in steel 1 as a function of temperature. It can be seen that the total solution temperature of NbC in this steel is about 1250°C. Therefore, at the experimental solution temperature 1390°C NbC should be completely dissolved in the austenite. The mole fraction of NbC particles increases sharply from 1250°C to 1000°C while the Nb level in austenite diminishes rapidly. The relative mild
reduction of C content in the matrix is due to the high overall C to Nb mole ratio. Upon further cooling, the amount of precipitates increases slowly due to the gradual depletion of Nb in the matrix. From the Fig.5.2, it can be concluded that the mole fraction of NbC depends not only on the sum of Nb and C content but also the atomic ratio of Nb to C. For a given total amount of Nb and C, it can be readily proved that the stoichiometric ratio Nb/C = 1 gives the maximum possible amount of precipitation and this maximum is a strong function of undercooling.

5.4.2.2 Mole Fraction of (TiNb)(CN) Precipitates

Fig.5.3 shows the calculated mole fractions of \((\text{Ti}_x\text{Nb}_{1-x})(\text{C}_y\text{N}_{1-y})\) in terms of the accumulation of binary compounds in the temperature range 800°C to 1500°C for steels 2 to 4. The overall mole fraction of carbonitride (as defined by the TiC solid contour line) and proportions of each type of binary carbides/nitrides in the multicomponent compound strongly depend on the composition of the steels and the temperature. It can be seen that none of the three steels are completely free from precipitates in the austenite phase field (910°C - 1395°C). At very high temperature the precipitates are mainly \((\text{Ti}_x\text{Nb}_{1-x})\)N (TiN and NbN) and their amount increases slowly with decreasing temperature because of rapid depletion of N. Steel 3 with both relatively higher Ti and N contents is expected to contain the larger fraction of undissolved (TiNb)N at 1390°C. However, with further cooling along the abscissa of Fig.5.3 through typical thermomechanical processing temperature (1200 - 900°C), the compound \((\text{Ti}_x\text{Nb}_{1-x})\)C consisting of a mixture of TiC and NbC, although intimately mixed with \((\text{Ti}_x\text{Nb}_{1-x})\)N, dominates the precipitation reaction, and this results in a sharp increase of the mole fraction of carbonitride particles in such steels due to rapidly coming out of TiC and NbC.
For steel 2 with high Ti, Nb and C and very low N, the TiC and NbC start to rapidly increase their proportion around 1275°C; for steel 3, they start to proportionate around 1200°C. However; for steel 4 with low Ti, Nb and C and relatively higher N levels, it is not until about 1000°C that the amount of carbides begin to significantly increase. As a result, the mole fraction of precipitates (mainly TiC and NbC) in steel 2 with the higher levels of total solutes is highest at the aforementioned rolling temperature and it is the least in steel 4 due to its relatively lower total amount of solutes. (TiNb)C precipitates of this kind are considered to be the major contributor to the retardation of recrystallization and grain growth in austenite during hot rolling.

It is worth noted that with cooling below 1300°C the amount of (TiNb)N is almost unchanged due to the matrix depletion of N. Also Fig.5.3 shows the repartitioning of TiN and NbN resulting from the strongly preferential entry of Nb into carbonitride at low temperature.

5.4.2.3 Compositions of the Complex Carbonitride Precipitates

The particle composition changes (i.e. x and y in (Ti$_x$Nb$_{1-x}$)$_{(C_yN_{1-y})}$) with temperature for steels 2 to 4 are presented in Fig.5.4. It is evident that for all three steels near the solution temperature the x values approach unity and the y values zero. Thus the precipitates are chemically close (TiNb)N same as indicated in Fig.5.3. Therefore, Ti and N are the dominant elements in the quaternary carbonitride at higher temperatures. By contrast as temperature decreases, the x decreases and y goes the opposite way, i.e., the proportions of Nb and C in the compound increase. The inversion of the x value at around 1220°C in steel 2 occurs and this is due to the sharp increase in TiC in steel 2. The precipitate may be
considered as Ti-Nb carbide.

Since at the temperature of complete dissolution of the particles, the composition in the equilibrium case will be strongly biased towards the most stable compound TiN, the ultimate dissolution temperature should not be significantly affected by the mixing effects, i.e., it can be estimated at the point of complete dissolution of TiN (which is slightly underestimated). At lower temperatures however, calculations [9] showed that mixing effects give rise to an increase in precipitate mole fraction.

### 5.4.2.4 Concentrations of Residual Solutes in the Austenite

The concentrations of the remaining Ti, Nb, C and N in the steels as a function of temperature were also calculated and these are presented in Fig.5.5 and 5.6. Mass balance equations indicate that the concentrations of the remaining solutes depend directly on the mole fractions of the precipitates and on the overall concentrations of the steels. Therefore, the solute concentrations change with temperature are consistent with the inverse trend of the mole fraction change. It may be noted that N is almost depleted at very high temperature, or most of TiN comes out at above 1300°C. Although the concentrations of the remaining N in austenite are very low at solution temperature, they can significantly influence the chemical driving force for precipitation nucleation, as will be shown later in this chapter. The temperature for the onset of the rapid decrease of Ti, Nb and C content in austenite correspond directly to the temperature at which TiC and NbC start to emerge rapidly, as can be seen in Fig.5.3.
5.4.2.5 Effective Concentrations of the Solutes

In the previous section, we have calculated the equilibrium mole fraction of precipitates using the overall compositions. While the calculated results show that there exist undissolved carbonitrides at the solution temperature in steels 2 to 4, as was proved early by experimental observations in Ch.4, the solutes fixed in these carbonitrides make no contribution to the newly-formed (or reprecipitating) carbonitride precipitates during aging. Hence the solutes in the austenite must be corrected for the undissolved part. Accordingly, the effective concentrations of the precipitate-forming solutes are defined as the dissolved concentrations of solutes in austenite at the solution temperature 1390°C so that only they can play a role in a subsequent precipitation reaction as the matrix is cooled down. The undissolved particles at 1390°C were thus eliminated from further consideration. It is assumed that following solution treatment the equilibrium between austenite and carbonitride is sufficiently closely approached, whence the concentrations of dissolved solutes are calculated from the the thermodynamic analysis presented above and recorded in Table 5.2. These values were used as the effective concentrations of the precipitate forming elements in further calculations of the mole fractions and compositions of the newly formed precipitates and the chemical driving forces for precipitation.

The parameters used in the computations are estimated in the following ways. The matrix concentration is estimated as the equilibrium value at 1390°C based on the assumption that the large undissolved particles (~50 nm) are equilibrated. The molar volume of the matrix \( V_m = 7.31 \times 10^{-6} \text{m}^3/\text{mole} \) was calculated from the lattice parameter of austenite \( a = 0.365 \text{ nm} \), and the molar volume of carbonitride, \( V_p \), was calculated from the lattice parameter which varies with the
composition of the particle. To accommodate this variation it is assumed that the lattice parameter of mixed carbonitride proportionates as the mole fraction of each binary compound according to the law of mixing, that is

\[ a_{(TiN)(CN)} = xy_a_{TiC} + (1-x)y_a_{NbC} + x(1-y)a_{TiN} + (1-x)(1-y)a_{NBN} \]  

(6.63)

where the \( a_{MX} \) are the lattice parameters of MX. Here \( x \) and \( y \) are calculated from the isothermal equilibrium model. The lattice parameters for the stoichiometry binary carbides and nitrides are obtained from Tables 2.1 and 2.2. The corrected Ti, Nb, C and N concentrations in austenite at 1390°C (see Table 5.2) are employed as the initial compositions \( X_i^o \) for reprecipitation during aging. The interfacial energy was taken to be 0.3 J/m² (with reference to data on the austenite/ Cr₂₃C₆ interface [136]).

5.4.2.6 Mole Fraction of the Newly-Formed Precipitates

In this section the mole fractions and compositions of precipitate refer to the maximum amount of newly formed precipitate which comes out during isothermal aging below the solution temperature.

The predicted mole fraction of new particles is plotted in Fig.5.7 the total amount of newly formed precipitates is less than that in Fig.5.3 at a given temperature since the undissolved carbonitride at solution temperature is excluded. Steel 3 is affected the most because of its highest undissolved amount of (TiNb)N at 1390°C. But in all three alloys the general trend and shape remain similar. The calculation results also show that the solute compositions change with temperature keeps to the same trend as in Fig.5.5 and 5.6. The carbonitride precipitated in steel 2 is almost Ti-Nb carbide. However, compared with steels 2 and 3, steel 4 has
an extended (TiNb)N range.

So far it has not been possible to obtain estimates of the volume fraction of the precipitates from carbon replicas in microalloyed steels because of grain to grain variability in the etching response of the steel and the sensitivity of the extraction process to etching time of the specimen. Furthermore after etching, the exposed particles are sitting on a very rough surface, and as a result the electron micrographs pertain to the projection of particles from this surface which implies a density greater than the true two dimensional value.

5.4.2.7 Compositions of the Newly-formed Precipitates

The experimental and predicted compositions of the reprecipitated (TiNb)(CN) as a function of aging temperature and effective steel compositions is presented in Fig.5.8. In comparison with Fig.5.4, the general trend remains similar but a significant shift of the curves is evident, unlike the mole fractions and matrix compositions. All the alloys showed the expected increase in Ti content of the particles with increasing aging temperature. Although the experimental results are limited, they show very good reasonable agreement with the prediction for steels 2 and 3 and reasonable agreement for steel 4. First for steel 2 the results obtained confirm the reversion of x as calculated.

Most of the experimental results are based on the EDX measurements on 60 s aged specimens, which definitely remain some distance from quasi-equilibrium. Detailed microanalysis has been made on the 100 hr aged specimens of steel 4 which should nearly reach the equilibrium. The measured x average values from cubic particles is higher for aging 100 hr at 1000°C than that from spherical particles; while both values are greater than that for aging 60 s. On the other hand, the deduced y values are opposite for cubic and spherical particles. This could be an
indication that the transferring of Ti and Nb from the undissolved particles to the newly-formed particles happened so as to reach the equilibrium. At 1000°C overall equilibrium, including the undissolved (TiNb)N can not be reached by holding even for 100 hr. On the other hand, at 1100°C the overall equilibrium, including the undissolved (TiNb)N may be reached by holding for 100 hr since almost all of the particles are cuboids.

5.4.2.8 Compositions of Critical Nuclei

The calculated dependence of the compositions of the critical nuclei on precipitation temperature and steel composition is shown in Fig.5.9.a. In contrast to the equilibrium compositions of the carbonitride, the x value of the carbonitride nucleus increases with decreasing temperature, and the y value goes in the opposite way. This may be explained by the variations of the supersaturation ratio, \( k_s \), for individual binary carbides and nitrides with temperature as shown in Fig.5.9.b. It can be seen that for the same undercooling, the matrix has the highest supersaturation with respect to TiN, and furthermore \( k_s \) for TiN increases faster with decreasing temperature than for the other binary compounds. Since the calculation starts from the solution temperature, the relative supersaturation of TiN increases with undercooling so that the x value for the critical nucleus increases with decreasing temperature and y goes the opposite way. But the final equilibrium compositions of the complex carbonitride are determined by the amount of each solute available for precipitation which yield the Fig.5.8.
5.4.2.9 Chemical Driving Forces for Nucleation and Critical Nucleus Sizes

The calculated chemical driving forces for the precipitate nucleation of Nb carbide and Ti-Nb carbonitride and their critical radii in the four steels are plotted in Fig. 5.10. Fig. 5.10.a shows that the driving force, $\Delta G_v$, is directly proportional to the undercooling. It is to be noted that the slope for (TiNb)(CN) is much deeper than for NbC, which is directly due to the effect of the mixing of binary compounds. Therefore, for the same undercooling, the mixing of carbides and nitrides significantly increases the driving forces for nucleation. This may explain the experimental results [131] that the required supercooling for precipitation of NbC in Fe-Nb-C steels is much larger than that for Nb(CN) in Fe-Nb-C-N steels.

Fig. 5.10.b shows the calculated radius of the critical nucleus as a function of temperature. According to classical nucleation theory, the critical radius is inversely proportional to the chemical driving force. Fig. 5.10.b demonstrates that the calculated critical nucleus size is not very sensitive to initial compositions at the aging temperatures. For example in steels 2 to 4 which have different initial compositions, the calculated critical sizes are about the same at 1000°C.
CHAPTER VI

PRECIPITATION KINETICS

In the previous chapter we have considered an essentially equilibrium approach to study the compositions and mole fractions of the complex carbonitrides in microalloyed steels. In metallurgical practice, however, systems are rarely given time to attain their equilibrium condition as for example in thermomechanical processing. It is thus essential to bring kinetics into the model. Diffusion of the alloying elements will of course play an important role in cases where time is limited.

It is now the further intention to establish a model to predict the growth kinetics of carbides, nitrides and carbonitrides, and composition variation within the precipitates, for steels containing low levels of Nb, Ti, C and N. That is, given a steel composition and temperature, we would like to estimate the precipitate growth process, composition distribution within the particles and precipitate volume fraction with time.

6.1 KINETICS OF NUCLEATION OF NBC (TINB)C AND (TINB)(CN) IN AUSTENITE

6.1.1 Nucleation Rate

Nucleation, the first stage of carbcnitride precipitation, has received
less attention both theoretically and experimentally. It is only recently that Dutta and Sellars [116] have proposed a kinetic model for NbC and Nb(CN) precipitation by conversion of N to equivalent of C based on classical nucleation theory, and Liu and Jonas [137] further developed a modified model for Ti(CN) precipitation. In this section we will follow their approach to develop a model for (TiNb)(CN) precipitation.

The equations for the steady state \( J_s \) and transient \( J(t) \) rates of nucleation \( \text{nuclei/m}^3 \text{s} \) are expressed by the classical theory of diffusion controlled nucleation in solids as [138,139]

\[
J_s = Z\beta^*N \exp \left[ -\frac{\Delta G^*}{k_B T} \right] \tag{6.1}
\]

\[
J(t) = J_s \exp \left[ -\frac{\tau}{t} \right] \tag{6.2}
\]

where \( Z \) is Zeldovich non-equilibrium factor, \( \beta^* \) is the rate at which atoms or molecules are added to the critical nucleus, \( N \) is the number of atomic nucleation sites (of a particular type) per unit volume, \( \Delta G^* \) is Gibbs free energy upon forming the critical nucleus, \( \tau \) is the incubation time for establishing steady state nucleation conditions and \( k_B T \) is Boltzmann's constant times absolute temperature. Although the form of the equations for \( J_s \) and \( J(t) \) do not change, the quantities \( Z \), \( \beta^* \), \( \Delta G^* \) and \( \tau \) are all specific to the system and to the type of nucleation process considered. They must be developed on something of an individual basis. For homogeneous nucleation in the absence of crystallographic effects the parameters \( Z \), \( \beta^* \), \( \Delta G^* \) and \( \tau \) can be written as follows [139]:

\[
Z = \frac{V_p \Delta G^2}{8\pi (k_B T K \sigma^3)^{1/2}} \tag{6.3}
\]
\[ \beta^* = \frac{16\pi\sigma^2 D_M X_M L}{a^4 \Delta G_v^2} \]  

(6.4)

\[ \Delta G^* = \frac{16\pi K \sigma^3}{3(\Delta G_v - \Delta G_s)^2} \]  

(6.5)

\[ \tau = \frac{8k_B T K \sigma a^4}{D_M X_M V^2 \Delta G_v^2 L} \]  

(6.6)

where \( a \) is matrix lattice parameter, and \( K \) and \( L \) are factors describing morphology of critical nuclei, \( D_M \) and \( X_M \) are the diffusivity and concentration of the slowest-diffusing solute (i.e. the rate controlling element like Ti and Nb). For a cap shaped morphology, \( K \) and \( L \) are written as

\[ K = \frac{1}{4} (2 - 3 \cos \theta + 4 \cos^2 \theta) \]  

(6.7)

\[ L = (1 - \cos \theta) \]  

(6.8)

where \( \theta \) is the contact angle between a carbonitride and austenite grain boundary. \( \Delta G_s \) is the misfit strain energy per unit volume of precipitate. The parameter \( \Delta G_v \) is the volume free energy change upon forming critical nuclei, i.e. the chemical driving potential for nucleation as described in §5.3.

Nucleation may occur homogeneously (at random on the available lattice sites) or heterogeneously (catalyzed by defects such as interfaces and dislocations). In practice, the emphasis should be on developing simple, reasonably accurate rate equations which may easily be employed to compare with or to predict experimental behaviors. For diffusion controlled nucleation in dilute substitutional solutions, the derivation of the induction period gave an expression
of the form [138]:

\[ Z\beta^* = \frac{D_M X_M}{a^2} \]  \hspace{1cm} (6.9)

Diffusion data in Table 6.1. by several authors show that in the temperature range of interest diffusivities of interstitials are 4 to 6 orders of magnitude faster than those of substitutional elements. Therefore, the rate-limiting elements are expected to be Nb and Ti. This simplified form of \( Z\beta^* \) will be adopted in our simulation and the resulting expressions are substantially simplified. Therefore the steady state nucleation rate \( J_s \) can be expressed as

\[ J_s = \frac{N}{a^2} D_M X_M \exp \left(-\frac{\Delta G^*}{k_B T} \right) \]  \hspace{1cm} (6.10)

for NbC

\[ J_s = \frac{N}{a^2} D_{Nb}^{o} X_{Nb} \exp \left(-\frac{Q_{Nb}}{RT} \right) \exp \left(-\frac{\Delta G^*}{k_B T} \right) \]  \hspace{1cm} (6.11)

where \( D_{Nb}^{o} \) and \( Q_{Nb} \) are the diffusion frequency factor and activation energy of Nb in austenite, respectively.

However for the nucleation of \((Ti_xNb_{1-x})C\) and \((Ti_xNb_{1-x})(C_yN_{1-y})\), both Ti and Nb are the rate limiting elements. Analogously to the above considerations, Eq.(6.11) can be modified for precipitation of these complex carbonitrides as

\[ J_s = \frac{N}{a^2} (xX_{Ti} D_{Ti} + (1-x)X_{Nb} D_{Nb}) \exp \left(-\frac{\Delta G^*}{k_B T} \right) \]  \hspace{1cm} (6.12)

where \( x \) is the Ti/(Ti+Nb) atomic ratio in the critical nuclei as defined in §5.3.

6.1.2 Estimation of Precipitation Start Time

Lattice parameters of austenite and carbides/nitrides show that there is
more than a 20% mismatch in lattice spacings. Therefore, carbonitride precipitate surfaces are expected to be incoherent with the austenite matrix. Accordingly the misfit strain energy, $\Delta G_s$, may be neglected.

Two types of nucleation mechanisms can be considered for the homogeneous precipitation of a new phase which is different in composition than the matrix. One is the growth of embryos possessing the same composition as the stable phase; the other is the condensation of solute atoms in solute-rich atom groups which are formed by the fluctuation of composition. The first mechanism is chemically impossible for the nucleation of carbonitrides in the Fe-M$_j$-X$_j$ systems due to the high interfacial energy, since $\Delta G^*$ is proportional to $\sigma^3$. The second seems tenable but is also of low probability for homogeneous nucleation because of the large difference of composition between the carbonitride and the matrix. Accordingly, nucleation will most likely be triggered by the fluctuation of composition at defects, particularly at edge dislocations (jogs). The density of precipitates will depend on the frequency whereby the fluctuation of composition at defects is large enough to represent a stable new phase. In the present case, it can be assumed that nucleation take place mainly on dislocations. For incoherent nucleation at dislocations [138]

$$\Delta G^* = \frac{16\pi \sigma^3 F}{3(\Delta G_v^2)}$$  \hspace{1cm} (6.13)

where $F \ll 1$ is a modifying factor that arises for nucleation at dislocations due to the release of the strain energy of the lattice. $F$ of course equal to unity for homogeneous incoherent nucleation in the matrix.

In the case of nucleation on dislocations, the volumetric nucleation site density, $N$, equals the dislocation line density, $\rho_d$, multiplied by the number of
sites per unit length corrected for geometry, viz,

\[ N = \sqrt{2} \rho_d / a \]  \hspace{1cm} (6.14)

For a typical quenched steel with a lath martensite structure in this study, \( N \approx 5 \times 10^{25} / \text{m}^3 \) [146], which is a factor of \( \sim 10^4 \) less than for homogeneous nucleation. Considering that a critical number \( N^* \) of nuclei per unit volume must be formed in time \( t_s \) for nucleation to be detected, then

\[ t_s = \frac{N^*}{J(t)} \]  \hspace{1cm} (6.15)

This expression is a good approximation as long as the precipitate volume fraction is sufficiently small at the time \( t_s \).

From diffusion theory, Shewmon [147] gave the following simplified expression for the incubation time

\[ \tau = \frac{1}{2Z^2 \beta^*} \]  \hspace{1cm} (6.16)

For homogeneous nucleation of second phase particles \( \tau \approx 100 \) sec. But for heterogeneous nucleation, \( \tau \) is decreased greatly. According to our experimental observations, the incubation times for carbonitride precipitation in the present treatment are less than one second and so can be neglected whence \( J(t) \) can approximately be \( J_s \) and Eq. (6.15) can be rewritten as

\[ t_s \approx \frac{N^*}{J_s} \]  \hspace{1cm} (6.17)

For \((\text{Ti}_x\text{Nb}_{1-x})\text{C}\) and \((\text{Ti}_x\text{Nb}_{1-x})(\text{C}_y\text{N}_{1-y})\)
\[ t_s = \frac{N^*}{N} a^2 \{ X_{Ti} D_{Ti} + (1-x)X_{Nb} D_{Nb} \}^{-1} \exp \left( \frac{\Delta G^*}{k_B T} \right) \]  

(6.18)

Following Dutta and Sellars [116] for NbC precipitation in the Fe-Nb-C matrix

\[ t_s = C \ \frac{X_{Nb}^{-1}}{\exp \left( \frac{270000}{RT} \right) \exp \left( \frac{B}{T^3 (1n\ k_s)^2} \right)} \]  

(6.19)

where \( k_s \) is the supersaturation ratio, \( C = 1 \times 10^{-13} \) (if \( N^*/N = 0.1 \)) and \( B = 16\pi F_0^3 V_p^2 N_o/3R^3 \) (\( N_o \) is the Avogadro constant). In this way, \( t_s \) can be considered as the overall onset of the complex carbonitride precipitation at the expense of matrix solute.

6.2 KINETICS OF PRECIPITATE GROWTH

It is much more difficult to deal with multicomponent diffusion involving a moving boundary than involving the single phase problem with a stationary boundary. The many variables complicate the diffusional precipitation kinetics to an extent that analytic mathematical solutions are infeasible. Thus the appropriate methodology for theoretical prediction of precipitation behavior in microalloyed steels is by numerical integration using a computer. The numerical treatment of diffusion controlled phase transformation in multicomponent alloys involves the simultaneous solution of a set of diffusional, equilibrium and mass balance equations. These equations are non-linear and transcendental so iterative methods have to be used.
6.2.1 Simulation of Carbide and Nitride Precipitation in the Fe-M-X Alloys

6.2.1.1 Assumptions and Mathematical Formulations

Consider a ternary Fe-M-X system and select M and X as the independent components, i.e., consider solute M and X in solvent Fe. At temperature $T_1$, a specimen of uniform composition ($C_M^0$, $C_X^0$) is in a single-phase $\gamma$ region. This specimen undergoes an instantaneous quench to room temperature and is then up-quenched to a temperature $T_2$, at which the composition ($C_M^C$, $C_X^C$) is in a two-phase, $\gamma$-Fe + MX, field. The problem is to investigate the diffusional growth of carbide/nitride precipitates in the matrix.

After up-quenching to the transformation temperature $T_2$, the supersaturated austenite will contain a high density of heterogeneous nucleation sites. For simplicity we assume that all nuclei form right at the beginning of precipitation (i.e., site saturation) and possess the same growth rate as illustrated in Fig.6.1. The MX particles are very fine and well-separated in comparison with their sizes. These particles will be approximated as spheres, although they may actually in some cases be discs and cubes in shape. The precipitate particles are actually randomly distributed but it is not unreasonable to approximate this configuration by a uniform distribution forming a face-centered cubic space lattice, i.e. Wigner-Seitz array (Fig.6.2). According to the above simplifying assumptions, all MX particles are of the same size and are uniformly spaced. The Fe-M-X matrix is taken to be divided into equi-sized cells such that diffusion between cells does not occur, i.e., $\nabla C$ will be zero across cell walls. Therefore by symmetry there will be no net flux into or out of each cell. The problem of precipitation kinetics is thus simplified so as to require dealing with only one cell.
6.2.1.2 The Growth of Spherical $M_{X_{y}}$ Precipitates

From the foregoing model, the mathematical description of the solution can be further simplified without significant loss of accuracy if the cell boundary consisting of segments of planes is replaced by a sphere of equivalent volume. The radius of this equivalent sphere is denoted as $R_o$ as shown in Fig.6.2. Then it can be assumed that the diffusive field around a precipitate has spherical symmetry.

The growth of a precipitate is achieved by the motion of the MX and matrix interface caused by a net flux of matter across the interface with due regard to the difference in partial volumes between the two.

A further assumption is made that local equilibrium is maintained at the precipitate/matrix interface. For the local equilibrium condition, the interface composition, $X_M^e$ and $X_x^e$, depends on the condition set by the capillarity dependent solubility product, viz.

$$X_M^e X_x^e = K_{MX}^e = K_{MX_y}^e \exp \left( \frac{4\sigma V_p}{RT r} \right)$$  \hspace{1cm} (6.20)

where $K_{MX_y}^e$ is the solubility product for a spherical carbide (i.e. with the inclusion of capillarity effect).

Now let us consider the initial period of precipitation when the diffusion field is small relative to the size of the equivalent sphere. In addition, we note that the relative supersaturation, $k(t)$, of $M$ is

$$k(t) = \frac{C_M^o - C_M^e}{C_M^p - C_M^e}$$  \hspace{1cm} (6.21)

where $C_M^p$ is the $M$ concentration in the carbide particle. One should be aware that $C_M^e$ varies as a function of time and the same for $k(t)$. Then by the mass balance, we
can see that the radius, \( \varphi(t) \), of the spherical precipitate will advance at a rate much slower than the expansion of the surrounding diffusive field because \( k(t) \ll 1 \). Consequently, we can assume that the actual solution near \( \varphi(t) \) can be approximated by a quasi-steady solution with fixed boundary within each time increment. This solution will satisfy the boundary conditions

\[
C_M = C_M^0, \quad \text{at } r = R_o
\]

(6.22a)

and

\[
C_M = C_M^c, \quad \text{at } r = \varphi(t)
\]

(6.22b)

The diffusion equation in spherical coordinates will be

\[
\frac{\partial C_M}{\partial t} = D_{MM} \left[ \frac{\partial^2 C_M}{\partial r^2} + \frac{2}{r} \frac{\partial C_M}{\partial r} \right]
\]

(6.23)

For the quasi-steady state, this has the following solution

\[
C_M = A + \frac{B}{r}
\]

(6.24)

where \( A \) and \( B \) are constants to be determined by the boundary conditions. Using the given boundary conditions and assuming \( \varphi(t) \ll R_o \) we obtain

\[
C_M = C_M^0 - \frac{(C_M^0 - C_M^c) \varphi(t)}{r}
\]

(6.25)

where the sphere radius \( \varphi(t) \) is a very slowly varying function of time.

The flux of \( M \) at the interface is

\[
J_M \bigg|_{r=\varphi} = -D \frac{\partial C_M}{\partial r} \bigg|_{r=\varphi} = -D \frac{C_M^0 - C_M^c}{\varphi}
\]

(6.26a)
or

\[ J_M = -\frac{D_{MM}}{V_m} (X^o_M - X^e_M) \frac{1}{\phi} \]  
(6.26b)

where \( V_m \) is the molar volume of the matrix. Referring to Eq.(2.46), we obtain

\[ J_x = -\frac{D_{xx}}{V_m} \left[ (X^o_x - X^e_x) - \varepsilon_x^e M X^e_x (X^o_M - X^e_M) \right] \frac{1}{\phi} \]  
(6.26c)

Taking account of the stoichiometry \( y \) in \( MX_y \), the fluxes at the interface are related as follows

\[ J_x + vC_x^e = y (J_M + vC_M^e) \]  
(6.27a)

where \( v \) is the growth rate. Compared with \( J_x \), the \( vC_x^e \) term can be neglected. Then the equation is rewritten to

\[ J_x = yJ_M \]  
(6.27b)

Combining Eq.(6.20) and Eqs.(6.26b,c) with (6.27b), one obtains the family of equations

\[ X^e_M X^e_x = a \]  
(6.28a)

and

\[ bX^e_x + cX^e_M = d \]  
(6.28b)

where

\[ a = K_{MX}^* \]  
(6.29a)

\[ b = 1 - \varepsilon_x^e X^o_M \]  
(6.29b)

\[ c = -y \frac{D_{MM}}{D_{xx}} \]  
(6.29c)

\[ d = X^o_x - y \frac{D_{xx}}{D_{MM}} - \varepsilon_x^e K_{MX}^* \]  
(6.29d)
Applying the conservation of solute M to the whole particle of volume \( V = \frac{4}{3} \pi \varphi^3 \) and surface area \( A = 4 \pi \varphi^2 \) we have

\[
\frac{dM_M}{dt} = (C^e_M - C^p_M) \frac{dV}{dt} = A(-J_M)
\]

(6.30a)

i.e.

\[
(C^e_M - C^p_M) \frac{d}{dt} \left[ \frac{4}{3} \pi \varphi^3 \right] = 4 \pi \varphi^2 D_{MM} (C^o_M - C^p_M) \frac{1}{\varphi}
\]

(6.30b)

The velocity of growth of spherical precipitates will therefore be

\[
v = \frac{d\varphi}{dt} = k(t)D_{MM} \frac{1}{\varphi}
\]

(6.31a)

or

\[
d\varphi = k(t)D_{MM} \frac{1}{\varphi} \, dt
\]

(6.31b)

Eq.(6.31b) can be now used for the evaluation of \( \varphi(t) \) by numerical integration methods.

The average spacing between particles in practical steels is expected to be around 100 nm. Therefore, the M diffusional field of two particles can impinge as little as in less than one second at the aging temperatures. Consequently it is more accurate to replace initial compositions of \( X^o_M \) and \( X^o_X \) at the cell boundary with the average compositions \( \bar{X}_M \) and \( \bar{X}_X \) which are obtained from the following equations.

\[
\bar{C}_M = \frac{V_{cel l} C^o_M + V_{ppt} C^p_M}{V_{cel l} + V_{ppt}}
\]

(6.32)
where $V_{\text{ppt}}$ is the average precipitate volume in one cell, $V_{\text{cell}}$ is the volume of a single cell. Since $V_{\text{cell}} \gg V_{\text{ppt}}$ and $C_i = X_i/V_m$, we have

$$\bar{X}_M = \frac{V_{\text{cell}} X^o_M - V_{\text{ppt}} X^p_M}{V_{\text{cell}}} = X^o_M \cdot \frac{V_{\text{ppt}}}{V_m} \left(\frac{\phi}{R_o}\right)^3 \quad (6.33a)$$

Similarly,

$$\bar{X}_X = X^o_X \cdot y \frac{V_{\text{ppt}}}{V_m} \left(\frac{\phi}{R_o}\right)^3 \quad (6.33b)$$

This will be compared with the finite difference method in a later section.

6.2.2 Simulation of Complex Carbonitride Precipitation in the Fe-M$_i$-X$_j$ Alloys

6.2.2.1 Multicomponent Diffusion Equations

According to Onsager's form of the thermodynamics of irreversible process, the generalized multicomponent diffusion equations for an n-component system (n is the solvent) can be written as

$$J_i = -\sum_{j=1}^{n-1} D_{ij} \nabla C_j \quad (6.34)$$

For dilute Fe-M-X ternary systems ($X_m, X_x \ll 1$), it has been shown [105] that

$$D_{XM} \approx \varepsilon_{X}^{X} X_{x} D_{xx} \quad (6.35a)$$

$$D_{MX} \approx \varepsilon_{X}^{X} M_{x} D_{MM} \quad (6.35b)$$

Where the $\varepsilon_i^j$ are the constant Wagner interaction parameters. It should be a very
good approximation to extend this formula to dilute Fe-Ti-Nb-C-N pentenary system, that is

\[ D_{ij} = \varepsilon_{ij}^{i} D_{ii} \]  

(i \neq j) \hfill (6.36)

In this system, the fact that \( D_{xx} \gg D_{mm} \) assures that the effect of \( D_{xm} \) on the interstitial fluxes will be large and that of \( D_{mx} \) on the corresponding substitutional fluxes can be neglected. \( D_{cn}, D_{nc}, D_{nbt_i}, \) and \( D_{tiny} \) can also be neglected since the cross interactions between Ti and Nb, and C and N are moderated by the near equality of on-diagonal \( D \)'s. Thus the fluxes can be approximately represented as:

\[ J_{C} = - D_{cc} (\nabla C_C + \varepsilon_{Ti}^{Ti} X_C \nabla C_Ti + \varepsilon_{Nb}^{Nb} X_C \nabla C_{Nb}) \]  \hfill (6.37a)

\[ J_{N} = - D_{nn} (\nabla C_N + \varepsilon_{Ti}^{Ti} X_N \nabla C_Ti + \varepsilon_{Nb}^{Nb} X_N \nabla C_{Nb}) \]  \hfill (6.37b)

\[ J_{Ti} = - D_{ni} \nabla C_{Ti} \]  \hfill (6.37c)

\[ J_{Nb} = - D_{nb} \nabla C_{Nb} \]  \hfill (6.37d)

With these diffusion equations in mind we can now proceed the computer modelling.

6.2.2.2 Computer Modelling of the Growth of (TiNb)(CN) Precipitates

A finite difference model will be developed for predicting the growth of complex carbonitride precipitates in microalloyed austenite and compared with the previous model in a later section. This proposed model is based on most of the assumptions in previous model as summarized below

1). The rate of the precipitation process is controlled by the volume diffusion of the Ti, Nb, C and N atoms in austenite.
2). Local equilibrium, including the effect of capillarity, holds at the interface.

3). The particles are spherical.

4). The interfacial energy, \( \sigma \), is a constant.

5). There is no diffusion within the particle.

It is also assumed that all the nuclei form immediately after the up-quenching with the same growth rate and are uniformly distributed in the form of Wigner-Seitz array (Fig.6.2) such that the fluxes vanish at the cell limits \( (R_o) \). The problem is again simplified, so one needs to deal with only one cell.

Following the method of Voice and Faulkner [148] for carbide dissolution, a modified computation process is constructed subject to the above assumptions. In one cell a carbonitride nucleus is considered to exist in a matrix of initial uniform compositions of \( C^0_{Ti} \), \( C^0_{Nb} \), \( C^0_C \) and \( C^0_N \) (Fig.6.3.a). The \( Fe-M_i-X_j \) matrix is theoretically divided into shells of equal thickness radiating from the center of the particle (usually of the order of 2 nm thickness). An initial concentrations of solutes \( M \) and \( X \) are then assigned to each shell, irrespective of whether it is in a particle or matrix region (Fig.6.3.b). The one-dimensional form of Eqs.(6.37) is modified to the three-dimensional reality by weighting diffusion from one shell \((i+1)\) to \(i\) across the spherical interface of local area \(A_i\). Accordingly the solute transferred through the interface \(A_i\) can be presented by

\[
\text{ith solute transferred/\(\Delta t\) = } J_i A_i = - A_i \sum_{k=1}^{4} D_{ik} \frac{dC_i}{dx} \tag{6.38}
\]

where \(dC_i/dx\) is the concentration difference/shell width, and \(\Delta t\) the time interval. This equation may be approximated by replacing \(C_i\) by \(X_i/V_m\) whence
ith solute transferred/\Delta t = - \frac{A_i D_i}{V_m \Delta x} \left\{ \left[ X_{i+1}^i - X_i^i \right] + \sum_{j=1}^{4} \varepsilon_{ij} \left[ X_{i+1}^j - X_i^j \right] \right\}. \quad (i \neq j) \quad (6.39)

where subscript \( i \) stands for the ith shell, superscript \( i \) and \( j \) stand for the ith and jth elements (e.g. \( X_i^j \) is the mole fraction of jth solute in the ith shell), \( \Delta x \) is the thickness of the shell, and the \( V_m \) is the molar volume of the austenite matrix. The transferred solutes are subtracted uniformly from the (i+1)th shell and added to the ith shell when its atoms transfer to the (i-1)th shell in a similar way, and finally the diffused solutes are added to the particle surface. Diffusion to the interface is carried out in a time interval, \( \Delta t \), determined by the stability requirements of the computation. This process maintains an even concentration profiles and is repeated until an iterative equilibrium is reached (as in Fig.6.3.c).

The fluxes of \( M \) and \( X \) at the austenite/precipitate interface can be written approximately in accord with Eq.(6.37) as

\[
J_C = - \frac{D_C}{V_m} \left\{ \frac{X_C - X_C^*}{\Delta x} \right\} \quad \left( \frac{X_{Ti} X_{Ti} - X_{Ti}^*}{\Delta x} \right) + \frac{\varepsilon_{Ti} \varepsilon_{Ti} X_{Ti} X_{Ti}^*}{\Delta x} + \frac{\varepsilon_{Nb} \varepsilon_{Nb} X_{Nb} X_{Nb}^*}{\Delta x} \quad (6.40a)
\]

\[
J_N = - \frac{D_N}{V_m} \left\{ \frac{X_N - X_N^*}{\Delta x} \right\} + \frac{\varepsilon_{Ti} \varepsilon_{Ti} X_{Ti} X_{Ti}^*}{\Delta x} + \frac{\varepsilon_{Nb} \varepsilon_{Nb} X_{Nb} X_{Nb}^*}{\Delta x} \quad (6.40b)
\]

\[
J_{Ti} = - \frac{D_{Ti}}{V_m} \left\{ \frac{X_{Ti} - X_{Ti}^*}{\Delta x} \right\} \quad (6.40c)
\]

\[
J_{Nb} = - \frac{D_{Nb}}{V_m} \left\{ \frac{X_{Nb} - X_{Nb}^*}{\Delta x} \right\} \quad (6.40d)
\]

where the local equilibrium compositions \( X_i \) are assigned to the shell next to the
particle and the $X_i^*$ are the compositions of solutes in the second shell next to the austenite/precipitate interface.

The stoichiometry restrictions in $(\text{Ti}_x \text{Nb}_{1-x})(\text{C}_y \text{N}_{1-y})$ require that the diffusional fluxes at the precipitate/matrix interface must satisfy the following three equations

$$(1-x) \left[ J_{\text{Ti}} + vC_{\text{Ti}}^e \right] = x \left[ J_{\text{Nb}} + vC_{\text{Nb}}^e \right] \quad (6.41a)$$

$$(1-y) \left[ J_{\text{C}} + vC_{\text{C}}^e \right] = y \left[ J_{\text{N}} + vC_{\text{N}}^e \right] \quad (6.41b)$$

$$\left[ J_{\text{Ti}} + vC_{\text{Ti}}^e \right] + \left[ J_{\text{Nb}} + vC_{\text{Nb}}^e \right] = \left[ J_{\text{C}} + vC_{\text{C}}^e \right] + \left[ J_{\text{N}} + vC_{\text{N}}^e \right] \quad (6.41c)$$

However, for microalloyed steels the $vC_{i}^e$ terms make a much smaller contribution compared with $J_i$ and can be neglected. Then the expressions are simplified to

$$(1-x) \ J_{\text{Ti}} = x \ J_{\text{Nb}} \quad (6.42a)$$

$$(1-y) \ J_{\text{C}} = y \ J_{\text{N}} \quad (6.42b)$$

$$J_{\text{Ti}} + J_{\text{Nb}} = J_{\text{C}} + J_{\text{N}} \quad (6.42c)$$

Eqs.(5.21a-c) and (6.42) are six equations in six unknowns ($x$, $y$ and four $X_i$) which can be solved numerically by jointing with Eqs.(6.37). By applying the conservation of M solutes to the whole particle, the velocity of growth of a spherical (TiNb)(CN) precipitate will therefore be

$$v(C_{\text{Ti}}^p + C_{\text{Nb}}^p) = \left[ J_{\text{Ti}} + vC_{\text{Ti}}^e \right] + \left[ J_{\text{Nb}} + vC_{\text{Nb}}^e \right] \quad (6.43)$$

where $C_{\text{Ti}}^p = \frac{x}{V_p}$ and $C_{\text{Nb}}^p = \frac{1-x}{V_p}$; and neglecting $vC_{i}^e$ gives
\[ v = \frac{dr}{dt} = V_p (J_{Ti} + J_{Nb}) \]  \hspace{1cm} (6.44)

Eqs.(5.21a-c) and (6.42) are solved at the beginning of each time increment \( \Delta t \), and at the same time the fluxes at the interface are calculated by Eq.(6.40). After the solution of the equilibrium and diffusion equations, the position of the interface is then updated by Eq.(6.44) simply adding \( v \Delta t \) to the previous value, i.e., the precipitate size with time is obtained. Simultaneously the internal composition parameters, \( x \) and \( y \), at a certain position \( r \) in the Ti-Nb carbonitride particle are obtained.

6.3 COMPUTATION RESULTS

The six non-linear simultaneous equations which represent the local equilibrium and flux equalities at the austenite - (Ti\(_{\frac{x}{x}}\), Nb\(_{\frac{1-x}{1-x}}\), C\(_{\frac{y}{y}}\), N\(_{\frac{1-y}{1-y}}\)) interface are summarized as follows:

\[
RT\ln[X_{Ti} X_C] = \Delta G^0_{TiC} + RT\ln[xy] + \Delta G(1-x)(1-y) + \Omega_{CN} (1-y)^2 + \frac{4\sigma V_p}{r}
\]

\[
RT\ln[X_{Nb} X_C] = \Delta G^0_{NbC} + RT\ln[(1-x)y] - \Delta G(x)(1-y) + \Omega_{CN} (1-y)^2 + \frac{4\sigma V_p}{r}
\]

\[
RT\ln[X_{Ti} X_N] = \Delta G^0_{TiN} + RT\ln[x(1-y)] - \Delta G(1-x)(y) + \Omega_{CN} y^2 + \frac{4\sigma V_p}{r}
\]

\[
(1-x) J_{Ti} = x J_{Nb}
\]

\[
(1-y) J_C = y J_N
\]
\[ J_{\text{Ti}} + J_{\text{Nb}} = J_{\text{C}} + J_{\text{N}} \]

The Newton-Raphson technique was applied to solve the six non-linear simultaneous equations.

6.3.1 The Evolution of Composition Profiles of Solutes Across the Matrix

The computer output plots shown in Figs.6.4 to 6.7 represent the concentrations of solutes in terms of atom density (atom/nm\(^3\)) in the matrix to distance from the center of cell during the simulated growth (similar to Fig.6.3.c). The curves are plotted for different aging times. The starting points of the curves in the y direction, which is in fact close to the particle edge in the x direction, are the solute local equilibrium concentrations. It can be seen from these figures that the diffusion fields from two particles can overlap in one second. After the overlapping, it is much more difficult for new particles to nucleate due to the draining up of solutes. This suggests our original site-situation proposition that most precipitates will nucleate within a second.

The compositions at the interface are reduced quickly (some even below the final equilibrium levels) during the initial fast growth and recovered up when approaching equilibrium in some cases. This results from the fact that the C and N diffuse much faster than Ti and Nb. Therefore, their concentration profiles are almost flat, which depresses the Ti and Nb concentrations further at the interface in the early stages of carbonitride precipitation.

Consider the typical Nb profile in Fig.5.4. It can be seen that the austenite equilibrium Nb concentration at the precipitate-matrix interface is about half way between the initial and final equilibrium levels of Nb (1000°C at \( t = 0.1 \))
s for steel 3). This is due to the curvature effect of the small particle and leads to a reduced growth rate as shown in later section. As the particle grows, $C_{\text{Nb}}^e$ decreases quickly to a level which may be even below the final equilibrium concentration (also Ti profile in Fig.6.4), which in turn increases the Ti and Nb concentration gradients at the interface and accelerates the growth rate. As particle continues to expand, the gradients of the solutes in austenite decrease, which in turn results in the reduced growth rate of the particles. By the time of 60 s the growth at the expense of matrix solutes ends due to the vanishing of the concentration gradient. In this condition, the precipitates and the austenite reach a capillarity controlled thermodynamic equilibrium. In the actual cases of course, the equi-sized and spacing particles do not exist, and in long periods of time the continued growth, so-called Ostwald ripening, takes place with little change in particle volume fraction (see Ch.7).

By comparison of Figs.6.4 and 6.6, Figs.6.6 and 6.7, it can be seen that the less of solute level and the higher of aging temperature, the faster the equilibrium is reached.

### 6.3.2 Composition Profiles in the Complex Carbonitrides

Figs.6.8 and 6.9 show the predicted composition profiles within the complex carbonitride particles (i.e. $x$ and $y$ in $(Ti_x Nb_{1-x})(C_y N_{1-y})$). They indicate that the core of the particle is almost pure TiN, and as it is growing, the outer shell is richer in Nb and C. The experimental results (Fig.4.28 to 4.32) showed that the younger and smaller particles have a higher Ti composition, which to some extent indirectly support the predicted Ti and Nb composition profiles in the particles. These conclusions depend on the assumption that there is no diffusion of the Ti and
Nb in the carbonitride at the aging temperature. While calculations suggest that
the diffusion of Ti and Nb is negligible even in such small particles for very
short aging times.

During nucleation and growth, the composition of newly formed carbonitride
precipitates is determined by both the thermodynamics and kinetics of the solutes
(i.e. local equilibrium and diffusion). Depending on the temperature at which a
given particle has nucleated, its composition is the result of the balance of
equilibrium thermodynamics that determine the composition as a function of
temperature and the diffusional kinetics of the process that change the composition
as function of time. This can be understood qualitatively by noting that the matrix
has the highest supersaturation with respect to TiN, and also Ti diffuses faster
than Nb. Therefore, the nuclei or the core of the precipitates should have a higher
Ti and N content and low Nb and C. However, after Ti and N are depleted in the
matrix Nb and C become the major diffusion element, and the particles have a
NbC-rich shell.

6.3.3 Effects of the Diffusion Interactions

We have chosen to examine the effect of the multicomponent diffusion
interaction in the model in detail for steel 3. This was chosen for its expected
large cross effect. As a sensitivity test we have repeated the calculation setting
ε = 0 yielding the dashed line for the interstitials (Fig.6.5). For ε = 0, the C
and N profiles are almost flat. However, for ε ≠ 0 we note the expected depression
of the profiles C and N in the matrix matching the Ti and Nb profiles near the
interface, and this local redistribution of the interstitials is directly due to
the cross-interaction terms in the Eqs.(6.37). The Ti and Nb profiles (Fig.6.4) are
essentially independent of the cross-interaction. Fig.6.9 shows the effect of cross
interaction on the composition profiles in the particles. It is noted that the
cross-interaction has a stronger effect on the y profile in the carbonitride than
on the x one. As can be seen there is a significant multicomponent diffusion effect
on the interstitial profiles in the austenite and in the particle. However
calculation shows there is a very weak effect on the interface motion (growth rate)
since this is controlled by the slow-diffusing elements of Ti and Nb.

6.3.4 Precipitation-Time-Temperature Curves -- PTT Curves

The progress of an isothermal precipitation reaction can be conveniently
represented by plotting the fraction of precipitate \( f_p \) as a function of time, and
\( f_p \) may be defined as the volume of precipitate at any time divided by its final
volume. \( f_p \) varies from 0 to 1 from the beginning to the end of the reaction.
Figs.6.10 and 6.11 show the calculated volume fractions of particles as a function
of aging time in the four steels at 1000°C and 1100°C, respectively. They indicate
that most of the volume of precipitates comes out within 20 s, which is in good
agreement with the present experimental results. The equilibrium can be approached
in such short aging time because the high density of nucleation sites reduces the
solute diffusion distance. Unfortunately, it has not been so far possible to obtain
a accurate measurement of the volume fraction for these tiny particles.

The overall transformation kinetics of precipitation can be represented by
plotting the precipitation fraction \( f_p \) as a function of time and temperature,
i.e., a PTT diagram defined by \( f_p(t, T) \). Conventionally, the criteria of \( f = 5\% \) has
been chosen as the beginning point of a transformation. However for simplicity in
the calculation, we choose the forming of 10% nuclei \( (N^*/N = 0.1) \) as the starting
time, \( t_1 \), for precipitation.

The calculated \( t_1 \) for different F values on the four steels are shown in Figs.6.12 and 6.13. These curves are of the classical C-shape and illustrate that the temperature of the nose and the time to the nose for NbC in steel 1 are very sensitive to the value of F and therefore to the nature of the heterogeneous nucleation, but are less sensitive for (TiNb)(CN) in steels 2 to 4. This is because that the high undercooling of steels 2 to 4 and the effect of mixing binary compounds result much higher driving force for carbonitride nucleation which reduces the reliability of nucleation on defects. In comparison with experimental results in these figures, it can be seen that the reasonable fitting F values for NbC is 0.1 and for (TiNb)(CN) is 0.3, with their noses at minimum times of about 1.5 s at 1100°C for NbC; and the noses of (TiNb)(CN) are at minimum times of about 0.5 s at 1200°C much higher than that of NbC due to the same effects mentioned above. Combining with the computer program, the finished C curve for carbonitride particle at the initial stage of precipitation can be evaluated.

6.3.5 Comparison Between Predicted and Observed Growth Rates

The parameters used in the computations are estimated in the following ways. The molar volume \( V_p \) for NbC was calculated from the lattice parameter of NbC\(_{0.9}\) in reference [149], i.e., 1.340x10\(^{-5}\)m\(^3\)/mol. The diffusion coefficients and the interaction parameters in C, N, Ti and Nb in austenite are given in Tables 6.1 and 2.5. All the others are the same as adopted in §5.4. The corrected Ti, Nb, C and N concentrations in austenite at 1390°C (see Table 5.2) are employed as the initial compositions \( X_i^0 \). An integration shell spacing of 2 nm was used throughout the calculations, and a different time interval of 10\(^{-6}\) to 10\(^{-4}\)s was used depending
on the stability requirements of the computation. It is assumed that for our very thin samples (~0.5 mm) that the aging temperature is achieved instantaneously and that the kinetic barrier for nucleation is negligible (site saturation). The half spacing, $R_o$, between particles, is estimated to be 40 nm at 1000°C for four steels, and 45 nm at 1100°C for steel 1 and 50 nm for steels 2 to 4 according to following self-consistent method. Considering one cell, we have

$$Z = \frac{(V_{ppt}/V_p)}{(V_{cell}/V_m)}$$  

(6.45)

where $V_{ppt}$ is the average precipitate volume in one cell, $V_{cell}$ is the volume of single cell. Rearranging gives

$$R_o = \left(\frac{V_m}{ZV_p}\right)^{\frac{1}{3}} \bar{r}$$  

(6.46)

where the equilibrium mole fraction of carbonitride, $Z$, is calculated from Eqs.(5.21a-c) and (5.22) and $\bar{r}$ is assigned the value of the average particle radius for 60 s aging at 1000°C and 20 s aging at 1100°C obtained in this study. The critical radius of precipitate, $r_c$, is calculated from Eqs.(5.21a-c) by substituting the initial compositions $X_i^0$. We then set $r = 1.01 \, r_c$ to start the computation.

Figs.6.14 to 17 show the plots of the mean particle size against aging time in the fast growing stage for the two experimental temperatures (the error bars denote the standard deviation of the mean on about 200 particles). The solid lines are the growth rates calculated from the diffusion models proposed in this study. The predicted growth rate is close to that observed. Both the experimental and predicted results have proved that the rapid growth of NbC, and complex (Ti,Nb)C precipitates at the expense of matrix solutes lasts only about a minute and that the equilibrium volume fraction is approached in a very short aging
time; then the very slow coarsening process ensues. It should be noted here that the equilibrium is between austenite and newly precipitated particles with the exclusion of undissolved particles. Since the (TiNb)(CN) is the only stable precipitation phase with austenite at the aging temperatures, the equilibrium here is actually the quasi-equilibrium defined by the very slow kinetic process of composition and volume fraction change of undissolved large (TiNb)N particles.

As a sensitivity analysis for the effect of surface tension we have repeated the calculation setting \( \sigma = 0 \) and \( r_c = 0.1 \text{ nm} \) yielding the dashed line in Fig.6.16 at 1000°C. This calculation demonstrates that the inclusion of surface tension decreases the particle size by about 10% for the same aging time. After trying integration shell thicknesses of 0.5 and 1 nm, it was found that the particle growth rate is not very sensitive to the shell thickness (\( \leq 2 \text{ nm} \)).

In the calculations for all four steels, the same precipitate spacing, \( R_0 \), has been assumed for the same aging temperatures, i.e., the density of nucleation sites which is directly related to the dislocation density is assumed to be the same in the quenched specimens. This assumption is supported by the fact that approaching equilibrium after aging for about 60 s the average size of particles is larger in proportion to the concentration of the dissolved solutes (in the sequence of steels 1, 2, 3 and 4). Of course, the ratio of M to X is also an important factor affecting the molar fractions of precipitates.

There are a number of reasons why the predicted growth rate deviates slightly from that observed in some cases. For one thing the incubation time should not be ignored in the model. Experimental results show that the incubation time of precipitation at 1100°C is less than 3 s, and is larger than 3 s at 1000°C for steel 1; while for steels 2 to 4, the incubation time is less than 1 s and is larger than 1 s at 1000°C for steel 4. Secondly we have not made a correction for
the gradual heating to the aging temperature. For the very short aging times, the
temperature may not even reach the aging temperature by the end of aging period.
However, heat transfer data of iron suggest that it should take less than one
second to reach the aging temperature for up-quenching in a salt bath. Furthermore
in the semi-analytic model for NbC, another reason of deviation may be that using
the approximation $\Delta C/\varphi$ as composition gradient, which is close to the true gradient
for the shorter times (a few seconds), gives a value greater than the real value
after the onset of impingement of the diffusion field between two growing
particles. We have partially corrected for this error by the replacement of average
compositions for initial compositions at the cell boundary. On the other hand,
these potential errors are offset by the fact that dislocation densities and
quenched-in excess vacancy concentrations are very high in the quenched specimens
so that the nucleation and early growth of precipitates are enhanced before these
defects are annealed out.

Two growth models have been developed in this chapter, one is the
semi-analytic model applied to MX particles and the other is the finite difference
model applied to (TiNb)(CN) particles. According the Fig.6.14 for steel 1, the
first one gives a predicted growth rate slightly higher than that observed due to
the underestimation of diffusional impingements. The finite difference model can
overcome this limitation and yield a closer simulation of the observed growth (see
Fig.6.15 to 6.17). This model also gives more information, including the
concentration profiles of solutes across the matrix. However, the major
disadvantage of this model is that it requires much more computation time than the
first one. Therefore, the first model is suitable for a microcomputer without great
loss of accuracy and the second is suitable for mainframe application where
rigorous simulation is desired.
CHAPTER VII

DISCUSSION

The salient features of the experimental and modelling results can be briefly summarized as follows:

(a) In most cases the precipitate growth and coarsening are diffusion controlled. Both experimental results and prediction show that pre-coarsening growth at the expense of matrix solutes is very rapid and lasts about 60 s; then slow particle coarsening takes place.

(b) The detailed morphology of the precipitates have been studied. An evolution of carbonitride morphologies from an initial spherical shape to polyhedral and then in some cases to spherical again, and some to a cubic shape has been observed.

(c) A strong relationship between steel and particle compositions has been found and the size dependence of particle composition has been observed. The thermodynamic model has predicted that the higher is the temperature the higher is the Ti content in the carbonitrides. The kinetic model predicted that the cores of carbonitride precipitates are Ti rich and the outer layers are Nb rich in the steels studied.

It is the purpose of this chapter to try to explain these experimental results using as a basis the thermodynamic and kinetic modelling developed in Ch. 5 and 6. We also attempt to discuss in more general terms the diffusion within the particles, effects of cross interactions of solutes and the comparison of the
present experimental procedure with thermomechanical processing.

7.1 NUCLEATION, GROWTH AND COARSENING OF PRECIPITATES

The second phase precipitation from a supersaturated solid solution may generally be regarded as taking place in three stages:

1). The formation of nuclei of the second phase (assuming negligible incubation time).

2). Initially rapid growth at the expense of matrix solutes until the matrix contents reach nearly to equilibrium values (the termination of precipitation).

3). Capillarity-induced coarsening (or Ostwald ripening), where the larger, more stable particles grow by cannibalizing the smaller, less stable particles to decrease the total interfacial energy with the volume fraction of particles remaining approximately constant.

Consecutive or competing reactions may complicate this simple picture and in reality this sequence of events could be taken as a continuous (or even simultaneous) process.

7.1.1 Nucleation of Precipitates

It is widely known that carbonitride precipitation in microalloyed austenite takes place by diffusion controlled nucleation and growth. Understanding the nature of these processes is therefore important in designing the thermomechanical processing in order to obtain desirable microstructure and properties of steels. The calculated precipitation-time-temperature (PTT) diagrams
in Ch.6 show that heterogeneous nucleation is increasingly sensitive to defects for the low driving force which is common in thermomechanical processing.

Homogeneous incoherent nucleation in the matrix almost never occurs due to the high interfacial energy, since $\Delta G^*$ is proportional to $\sigma^3$. In practice heterogeneous nucleation exists in almost all phase transformations in solid solutions. The favorable nucleation sites are non-equilibrium defects such as excess vacancies, dislocations, grain boundaries etc., all of which increase the free energy of the material. If the creation of nucleation results in the destruction of defects, some free energy will be released thereby reducing the activation barrier for nucleation. Another important factor in nucleation at defects is the microsegregation of solute to defects which speed up the nucleation rate.

When an alloy is quenched from a high temperature, excess vacancies are retained during the quench. These vacancies can assist nucleation by increasing diffusion rates, or by relieving misfit energies (e.g., Al-Ge alloy [150]). From the alternative two-zone furnace treatment it seems that the excess vacancies themselves do not lead to the nucleation of carbonitrides in austenite, probably due to the large interfacial energy and the high volume strain energy between matrix and particles. In addition to contributions of this kind, dislocations can speed up nucleation by solute segregation which can raise the composition of the matrix nearer to that of the precipitate. The growth of an embryo beyond the critical size can also be enhanced by providing such a fast diffusion pipe.

The driving forces for NbC and (TiNb)(CN) nucleation were calculated with the aid of a thermodynamic model. With the adoption of effective compositions the results (see Fig.5.8) show that small amounts of remaining Ti and N in austenite can significantly increase the chemical driving force for (TiNb)(CN) nucleation
and thereby greatly accelerate the rate of precipitation.

7.1.2 Growth of Precipitates

In Ch.4 the observations show that the evolution of the particle size distribution during aging can be divided into two stages: growth and coarsening. The growth of a stable particle can only occur after its nucleation. In most cases of phase transformation, nucleation takes place gradually over a time period rather suddenly and completely at $t = 0$. This means that each precipitate present at time $t$ has undergone a different growth time. However, the present observations show that the incubation time is less than 1 s and the calculation suggests that the diffusion fields of two growing particles begin to overlap (soft impingement) after about 1 s, so that the saturation of the nucleation sites happens within 1 s in the present systems. Therefore, it is reasonable to neglect the incubation time in this theoretical study. The experimental results demonstrate that the initial growth of precipitates at the expense of matrix solutes is very fast until the matrix contents reach nearly to equilibrium values. Then the growth rate drops continuously until the excess solutes are exhausted and precipitation is finished. After this time, growth does not actually stop, but now proceeds by a coarsening process in which the larger particles grow at the expense of the smaller ones so to reduce the total interfacial energy. It is to be noted that the variation of the mean NbC and (TiNb)(CN) particle size during the initial fast growth stage followed the diffusion controlled growth law. This stage can be adequately predicted using the kinetic models proposed in this study. The growth rate starts to disobey this model at around 60 s which can be considered as the precipitation finish time and the time of onset of coarsening.
The sensitivity analysis for the effects of surface tension in Ch.6 shows that the inclusion of surface tension decreases the particle size by about 10% for the same aging time. This can be understood in the fact that the capillarity effect results in an increase of the equilibrium compositions in the matrix at the interface, thus this reduces the growth rate of precipitates due to the decrease of concentration gradient at the interface (see Fig.6.4). Secondly as discussed in §2.2.3, the surface tension reduces the "equilibrium" molar fraction of precipitates by about 10% for a average size of 5 nm.

7.1.3 Ostwald Ripening - Precipitate Coarsening

Since high curvature raises the surface chemical potential or concentration solute tends to flow from small to large particles and the latter to grow at the expense of the former. This process is called Ostwald ripening. The coarsening kinetics of second phase particles in the late stages have been investigated extensively, both experimentally and theoretically. It has been demonstrated [14,108,151-153] that the coarsening kinetics of MX particles can be adequately described by the Lifshitz-Wagner equation [125,126] in the general form of

\[ r^n - r_0^n = kt \]  

(7.1)

where \( n \) has the value of either 2, 3, 4 and 5 depending on whether the coarsening process is interface reaction controlled [125], bulk diffusion controlled [125,126], grain boundary diffusion controlled [154], or dislocation pipe diffusion controlled [154,155], respectively. It has been verified in many binary systems that the observed growth rate of second phase particles for the diffusion controlled case is well described by
where \( r_o \) is the average particle radius at the onset of coarsening, \( V_p \) the volume of the particle per one mole of alloying element \( M \), \( D_M \) the diffusivity of \( M \) atoms in matrix, \( X_M \) the solubility of \( M \) atoms and \( y \) the stoichiometric factor depending on the composition of precipitates. However for the growth of \( M_aX_b \) interstitial carbides in ternary Fe-M-X alloys, the equation must be modified to the following formulas [27]

\[
\bar{r}^3 - \bar{r}_o^3 = \frac{8(\alpha + \beta)\sigma V_p^2 D_M u_M^\gamma}{9aRT(u_C - u_M^\gamma)^2} t
\]  

(7.3)

where the \( u_M^C \) and \( u_M^\gamma \) are the concentration parameters in ternary alloys which are defined as [156]

\[
u_M = \frac{X_M}{1 - X_X}
\]  

(7.4)

Generalizing this equation to multicomponent systems such as considered in this study is a complex problem [153,157], involving a complicated interplay between thermodynamics, kinetics and mechanics, and it will not be discussed further.

Fig.7.1.a is a plot of the average particle size of NbC versus heating time for steel 1 during coarsening at 1000\(^\circ\)C and 1100\(^\circ\)C, the solid line is calculated from Eq.(7.3) and the up-triangle represents the experimental data. For the calculation \( u_M^\gamma \) is set to be 0.0002 and \( u_M^C \) to be 1 with reference to Wey [27] and \( \bar{r}_o \) to be 4 nm according to experimental data. This figure illustrates that the
diffusion controlled Ostwald ripening theory adequately describes the growth of NbC particles at 1100°C. However, the coarsening rate is extremely low at 1000°C (reaching 16.4 nm on the average after 200 hr). This may result from the limitation by a strong interfacial reaction, which is consistent with the stable polyhedral shapes observed throughout the aging.

The average particle size of (TiNb)(CN) in steels 2 to 4 as a function of holding times is shown in Figs.7.1.b and 7.2. The carbonitride coarsening rates in steels 2 and 3 at 1000°C and 1100°C are similar to that in steel 1. However when comparing these figures, it is to be noted with surprise that the particle growth rate in steel 4 is almost the same at 1000°C as for 1100°C. Furthermore, the carbonitride coarsening rate is higher at 1000°C in steel 4 than those in steels 1 to 3 and the rate is much slower at 1100°C in steel 4 than those in steels 1 to 3. Micrographs from the specimens in steel 4 (Fig.4.15) show that most of particles have transformed from a spherical shape to a cubic shape at 1100°C for 100 hr but only about half have transformed at 1000°C. It is believed that before the morphological transformation the coarsening rate of spherical carbonitrides in steel 4 is diffusion controlled. The observations indicate that the diffusion-controlled stage lasted about 100 hr at 1000°C; but this stage lasted about 10 hr at 1100°C and afterwards sluggish interface reaction controlled growth took place.

7.2 MORPHOLOGICAL EVOLUTION

Various morphologies of NbC and (TiNb)(CN) particles have been observed in this study (see Figs.4.2 to 4.15). Some typical morphologies of particles are
shown in Fig.7.3. An evolution from initial spherical particles to polyhedral and then some to spherical again and some to cubic was evident in this study.

The equilibrium shape of an isolated single particle (crystal) can be theoretically predicted from a $\sigma$-plot, which is usually expressed as the variation of interfacial energy, $\sigma$, with surface orientation in three dimensions. A section through such a plot is shown in Fig.7.4.a (the curved line). The equilibrium shape has the property that the total surface energy is minimum and the shape that satisfies this condition is determined by the so-called Wulff construction (in Fig.7.4.a [150]). When the $\sigma$-plot contains sharp cusps the equilibrium shape is a polyhedron with the largest facets having the lowest interfacial free energy (in Fig.7.4.b). Of course when $\sigma$ is independent of orientation, as for liquid droplets, both the $\sigma$-plot and equilibrium shapes are spheres.

A stability theory with the assumption of isotropic interfacial energy was applied by Mullins and Sekerka [158] to growing spherical precipitates. They found that the sphere is a stable shape below a critical radius ($R_c$) which is about seven times the critical radius for homogeneous nucleation. Above $R_c$ the sphere is unstable. In this study the estimate of $R_c$ is around 4 nm for NbC. Above this value instability may play a role in the formation of polyhedra which tend to be stable. During the initial fast growth stage, solutes diffuse strongly towards the nuclei and add to them uniformly at the nucleus/matrix interfaces. This rapid dynamic process makes the growing particle tend to be a spherical shape.

When coarsening starts, the driving force for growth is much smaller than in the precipitation stage and the particles tend to have the equilibrium shape. The possible stabilizing factor for the polyhedral shape is the extreme anisotropy of the $\sigma$-plot cusp orientations which will strongly stabilize the interface against perturbations. A cube-cube orientation has been found for carbides and nitrides in
\(\gamma\)-Fe [159].

The evolution of precipitates from initial spheres towards polyhedra (and finally back to spheres at 1100°C in steel 1) was apparent in this study. This proves that the morphologies of precipitates are determined not only by the interfacial surface energy, but also by transport and kinetic factors, as well as temperature. Indeed the experimental results in this study indicate that particle compositions, aging times and temperatures are the most important factors to determining the morphology of particles. Firstly the interfacial energy is dependent on particle compositions, which may significantly change the \(\sigma\)-plot of the carbonitride. In the present work the morphologies of particles are in fact correlated to the variations of particle compositions from NbC to (TiNb)C and (TiNb)(CN) in steels 1 to 4. The carbides and the carbonitrides with low N in steels 1 to 3 have spherical shapes at 1100°C for 100 hr and a polyhedral shape at 1000°C; on the other hand, for the carbonitrides with high Ti and N in steel 4 their final stable shape tends to be cubic at both 1100°C and at 1000°C for 100 hr. We can further differentiate the effects of aging temperature and time. As an example for different holding times, the results showed that there is a fast transition from the distribution of initially formed spherical particles to the faceted particles, and then gradual conversion back to spherical particles at 1100°C in steel 1, but the latest conversion has not happened at 1000°C. The final question is: to what extent are the morphologies influenced by the kinetics? We have no complete answer at this juncture.
7.3 DIFFUSION WITHIN THE CARBONITRIDE PARTICLES

In the present model it was assumed that there is no diffusion in the carbonitride particles, i.e., the overall composition of the particle cannot adjust to the changes in the composition of the surrounding matrix. It remains now to consider the validity of the assumption with respect to complex carbonitrides. Generally speaking, metallic compounds like carbides and nitrides possess extremely low diffusivities, as can be expected from their inherent ionic structure. The metallic atoms can only diffuse through their own sublattices, which results in diffusivities nearly ten orders of magnitude lower than in the austenite. Although for short aging time (< 60 s) the particle size is very small (~ 5 nm), the redistribution of Ti and Nb in the tiny compounds is still not likely due to the extremely low diffusivities of Ti and Nb in (TiNb)C presented in Table 4.1. From Saria and Yu data in Table 4.1, the redistribution of Ti and Nb in the carbonitride may only occur after a very long aging time at isothermal temperatures. On the other hand the diffusion of C and N in carbonitrides is much faster than for Ti and Nb. Therefore, the ratio of C and N in the growing particles can adjust by the diffusion of C and N within the carbonitride to reach a quasi-stationary state of equal activity in the particles.

Now let us consider the undissolved particles. If the undissolved particle is to adjust its composition during the aging, it can only do so by dissolving and reprecipitation or by preferential diffusion of Ti and Nb within the particles and exchange with the matrix as the particle grows or shrinks. During the growth at the expense of matrix solutes due to the quite short time and large particle dimensions, the former process cannot occur. Since the rate of diffusion of Ti and Nb in carbonitrides is extremely slow at the aging temperature, the latter process
seems unlikely for short aging times. But both processes may take place for very long aging times (say, 100 hr).

7.4 EFFECTS OF DIFFUSIVE CROSS INTERACTIONS OF SOLUTES

The sensitivity analysis in §6.4.3 shows that the multicomponent effects are fairly significant despite the low concentrations of alloy additions. The phase transformation modeler in complex multicomponent systems must always confront a decision whether or not to include diffusion cross-effects. One might conclude in the first instance that when the matrix concentrations are very low these effects can be neglected on account of relations (6.36) where the effect is seen to vanish with concentration. However, it must be noted that the interaction parameters are related to free energies of formation and therefore are not independent of the solubilities. Indeed they tend to lie in an inverse relation of magnitudes as can be seen from the present and the Fe-Mn-C example quoted in §2.3.3. We are therefore inclined to conclude that for every multicomponent problem, where the solubility limit is exceeded, including those associated with alloy oxidation or sulfidation, the matrix cross-effect must be included for predictive precision. This of course, is predicated upon the assumption that other parameters are sufficiently accurately known and that accurate modelling has a technological significance.

7.5 RELATIONSHIP BETWEEN STEEL AND PARTICLE COMPOSITIONS

In the thermodynamic equilibrium and kinetic growth models presented in Ch.5
and 6, it has been assumed that the carbonitrides are in complete or local equilibrium with microalloyed steels. However, all the results obtained in this study, aging at both 1000°C and 1100°C, show that the attainment of true (overall) equilibrium, particularly at low temperatures, is unlikely. In the experiments we have already noted that the coexistence of coarse TiN and fine (TiN)(CN) particles cannot correspond to a true equilibrium situation. On the other hand, the undissolved TiN cuboids are sufficiently coarse and widely dispersed that local equilibrium between the fine carbonitride precipitates and austenite can be effectively dictated by the remaining solutes in matrix.

In both models as in others [9-15], it has been assumed that in microalloyed steels there is complete mutual solid solubility of Ti, Nb, C and N in a single carbonitride precipitate species of the form $\left(\text{Ti}_x\text{Nb}_{1-x}\right)\left(\text{C}_y\text{N}_{1-y}\right)$. As discussed in Ch.2, the fact that binary carbides and nitrides precipitated in steels have a similar fcc lattice structure suggests that mutual solid solubility is likely to occur. The present study has again confirmed this belief. It has been found from direct measurement of a large number of particles from different microalloyed steels that not only do the particle compositions strongly reflect the compositions of the steels, but that the average composition can be predicted reasonably well from thermodynamic and kinetic models. In previous chapters it has been shown that these models provide a very good description of the particle compositions in steels 2 and 3 and these particles turn out to be close to be Ti-Nb carbides. For the precipitates in steel 4, the predicted particle compositions deviate somewhat from the experimentally determined particles compositions for various aging temperatures. Referring to Figs.4.27 to 4.33, the experimental results show that the measurement scatter of particle compositions in steel 4 ($x \sim 0.95$ to 0.6) is fairly large which is in sharp contrast to the situation in steel 2
(x \sim 0.7 \text{ to } 0.65) \text{ and steel 3 (x \sim 0.4 \text{ to } 0.2). For long aging times this large scatter is to be associated with the partial transformation of spherical and polyhedral particles to cubic particles. The non-uniform compositions through the particles, in particular for plate-like particles, is another contribution to the scatter. The cuboids and the centers of plate-like particles are strongly Ti and N rich, but the spheroids and two ends of plate-like particles contain less Ti and N. These observations may indicate that a partial phase separation (i.e. carbides-spheroids and nitrides-cuboids) is happening. This was also suggested by Houghton et al [128] and supported by theoretical calculation [160].

It is concluded that for the complex particles in the size range studied here the diffusion rate within particles may not be high enough to bring about homogenization of Ti and Nb within particles for short times. However, some homogenization within particles may be reached and/or the solutes exchange between particles and matrix may happen for very long aging time at 1100°C. If this happens, then the carbonitride particles of the size range analyzed should not normally exhibit significant concentration gradients and all the particles should have similar compositions. This is in contrast to the experimental observations and may be explained by phase separation which allows the coexistence of different morphological and compositional particles. Any future attempt to model the complex carbonitride precipitation reactions in microalloyed steels must account for this as well for the unknown kinetic factors discussed above.

7.6 THE SIZE DEPENDENCE OF PARTICLE COMPOSITIONS

It has been observed that in our microalloyed steels, particle compositions
can vary from particle to particle. In addition, the variations are strongly affected by steel composition. For example, a certain particle size dependence on composition is detected in steel 4 for short aging times (see Figs. 4.30 and 4.32). The variations of compositions in steel 4 for aging 100 hr are associated with the coexistence of two different particles; the net result of the two distributions give a fairly large dispersion of compositions for both x and y values. It is seen when comparing Figs. 4.30 to 4.32 that the particle size dependence on composition at the low aging temperature is more pronounced than at the higher temperature.

Indeed, it has been claimed [17,19] that precipitate particles in Ti-Nb steels exhibit corening, forming shells or caps of a more Nb-rich compound on Ti-rich cores. This may well be true when a large amount of undissolved TiN particles exist after solution treatment. During the subsequent rolling process very high dislocation densities could exist around the undissolved particles due to the tangling of dislocation around the particles. Therefore, the effective diffusion coefficient around the undissolved particles can be much higher than the volume diffusion. This makes nucleation and growth of a Nb rich layer on the remaining particles (TiNb)N very likely and detectable even within a short holding time. However in the present work there is no directly visible evidence of nucleation and growth of the fine carbonitride particles on the large undissolved cubic particles for short aging times.

7.7 CLOSING REMARKS

Although our thermo-cycle is not exactly the same as in thermomechanical processing in industry, the sequence of microstructure change is about the same as
that in practice. In thermomechanical processing, solution treatment is followed by rolling. In the rolling process, a tremendous amount of dislocations are produced; these dislocations are the favoured nucleation sites. Subsequently, two competing processes occur: one is precipitation of second phase particles (carbonitrides), the other is recrystallization of the deformed matrix. Which comes first will greatly affect the final microstructures. If recrystallization occurs early, then the large reconstituted austenite grains will lead to coarser final ferrite grains, which is not good for the overall properties. If precipitation come first, then the dense distribution of tiny particles can greatly retard the recrystallization, and maintain a fine austenite grain size which helps to form fine ferrite grains during the subsequent transformation. So far in the present studies, the experiments and the modelling have between focused to investigate how long it takes for the nucleation of carbonitride and how fast these particles grow in the isothermal processes. Consideration should now be giving to the simulation and prediction of the nucleation and growth kinetics of carbonitride in thermomechanical processing of microalloyed steels as in controlled rolling of HSLA steel plate. In this continuous cooling process the precipitation kinetics is a function of temperature, time and strain (and strain rate).

For Ti and Nb bearing HSLA steels, the carbonitride is typically described in the form of \((\text{Ti}_x\text{Nb}_{1-x})(\text{C}_y\text{N}_{1-y})\). The variation of transition element to light element ratios with temperature in this complex compound has been theoretically predicted and experimentally measured as shown in Ch.5.4. It can obviously be seen that titanium nitride tends to form at high temperatures and niobium carbide goes to completion at low temperatures. The advantages of the use of several microalloying elements are that Ti may be effective as a nitride former during reheat cycles and high temperature thermal cycling as in welding, while the
carbides of Ti and Nb may both contribute at low temperatures (below 1200°C) to stop austenite grain growth and retard recrystallization during thermomechanical processing.

It is well known that a decrease in the number of particles per unit volume leads to an increase in grain size. In the simplest form, the relation between grain size, \( \bar{R} \), the mean particle size, \( \bar{r} \), and volume fraction of particles, \( V_f \), can be described by the well known Zener equation [161], in the form

\[
\bar{R} = \frac{2\bar{r}}{3V_f}
\]  

(7.5)

This equation indicates that the average grain size is directly proportional to mean particle size and inversely proportional to the volumes of particles. According to this relationship used in the design of microalloyed steels, it is obvious that during thermomechanical processing the grain size control is essentially achieved by the stable precipitate compounds. The results of this study show that the use of several carbonitride forming elements can give the best combination, i.e. small particle sizes and a certain volume fraction of particles as well as improved coarsening resistance of particles.
CHAPTER VIII

CONCLUSIONS

In the present investigation, a detailed study of the morphologies, distributions, compositions, particle size distributions and the kinetic behaviors (nucleation, growth and coarsening) of complex carbonitride particles in microalloyed steels has been carried out using TEM and STEM-based high magnification micrographs and microanalysis. The chemical compositions of the extracted particles were extensively investigated by three complementary techniques: EDX, EELS and electron diffraction. A thermodynamic model of the complex carbonitride has been constructed to calculate the equilibrium compositions and mole fractions of carbonitride. Models of precipitate growth at the pre-coarsening stages have been developed based on thermodynamics and kinetics to predict the precipitation behavior of carbonitrides, mole fractions of precipitates and the composition distribution in the particles. The main conclusions from this work are summarized as follows:

8.1) An evolution of precipitate morphologies from an initial spherical shape to polyhedral and then in some cases to spherical again and some to a cubic shape was evident in this study. It was found that the morphologies of niobium carbide and titanium-niobium carbonitride precipitates are related to the particle size, aging temperature and time. Nearly all of the newly formed fine particles at short aging
times (< 60 s) approach sphericity. In steel 1 NbC particles less than 7 nm look fairly spherical, and particles over 7 nm have evident polyhedral shapes. However, when the size exceeds roughly 40 nm, the shape changes back to the spherical form (at 1100°C after 5 to 10 hr). In steels 2 and 3 for long holding times, almost all of particles have ripened to spherical shape. On the other hand in steel 4 for long times, the early formed spherical and polyhedral particles were slowly converted to the faceted cuboidal morphology. These results suggest that particle compositions, aging times and temperatures are as important as anisotropic surface tension determining the morphology of particles. The growth rates of NbC and complex (TiNb)(CN) are correlated with the morphologies. For spherical shapes, diffusion controlled growth dominates and the particle dimension increases quickly. On the other hand, for polyhedral and cubic shapes sluggish interfacial reaction governs the coarsening process and the precipitates ripen very slowly.

8.2) The growth of carbides and nitrides before coarsening can be predicted using the semi-analytical model proposed in this study. The model has been used to estimate the growth process of niobium carbides and gives satisfactory agreement with observed growth rate. Both experimental and predicted results suggest that the fast growth of NbC_y lasts only a few minutes, then slow coarsening occurs. This is interpreted as a changeover from fast diffusion growth to slow interfacial reaction coarsening since this change is associated with a shape change from spheres to polyhedra. Furthermore, the growth of (TiNb)(CN) particles prior to coarsening can be adequately predicted using the finite difference model proposed in this study. The results indicate that the carbonitrides increase their average sizes in a monotone way with aging time, growing quite rapidly to an average size of about ~5 nm within 30 s with the further growth (coarsening) being slow.
8.3) Ostwald ripening starts after the completion of precipitation and this process is likely to be controlled by the volume diffusion of metallic elements. The equation for the growth of carbides in the stage of Ostwald ripening for the diffusional controlled case adequately describes the ripening of pure NbC\textsubscript{y} particles at 1100°C which have spherical shapes. On the other hand, the carbides coarsen very little at 1000°C, a characteristic which is associated with a persistent polyhedral shape. The observed coarsening behaviors of (TiNb)(CN) in steels 2 and 3 are similar to that of NbC in steel 1. However, it is surprising to find that the particle coarsening rates in steel 4 is is about the same at 1000°C as at 1100°C. Furthermore, it was unexpectedly found that the carbonitride ripening rate is higher at 1000°C in steel 4 than those in steels 1 to 3 and that the rate is much slower at 1100°C in steel 4 than those in steels 1 to 3. This is associated with cubic shape.

8.4) The distribution of precipitates was found to be nearly random. However in some cases, clustering of particles occurred, which probably resulted from over-etching and settling. The factor that can account for the normal type of distributions is the existence of a relatively uniform dislocation density serving as nucleation sites in the quenched alloys.

8.5) The NbC particle size distributions at 1000°C have been found to be broader than predicted by theory. At the shorter heating times the deviation from the predicted distribution is small, but this increases with aging time. The particle size trends as a function of aging time in steel 4 indicate that the distribution shifts to larger average very rapidly and then changes very slowly as it widens.

8.6) The EDX (X-ray spectrum) output indicated that no Fe or other residual
elements exist in the particles analyzed. During aging in steels 2 to 4, only the complex carbonitride precipitates of the form \( (\text{Ti}_x \text{Nb}_{1-x})(\text{C}_y \text{N}_{1-y}) \) were found in the newly nucleated and growing particles due to the mutual solid solubility of carbides and nitrides. From the microdiffraction pattern, the \( \text{NbC}_y \) precipitates in steel 1 are identified approximately as \( \text{NbC}_{0.85} \). The undissolved cubic particles were identified by microanalysis as \( (\text{Ti}_{0.91} \text{Nb}_{0.09})(\text{C}_{0.1} \text{N}_{0.9}) \) in steel 3 and as \( (\text{Ti}_{0.95} \text{Nb}_{0.05})(\text{C}_{0.05} \text{N}_{0.95}) \) in steel 4 which are in good agreement with the predicted equilibrium composition for precipitates at the solution temperature.

8.7) The variations of the compositions and mole fractions of the newly-formed (TINb)(CN) and the equilibrium matrix compositions as a function of aging temperature and effective steel compositions are predicted on the basis of a regular solution thermodynamic model involving the four elements Ti, Nb, C and N in iron. The calculated particle composition average with temperature is in satisfactory agreement with measured compositions. In particular, the thermodynamic model gives very good agreement with experiment for steels 2 and 3. Both experimental results and prediction show that titanium nitride tends to form at very high temperatures and titanium-niobium carbides go to completion at low temperatures.

8.8) The measured compositions of particles in steels 3 and 4 exhibit a certain size dependence for short aging times in that the smaller and younger nuclei are Ti-rich, but the trend of size dependence diminishes with long holding times. The results also indicated that the particle size dependence on composition at the low aging temperature is more pronounced than at the higher temperature. The composition profiles of Ti and Nb within the particles were calculated using the model presented in this study and it shows that the complex carbonitrides have
nitride rich cores with Ti rich and carbide rich shells with Nb rich. This is seen to be in qualitative accord with the experimental observations. For very long aging times in steel 4 composition gradients are observed in plate-like particles in which the center of precipitates are strongly Ti and N rich. This may be explained by a trend to phase separation.

8.9) During solution treatment, the Ti and N cannot be completely dissolved in matrix in steels 2 to 4 due to the persistence of the undissolved particles. Although the level of residual N in austenite after solution treatment is very low, depending on the Ti concentration, such small amounts of nitrogen can considerably increase the chemical driving force for (TiNb)(CN) nucleation because of the mixing effect. The diffusion controlled nucleation model was applied to estimate the precipitation-time-temperature diagrams and these were compared with a limited number of experimental points. The noses of the curves shift from about 1100°C for steel 1 (F = 0.1) to 1200°C for steels 2 to 4 (F = 0.3) due to very high driving forces for carbonitride nucleation. The incubation times for NbC nucleation in steel 1 was longer than 1 s and the times of (TiNb)(CN) nucleation were less than 1 s except for steel 4 at 1000°C.

8.10) A sensitivity analysis shows that the multicomponent effects are fairly significant despite the low concentrations of alloy additions. Therefore from this and other similar results, it is concluded that multicomponent diffusion effects should be accounted for in all relevant first order phase transformations. The kinetic calculation shows that the inclusion of surface tension decreases the particle size by about 10% for the same aging time.
REFERENCES


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### Table 2.1

Crystalgraphic Data on Ti, Nb and V Carbides [34]

<table>
<thead>
<tr>
<th>Carbide</th>
<th>Composition Range (at.%C)</th>
<th>Type</th>
<th>Lattice Parameter (Å)</th>
<th>Carbon Position</th>
<th>Carbon Distribution</th>
<th>Structure Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>33 - 50</td>
<td>fcc</td>
<td>4.296-4.326</td>
<td>Oct.</td>
<td>Random</td>
<td>NaCl (B1)</td>
</tr>
<tr>
<td>NbC</td>
<td>41.8 - 49.7</td>
<td>fcc</td>
<td>4.433-4.70</td>
<td>Oct.</td>
<td>Random</td>
<td>NaCl (B1)</td>
</tr>
<tr>
<td>VC</td>
<td>δ:38.6-49.7, ε:44.1-47.9</td>
<td>fcc</td>
<td>4.118-4.141, 4.154-4.165</td>
<td>Oct.</td>
<td>Random Order</td>
<td>NaCl (B1) Super-Structure</td>
</tr>
<tr>
<td>Nb₂C</td>
<td>30.7 - 33.3</td>
<td>hcp</td>
<td>a:3.126-3.128, c:4.965-4.972</td>
<td>Oct.</td>
<td>Random Order</td>
<td>Hex. L'3 $\epsilon$-Fe₂N</td>
</tr>
</tbody>
</table>
## TABLE 2.2

Crystalgraphic Data on Ti, Nb and V Nitrides

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<tr>
<th>Nitride</th>
<th>Composition (at.%C)</th>
<th>Type</th>
<th>Lattice Parameter (Å)</th>
<th>Structure Type</th>
<th>Reference</th>
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<td>Ti$_3$N</td>
<td>25</td>
<td>tetragonal</td>
<td>a=4.92, c=5.16</td>
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<td>Goldsch [6]</td>
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<tr>
<td>Ti$_2$N</td>
<td>33.33</td>
<td>tetragonal</td>
<td>a=4.945, c=3.034</td>
<td>TiO$_2$ Rutile</td>
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<td>TiN$_{0.38-1.2}$</td>
<td>27-52</td>
<td>fcc</td>
<td>4.221 at TiN$_{0.45}$</td>
<td>NaCl (B1)</td>
<td>Goldsch [6]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.244 at TiN</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VN$_{0.72-1.0}$</td>
<td>41.5-51</td>
<td>fcc</td>
<td>4.066 at VN$_{0.72}$</td>
<td>NaCl (B1)</td>
<td>Goldsch [6]</td>
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<td></td>
<td></td>
<td></td>
<td>4.139 at VN</td>
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<td></td>
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<td>V$_3$N - V$_2$N</td>
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<td>a=3.126, c=4.545, VN$_{0.48}$</td>
<td>e-Fe$_2$N</td>
<td>Goldsch [6]</td>
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<td></td>
<td></td>
<td></td>
<td>a=2.839, c=4.560, VN$_{0.50}$</td>
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<td>NbN$_{0.9-1.0}$</td>
<td>47.1-51.4</td>
<td>fcc</td>
<td>4.381 - 4.392</td>
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<td>Brauer [39]</td>
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<td>Nb$_2$N</td>
<td>28.5-33.3</td>
<td>hcp</td>
<td>a=3.056, c=4.957, Nb end</td>
<td></td>
<td>Brauer [39]</td>
</tr>
<tr>
<td>NbN$_{0.4-0.5}$</td>
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<td></td>
<td>a=3.056, c=4.995, N end</td>
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<td></td>
</tr>
<tr>
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<td>48.7</td>
<td>hcp</td>
<td>a=2.959, c=5.568</td>
<td>B-8</td>
<td>Schonberg [40]</td>
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<tr>
<td>NbN</td>
<td>42.9-44.1</td>
<td>hcp</td>
<td>a=4.385, c=11.272</td>
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<td>Guard [41]</td>
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<td>Nb$_4$N$_3$</td>
<td>42.9-44.1</td>
<td>distorted tetragonal</td>
<td>a=4.385, c=4.310, Nb end</td>
<td></td>
<td>Brauer [42]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>a=4.386, c=4.331, N end</td>
<td></td>
<td></td>
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</tbody>
</table>
### TABLE 2.3

**Solubility Products for Ti, Nb and V Carbides in Austenite**, defined as $\log[M\%][C\%] = A + B/T$

<table>
<thead>
<tr>
<th>MC</th>
<th>T Range (°C)</th>
<th>A</th>
<th>B</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbC</td>
<td>900 – 1200</td>
<td>3.11</td>
<td>−7520 *</td>
<td>Nordberg [54]</td>
</tr>
<tr>
<td></td>
<td>1000 – 1300</td>
<td>3.18</td>
<td>−7700</td>
<td>Mori [55]</td>
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<tr>
<td></td>
<td>1000 – 1300</td>
<td>3.40</td>
<td>−7920 *</td>
<td>Laksh [56]</td>
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<tr>
<td></td>
<td>900 – 1200</td>
<td>2.81</td>
<td>−7020 *</td>
<td>Sharma [52]</td>
</tr>
<tr>
<td></td>
<td>1050 – 1150</td>
<td>3.31</td>
<td>−7970</td>
<td>Koyama [57]</td>
</tr>
<tr>
<td></td>
<td>1050 – 1300</td>
<td>3.42</td>
<td>−7900</td>
<td>Narita [58]</td>
</tr>
<tr>
<td></td>
<td>900 – 1300</td>
<td>3.04</td>
<td>−7290</td>
<td>Meyer [59]</td>
</tr>
<tr>
<td></td>
<td>950 – 1050</td>
<td>4.37</td>
<td>−9290</td>
<td>Johansen [60]</td>
</tr>
<tr>
<td></td>
<td>1000 – 1300</td>
<td>3.7</td>
<td>−9100</td>
<td>Smith [61]</td>
</tr>
<tr>
<td></td>
<td>900 – 1200</td>
<td>−0.63</td>
<td>−2500</td>
<td>de Kazin [62]</td>
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<td>TiC</td>
<td>900 – 1200</td>
<td>2.75</td>
<td>−7000</td>
<td>Irvine [63]</td>
</tr>
<tr>
<td></td>
<td>900 – 1200</td>
<td>5.33</td>
<td>−10475</td>
<td>Narita [64]</td>
</tr>
<tr>
<td></td>
<td>1000 – 1300</td>
<td>4.03</td>
<td>−8720</td>
<td>Shiraiwa [65]</td>
</tr>
<tr>
<td>VC</td>
<td></td>
<td>6.72</td>
<td>−9500</td>
<td>Narita [58]</td>
</tr>
<tr>
<td>V$_4$C$_3$</td>
<td></td>
<td>5.36</td>
<td>−8000</td>
<td>Aronsson [66]</td>
</tr>
</tbody>
</table>

* The precipitate was assumed to be NbC$_{0.87}$.
### Table 2.4

Solubility Products for Ti, Nb and V Nitrides in Austenite, defined as \( \log[M\%][M\%] = A + B/T \)

<table>
<thead>
<tr>
<th>MN</th>
<th>T Range (°C)</th>
<th>A</th>
<th>B</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbN</td>
<td>1200 - 1350</td>
<td>4.04</td>
<td>-10230</td>
<td>Smith [67]</td>
</tr>
<tr>
<td></td>
<td>1250 - 1350</td>
<td>2.80</td>
<td>-8500</td>
<td>Narita [68]</td>
</tr>
<tr>
<td></td>
<td>1000 - 1300</td>
<td>3.79</td>
<td>-10150</td>
<td>Mori [69]</td>
</tr>
<tr>
<td></td>
<td>1000 - 1300</td>
<td>2.86</td>
<td>-7929</td>
<td>Sharma [52]</td>
</tr>
<tr>
<td></td>
<td>1050 - 1150</td>
<td>3.70</td>
<td>-10800</td>
<td>Hoogend [70]</td>
</tr>
<tr>
<td>TiN</td>
<td>1200 - 1300</td>
<td>3.93</td>
<td>-15180</td>
<td>Narita [68]</td>
</tr>
<tr>
<td></td>
<td>1100 - 1350</td>
<td>4.72</td>
<td>-16190</td>
<td>Sawamura [71]</td>
</tr>
<tr>
<td></td>
<td>1200 - 1300</td>
<td>3.82</td>
<td>-15020</td>
<td>Chino [72]</td>
</tr>
<tr>
<td></td>
<td>1150 - 1350</td>
<td>0.32</td>
<td>-8000</td>
<td>Matsuda [73]</td>
</tr>
<tr>
<td></td>
<td>900 - 1350</td>
<td>5.00</td>
<td>-14400</td>
<td>Roberts [74]</td>
</tr>
<tr>
<td></td>
<td>1100 - 1350</td>
<td>5.19</td>
<td>-15490</td>
<td>Kunze [75]</td>
</tr>
<tr>
<td></td>
<td>1200 - 1400</td>
<td>4.94</td>
<td>-14400</td>
<td>Wada [76]</td>
</tr>
<tr>
<td>VN</td>
<td></td>
<td>2.27</td>
<td>-7070</td>
<td>Forhberg [77]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.46</td>
<td>-8330</td>
<td>Irvine [63]</td>
</tr>
</tbody>
</table>

* The precipitate was assumed to be NbC\(_{0.87}\).*
Table 2.5
Wagner Interaction Parameters

<table>
<thead>
<tr>
<th>$\varepsilon_1^{i}$</th>
<th>Reference</th>
<th>$\varepsilon_1^{i}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_C^C$</td>
<td>Ban [87]</td>
<td>$\varepsilon_C^{Nn}$</td>
<td>Wada [94]</td>
</tr>
<tr>
<td>$\frac{-8890}{T}$</td>
<td></td>
<td>$\frac{-5070}{T}$</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_N^N$</td>
<td>Hille [90]</td>
<td>$\varepsilon_C^{Si}$</td>
<td>Wada [94]</td>
</tr>
<tr>
<td>$\frac{-6294}{T}$</td>
<td></td>
<td>$\frac{+7370}{T}$</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_{Nb}^{Nb}$</td>
<td>Sharm [52]</td>
<td>$\varepsilon_C^{Cr}$</td>
<td>Sharm [52]</td>
</tr>
<tr>
<td>$\varepsilon_{Nb}^{Nb} \approx -2$</td>
<td></td>
<td>$\frac{-21880}{T}$</td>
<td></td>
</tr>
<tr>
<td>$\frac{-13588}{T}$</td>
<td>Bala [37]</td>
<td>$\varepsilon_C^{Ni}$</td>
<td>Sharm [52]</td>
</tr>
<tr>
<td>$\frac{4600}{T}$</td>
<td></td>
<td>$\frac{-17870}{T}$</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_C^{C}$</td>
<td>Jarl [91]</td>
<td>$\varepsilon_C^{Nn}$</td>
<td>Sharm [52]</td>
</tr>
<tr>
<td>$\frac{-5790}{T}$</td>
<td></td>
<td>$\frac{-57700}{T}$</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_C^{Nb}$</td>
<td>Green [92]</td>
<td>$\varepsilon_C^{Si}$</td>
<td>Mori [95]</td>
</tr>
<tr>
<td>$\frac{-66257}{T}$</td>
<td></td>
<td>$\frac{-57700}{T}$</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_C^{Ni}$</td>
<td>Bala [37]</td>
<td>$\varepsilon_N^{Nn}$</td>
<td>Jarl [91]</td>
</tr>
<tr>
<td>$\frac{-79150}{T}$</td>
<td></td>
<td>$\frac{3336}{T}$</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_N^{Nb}$</td>
<td>Bala [93]</td>
<td>$\varepsilon_C^{Cr}$</td>
<td>Jarl [91]</td>
</tr>
<tr>
<td>$\frac{-406240}{T}$</td>
<td></td>
<td>$\frac{-65150}{T}$</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_N^{Ni}$</td>
<td>Bala [93]</td>
<td>$\varepsilon_N^{Nn}$</td>
<td>Jarl [91]</td>
</tr>
<tr>
<td>$\frac{-705,000}{T}$</td>
<td></td>
<td>$\frac{-5776}{T}$</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_N^{Kn}$</td>
<td>Sharm [52]</td>
<td>$\varepsilon_N^{Ho}$</td>
<td>Jarl [91]</td>
</tr>
<tr>
<td>$\frac{-305033}{T}$</td>
<td></td>
<td>$\frac{-2888}{T}$</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_N^{Si}$</td>
<td>Sharm [52]</td>
<td>$\varepsilon_N^{Si}$</td>
<td>Sharm [52]</td>
</tr>
<tr>
<td>$\frac{-77265}{T}$</td>
<td></td>
<td>$\frac{-57700}{T}$</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_N^{Nb}$</td>
<td>Sharm [52]</td>
<td>$\varepsilon_N^{Nn}$</td>
<td>Sharm [52]</td>
</tr>
<tr>
<td>$\frac{-216135}{T}$</td>
<td></td>
<td>$\frac{-40510}{T}$</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_N^{Cr}$</td>
<td>Sharm [52]</td>
<td>$\varepsilon_N^{Ni}$</td>
<td>Sharm [52]</td>
</tr>
<tr>
<td>$\frac{+141}{T}$</td>
<td></td>
<td>$\frac{+21.2}{T}$</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 3.1

Compositions in Weight Percent of the Alloys Studied

<table>
<thead>
<tr>
<th>Steel No.</th>
<th>Titanium</th>
<th>Niobium</th>
<th>Carbon</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0000</td>
<td>0.1420</td>
<td>0.0780</td>
<td>0.0004</td>
</tr>
<tr>
<td>2</td>
<td>0.0956</td>
<td>0.0965</td>
<td>0.0870</td>
<td>0.0010</td>
</tr>
<tr>
<td>3</td>
<td>0.0370</td>
<td>0.0756</td>
<td>0.0750</td>
<td>0.0088</td>
</tr>
<tr>
<td>4</td>
<td>0.0206</td>
<td>0.0246</td>
<td>0.022</td>
<td>0.0027</td>
</tr>
</tbody>
</table>

TABLE 3.2

Impurity Contents in the Alloys Studied

<table>
<thead>
<tr>
<th>Elements</th>
<th>ppm.</th>
<th>Elements</th>
<th>ppm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>&lt; 30</td>
<td>Sulphur</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>Manganese</td>
<td>&lt; 170</td>
<td>Copper</td>
<td>&lt; 29</td>
</tr>
<tr>
<td>Cobalt</td>
<td>&lt; 16</td>
<td>Tin</td>
<td>&lt; 16</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt; 3</td>
<td>Zirconium</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Calcium</td>
<td>&lt; 12</td>
<td>Magnesium</td>
<td>&lt; 2</td>
</tr>
</tbody>
</table>

Al, V, P, Ni, Mo, B, Sb, Ce, Cr, W Not detected (less than 1 ppm)
TABLE 4.1

Diffusion Coefficients of Ti, Nb and C in Interstitial Compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Species</th>
<th>$D_0$(cm$^2$/s)</th>
<th>$Q$(kJ/mol)</th>
<th>T Range(°C)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC$_{0.97}$</td>
<td>Ti</td>
<td>4.4×10$^4$</td>
<td>735.7</td>
<td>1475 - 2720</td>
<td>Sarian [117]</td>
</tr>
<tr>
<td>TiC$_{0.97}$</td>
<td>C</td>
<td>6.98</td>
<td>398.4</td>
<td>1745 - 2720</td>
<td>Sarian [118]</td>
</tr>
<tr>
<td>TiC$_{0.67}$</td>
<td>C</td>
<td>114</td>
<td>459.4</td>
<td>1745 - 2080</td>
<td>Sarian [118]</td>
</tr>
<tr>
<td>TiC$_{0.95}$</td>
<td>NB</td>
<td>2.4</td>
<td>351.5</td>
<td>1935 - 2170</td>
<td>Sarian [117]</td>
</tr>
<tr>
<td>(Ti$<em>{0.5}$Nb$</em>{0.5}$)</td>
<td>Nb</td>
<td>4.7×10$^2$</td>
<td>502.1</td>
<td>2170 - 2280</td>
<td>Sarian [117]</td>
</tr>
<tr>
<td>NbC$_{0.766-0.868}$</td>
<td>NB</td>
<td>4.54</td>
<td>585.2</td>
<td>2097 - 2387</td>
<td>Yu [119]</td>
</tr>
<tr>
<td>NbC$_{0.78-0.915}$</td>
<td>Nb</td>
<td>0.11</td>
<td>530.9</td>
<td>2290 - 2852</td>
<td>Andry [120]</td>
</tr>
<tr>
<td>NbC$_{0.868}$</td>
<td>C</td>
<td>2.59</td>
<td>519.7</td>
<td>2100 - 2387</td>
<td>Yu [121]</td>
</tr>
<tr>
<td>NbC$_{0.766}$</td>
<td>C</td>
<td>2.22</td>
<td>31.7</td>
<td>2100 - 2387</td>
<td>Yu [121]</td>
</tr>
<tr>
<td>Aging Time</td>
<td>$\bar{d}_s$ (nm)</td>
<td>$\bar{d}_v$ (nm)</td>
<td>Morphology</td>
<td>Growth Rate</td>
<td>Control Factor</td>
</tr>
<tr>
<td>------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>------------</td>
<td>-------------</td>
<td>----------------</td>
</tr>
<tr>
<td>10 s</td>
<td>3.0</td>
<td>2.8</td>
<td>spherical</td>
<td>very fast</td>
<td>diffusion</td>
</tr>
<tr>
<td>20 s</td>
<td>5.6</td>
<td>5.4</td>
<td>spherical</td>
<td>very fast</td>
<td>diffusion</td>
</tr>
<tr>
<td>1 min.</td>
<td>7.5</td>
<td>7.3</td>
<td>most-poly</td>
<td>fast</td>
<td>diffusion</td>
</tr>
<tr>
<td>10 min.</td>
<td>8.1</td>
<td>7.6</td>
<td>polyhedral</td>
<td>slow</td>
<td>interface reaction</td>
</tr>
<tr>
<td>1 hr.</td>
<td>11.8</td>
<td>11.5</td>
<td>polyhedral</td>
<td>very slow</td>
<td>interface reaction</td>
</tr>
<tr>
<td>10 hr.</td>
<td>11.5</td>
<td>11.0</td>
<td>polyhedral</td>
<td>very slow</td>
<td>interface reaction</td>
</tr>
<tr>
<td>44 hr.</td>
<td>14.5</td>
<td>14.3</td>
<td>polyhedral</td>
<td>very slow</td>
<td>interface reaction</td>
</tr>
<tr>
<td>100 hr.</td>
<td>15.1</td>
<td>14.7</td>
<td>polyhedral</td>
<td>very slow</td>
<td>interface reaction</td>
</tr>
<tr>
<td>200 hr.</td>
<td>16.4</td>
<td>16.1</td>
<td>polyhedral</td>
<td>very slow</td>
<td>interface reaction</td>
</tr>
<tr>
<td>Aging Time</td>
<td>( \bar{d}_a ) (nm)</td>
<td>( \bar{d}_v ) (nm)</td>
<td>Morphology</td>
<td>Growth Rate</td>
<td>Control Factor</td>
</tr>
<tr>
<td>------------</td>
<td>----------------</td>
<td>----------------</td>
<td>--------------</td>
<td>-------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>5 s</td>
<td>3.1</td>
<td>2.9</td>
<td>spherical</td>
<td>very fast</td>
<td>diffusion</td>
</tr>
<tr>
<td>20 s</td>
<td>5.6</td>
<td>5.3</td>
<td>most-sphe</td>
<td>very fast</td>
<td>diffusion</td>
</tr>
<tr>
<td>1 min.</td>
<td>8.8</td>
<td>8.5</td>
<td>polyhedral</td>
<td>fast</td>
<td>mixed</td>
</tr>
<tr>
<td>5 min.</td>
<td>9.6</td>
<td>9.0</td>
<td>polyhedral</td>
<td>very slow</td>
<td>interface reaction</td>
</tr>
<tr>
<td>10 min.</td>
<td>9.8</td>
<td>9.3</td>
<td>polyhedral</td>
<td>very slow</td>
<td>interface reaction</td>
</tr>
<tr>
<td>1 hr.</td>
<td>11.9</td>
<td>11.5</td>
<td>polyhedral</td>
<td>slow</td>
<td>interface reaction</td>
</tr>
<tr>
<td>5 hr.</td>
<td>18.2</td>
<td>17.6</td>
<td>most-poly</td>
<td>fast</td>
<td>mixed</td>
</tr>
<tr>
<td>10 hr.</td>
<td>49</td>
<td></td>
<td>most-spher</td>
<td>fast</td>
<td>interface reaction</td>
</tr>
<tr>
<td>52 hr.</td>
<td>177</td>
<td></td>
<td>spherical</td>
<td>fast</td>
<td>interface reaction</td>
</tr>
<tr>
<td>100 hr.</td>
<td>195</td>
<td></td>
<td>spherical</td>
<td>fast</td>
<td>interface reaction</td>
</tr>
<tr>
<td>200 hr.</td>
<td>290</td>
<td></td>
<td>spherical</td>
<td>fast</td>
<td>interface reaction</td>
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</table>
### TABLE 4.4

**K-Factors Obtained from the Standards in This Study**

<table>
<thead>
<tr>
<th>Microscopy</th>
<th>Voltage</th>
<th>No. of measurement</th>
<th>$K_{TinB}$ for EDS</th>
<th>Standard deviation</th>
<th>Mode of operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>20 kV</td>
<td>10</td>
<td>0.518</td>
<td>0.0289</td>
<td></td>
</tr>
<tr>
<td>TEM</td>
<td>120 kV</td>
<td>10</td>
<td>0.542</td>
<td>0.0089</td>
<td>100 nm beam</td>
</tr>
<tr>
<td>STEM</td>
<td>100 kV</td>
<td>25</td>
<td>0.559</td>
<td>0.0249</td>
<td>C3 condenser</td>
</tr>
<tr>
<td>SEM (life sci)</td>
<td>15 kV</td>
<td>6</td>
<td>0.973</td>
<td>0.0398</td>
<td></td>
</tr>
<tr>
<td>TEM</td>
<td>100 kV</td>
<td>15</td>
<td>0.123</td>
<td>0.017</td>
<td>C3 condenser</td>
</tr>
<tr>
<td>STEM</td>
<td>100 kV</td>
<td></td>
<td>$K_{Tin}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEM (CANMET)</td>
<td>120 kV</td>
<td>5</td>
<td>0.286</td>
<td>0.012</td>
<td>Diff mode</td>
</tr>
<tr>
<td>TEM</td>
<td>120 kV</td>
<td>4</td>
<td>0.287</td>
<td>0.014</td>
<td>Image mode</td>
</tr>
</tbody>
</table>
Table 5.1

Free Energies of Formation of TiC, NbC, TiN and NbN in Austenite

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta G_{\text{HX}}^0 ) (J/mole)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbC</td>
<td>( \Delta G_{\text{NbC}}^0 = -176335 + 8.6T )</td>
<td>†</td>
</tr>
<tr>
<td>TiC</td>
<td>( \Delta G_{\text{TiC}}^0 = -166923 + 14.64T )</td>
<td>Sharaiwa [65]</td>
</tr>
<tr>
<td>NbN</td>
<td>( \Delta G_{\text{NbN}}^0 = -147010 - 247.7T + 30.3TnT )</td>
<td>Bala [135]</td>
</tr>
<tr>
<td>TiN</td>
<td>( \Delta G_{\text{TiN}}^0 = -221560 - 238.2T + 30.3TnT )</td>
<td>Bala [135]</td>
</tr>
</tbody>
</table>

† Estimated using the data of Jonansen and Smith in Ref.60 and 61.

Table 5.2

Predicted Concentrations in wt.% of Dissolved Ti, Nb, C and N in austenite at 1390°C

<table>
<thead>
<tr>
<th>Steel No.</th>
<th>Ti</th>
<th>Nb</th>
<th>C</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.091</td>
<td>0.095</td>
<td>0.087</td>
<td>0.00057</td>
</tr>
<tr>
<td>3</td>
<td>0.013</td>
<td>0.070</td>
<td>0.075</td>
<td>0.0016</td>
</tr>
<tr>
<td>4</td>
<td>0.016</td>
<td>0.024</td>
<td>0.022</td>
<td>0.0014</td>
</tr>
</tbody>
</table>
Table 6.1

Diffusion Coefficients of the Solutes in Austenite

<table>
<thead>
<tr>
<th>Solute</th>
<th>$D_o$ (mm$^2$/s)</th>
<th>$Q$ (kJ/mol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>67</td>
<td>157</td>
<td>Smith [140]</td>
</tr>
<tr>
<td>N</td>
<td>91</td>
<td>169</td>
<td>Darken [141]</td>
</tr>
<tr>
<td>V</td>
<td>2500</td>
<td>264</td>
<td>Bowen [142]</td>
</tr>
<tr>
<td>Ti</td>
<td>15</td>
<td>250</td>
<td>Moll [143]</td>
</tr>
<tr>
<td>Nb</td>
<td>75</td>
<td>264</td>
<td>Kurok [144]</td>
</tr>
<tr>
<td>NB</td>
<td>$5.3 \times 10^4$</td>
<td>344.3</td>
<td>Sparke [145]</td>
</tr>
<tr>
<td>Nb</td>
<td>$9 \times 10^6$</td>
<td>472.8</td>
<td>Sparke [145]</td>
</tr>
<tr>
<td>Hf</td>
<td>$3.6 \times 10^5$</td>
<td>407</td>
<td>Bowen [142]</td>
</tr>
<tr>
<td>Hf</td>
<td></td>
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</tbody>
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Fig.2.1 Experimental (solid lines by Rudy [35]) and predicted (dotted lines by Balasubramanian and Kirkaldy [36]) Ti-C phase diagram.

Fig.2.2 Experimental (solid lines by Rudy [35]) and predicted (dotted lines by Balasubramanian and Kirkaldy [36]) Nb-C phase diagram.
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Fig. 6.11 Precipitation kinetics in steels 3 and 4.
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Fig. 6.13 Predicted PTT curves and experimental results in steels 3 and 4.
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Fig. 7.4  (a) A possible (110) section of σ-plot of an fcc crystal. Wulff planes at the cusps (B,C, etc) give the inner envelope of all Wulff planes and thus the equilibrium shape; (b) The equilibrium shape in three dimensions showing [100] (square faces) and [111] (hexagonal faces). After Porter et al [150].