# **Equilibrium Model of Precipitation in Microalloyed Steels**

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# ABSTRACT

The formation of precipitates during thermal processing of microalloyed steels greatly influences their mechanical properties. Precipitation behavior varies with steel composition and temperature history, and can lead to beneficial grain refinement or detrimental transverse surface cracks. This work presents an efficient computational model of equilibrium precipitation of oxides, sulfides, nitrides and carbides in steels, based on satisfying solubility limits including Wagner interaction between elements, mutual solubility between precipitates and mass conservation of alloying elements. The model predicts the compositions and amounts of stable precipitates for multi-component microalloyed steels in liquid, ferrite and austenite phases at any temperature. The model is first validated by comparing with analytical solutions of simple cases, predictions using the commercial package JMat-PRO, and previous experimental observations. Then it is applied to track the evolution of precipitate amounts during continuous casting of two commercial steels (1004 LCAK and 1006Nb HSLA) at two different casting speeds. This model is easy to modify to incorporate other precipitates, or new thermodynamic data, and is a useful tool for equilibrium precipitation analysis.

Key Words: equilibrium precipitation, solubility product, mutual solubility, Wagner interaction, steel

thermodynamics, computational model

# I. INTRODUCTION

Microalloyed steels are strengthened mainly by the dispersion of fine precipitate particles and their effects to inhibit grain growth and dislocation motion<sup>[1]</sup>. These precipitates include oxides, sulfides, nitrides and carbides, and form at different times and locations during steel processing. They display a variety of different morphologies and size distributions, ranging from spherical, cubic to cruciform shape, sizes from nm to µm and locations inside the matrix or on the grain boundaries, such as shown in Fig. 1<sup>[2-6]</sup>. If properly optimized, these precipitate particles act to pin the grain boundaries, serving to restrict grain growth and thereby increasing toughness during processes such as rolling and run-out table cooling. However, if large numbers of fine precipitate particles accumulate along weak grain boundaries at elevated temperatures, they can lead to crack formation, which plagues processes such as continuous casting<sup>[7]</sup>. There is a strong need to predict the formation of precipitates, including their composition, morphology and size distribution, as a function of processing conditions.

Precipitate formation for a given steel composition depends on the temperature history in thermal processes such as casting, and is accelerated by the strain history in processes with large deformation, such as rolling<sup>[8]</sup>.

The first crucial step to model precipitate behavior is to predict the equilibrium phases, compositions and amounts of precipitates present for a given composition and temperature. This represents the maximum amount of precipitate that can form when the solubility limit is exceeded. This is also critical for calculating the supersaturation, which is driving force for precipitate growth. Thus, a fast and accurate model of equilibrium precipitation is a necessary initial step towards the future development of a comprehensive model of precipitate growth.

Minimization of Gibbs free energy is a popular method to determine the phases present in a multi-component material at a given temperature. The total Gibbs energy of a multi-component system is generally described by a regular solution sublattice model<sup>[9,10]</sup>. In addition to the Gibbs

energy of each pure component, extra energy terms come from the entropy of mixing, the excess Gibbs energy of mixing due to interaction between components and the elastic or magnetic energy stored in the system. In recent years, many researchers have used software packages based on Gibbs Energy minimization, including Thermo Calc<sup>[11,12]</sup>, FactSage<sup>[6]</sup>, ChemSage<sup>[3]</sup> and other CALPHAD models<sup>[13,14]</sup>, to calculate equilibrium precipitation behavior in multi-component steels.

Gibbs free energy functions with self-consistent parameters for a Fe-Nb-Ti-C-N steel system have been given by Lee<sup>[14]</sup>. The carbonitride phase was modeled using a two-sublattice model<sup>[15]</sup> with (Fe,Nb,Ti)(C,N,Vacancy), where the two sublattices represent the substitutional metal atoms and the interstitial atoms separately. Since not all positions are occupied by interstitial atoms, vacant sites were introduced in this sublattice. Mutual interaction energies between components incorporated up to ternary interactions, and accuracy was confirmed by comparing predictions with thermodynamic properties of Nb/Ti carbonitrides measured under equilibrium conditions for a wide range of steel compositions.

Although these models based on minimizing Gibbs free energy can accurately predict the equilibrium amounts of precipitates, and have the powerful ability to predict the precipitates to expect in a new system, the accuracy of their databases and their ability to quantitatively predict complex precipitation of oxides, sulfides, nitrides and carbides in microalloyed steels is still in question. In addition, the solubility product of each precipitate is a logarithmic function of free energy, so a small inaccuracy in the free energy function could cause a large deviation in calculating the amount precipitated<sup>[16]</sup>. Finally, the free energy curves and interaction parameters are very interdependent and so must be refit to incorporate new data.

An alternative method to predict the equilibrium phases in a multi-component alloy is to simultaneously solve systems of equations based on solubility products, which represent the limits of how much a given precipitate can dissolve per unit mass of metal. The origin of this equilibrium constant concept can be traced back to Le Chatelier's Principle of 1888<sup>[17]</sup>. The incorporation of mutual solubility was first suggested by Hudd<sup>[18]</sup> for niobium carbonitride, and later extended by Rose and Gladman<sup>[19]</sup> to Ti-Nb-C-N steel.

Recently, Liu<sup>[20]</sup> developed a model to predict the equilibrium mole fractions of precipitates Ti(C,N), MnS and Ti<sub>4</sub>C<sub>2</sub>S<sub>2</sub> in microalloyed steel. The solubility products are calculated from standard Gibbs energies, and accounts for the interaction between alloying elements and the mutual solubility of Ti(C,N). The precipitation of complex vanadium carbonitrides and aluminum nitrides in C-Al-V-N microalloyed steels was discussed by Gao and Baker<sup>[21]</sup>. They utilized two thermodynamic models by Adrian<sup>[22]</sup> and Rios<sup>[23]</sup>, and produced similar results. Park<sup>[24]</sup> calculated the precipitation behavior of MnS in austenite including two different sets of solubility products for Ti<sub>4</sub>C<sub>2</sub>S<sub>2</sub> and TiS<sup>[11,20]</sup> and assuming sulfides and carbonitrides (Ti,V)(C,N) are mutually insoluble. In both works<sup>[21,24]</sup>, the solution energy of mixing for C-N was assumed to be constant (-4260J/mol) with all other solution parameters taken as zero. The Wagner interaction effect was neglected for this dilute system and ideal stoichiometry was assumed for all sulfides and carbonitrides.

Previous solubility-product based models often neglect effects such as the differences between substitutional and interstitial elements during precipitation, mutual solubility between precipitates and the Wagner effect between solutes, so are only suitable for particular steel grades and precipitates. Moreover, the analysis of molten steel and ferrite is lacking as most works only focus on precipitation in the austenite phase.

Although many previous attempts have been made, an accurate model of equilibrium precipitation behavior in microalloyed steel has not yet been demonstrated. The complexity comes from many existing physical mechanisms during precipitation processes, such as solubility limits of precipitates in different steel phases, change of activities due to Wagner interaction between elements, treatment of mutually exclusive and soluble properties among precipitates and mass conservation of all elements.

The current work aims to establish and apply such a thermodynamic model to efficiently predict the typical precipitates in microalloyed steels. Mutual solubility is incorporated for appropriate precipitates with similar crystal structures and lattice parameters. The model is applied to investigate the effect of mutual solubility. It is then validated with analytical solution of simple cases, numerical results from commercial package JMat-Pro and previous experimental results. Finally, the model is applied to predict equilibrium precipitation in two commercial microalloyed steels with different

casting speeds in practical continuous casting condition.

#### **II. MODEL DESCRIPTION**

The equilibrium precipitation model developed in this work computes the composition and amount of each precipitate formed for a given steel composition and temperature, based on satisfying the solubility products of a database of possible reactions and their associated activity interaction parameters. The database currently includes 18 different oxide, sulfide, nitride and carbide precipitates, (TiN, TiC, NbN, NbC<sub>0.87</sub>, VN, V<sub>4</sub>C<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Ti<sub>2</sub>O<sub>3</sub>, MnO, MgO, MnS, MgS, SiO<sub>2</sub>, TiS, Ti<sub>4</sub>C<sub>2</sub>S<sub>2</sub>, AlN, BN, Cr<sub>2</sub>N), and 13 different elements, (N, C, O, S, Ti, Nb, V, Al, Mn, Mg, Si, B, Cr), in Fe, and is easily modified to accommodate new reactions and parameters.

# **A. Solubility Products**

For each reaction between dissolved atoms of elements M and X to give a solid precipitate of compound  $M_x X_y$ .

$$xM + yX \leftrightarrow M_x X_y \tag{1}$$

the temperature-dependent equilibrium solubility product, K, is defined as

$$K_{M_x X_y} = a_M^x \cdot a_X^y / a_{M_x X_y}$$
<sup>[2]</sup>

where  $a_M$ ,  $a_X$  and  $a_{M_xX_y}$  are the activities of M, X and  $M_xX_y$  respectively. The solubility products in steels decrease with lower temperature, so there is usually a critical temperature below which precipitates can form, given sufficient time.

The solubility products of the precipitates in liquid steel, ferrite and austenite used in this study are listed in Table I. The solubilities in liquid are about 10-100 times larger than those in austenite, which are about 10 times greater than those in ferrite at the same temperature. These observed ratios are assumed to estimate unknown solubility products for oxides in solid steel and for the other precipitates in liquid steel. The solubility products generally decrease from carbides, to nitrides, to sulfides, to oxides, which corresponds to increasing precipitate stability. Thus, oxides generally precipitate first, forming completely in the liquid steel, where they may collide and grow very large, leaving coarse oxide particles (inclusions) and very little free (dissolved) oxygen remaining in the solid phase after solidification. In addition, oxide precipitates in the solid often act as heterogeneous nucleation cores of complex precipitates which form later at lower temperature<sup>[63,64]</sup>.

The solubilities and amounts of nitrides and carbides added to microalloyed steels typically result in these precipitates forming in the austenite phase as small (nm-scale) second-phase particles which inhibit grain growth. A notable precipitate is TiN, which is roughly 100-1000 times more stable than other nitrides and carbides. The large variations between the ratio of carbide and nitride solubility products also depends greatly on the alloying elements. This ratio is about 10 for niobium, so NbC<sub>0.87</sub> precipitates are commonly observed in steels because carbon is always relatively plentiful. This ratio is about 100-1000 for titanium and vanadium so these elements typically precipitate as nitrides. When the concentration of sulfur is high enough, the corresponding sulfides and carbosulfides are also observed in these steels.

For the low solute contents of the steels, the activity  $a_i$ , of each element *i*, (wt%) is defined using Henry's law as follows:

$$a_i = \gamma_i [\%i]$$
 where  $\log_{10} \gamma_i = \sum_{j=1}^{13} e_i^j [\%j]$  [3]

where  $\gamma_i$  is the activity coefficient,  $e_i^j$  is the Wagner interaction coefficient of element *i* as affected by alloying element *j*, and [%*i*] is the dissolved mass concentration of element *i* (wt%). The summation covers interactions from all alloying elements, including element *i* itself. This relation comes from the Taylor series expansion formalism first proposed by Wagner<sup>[65]</sup> and Chipman<sup>[66]</sup> to describe the thermodynamic relationship between logarithm of activity coefficient and composition of a dilute constituent in a multi-component system. Larger positive Wagner interaction parameters encourage more precipitation. If the alloying concentrations were higher, then higher-order interaction coefficients using the extended treatment by Lupis and Elliott<sup>[67]</sup> should be used. Since alloy additions are small in the microalloyed steels of interest in this work (<~1wt%), they are assumed to be dilute so only first-order interaction coefficients were collected. Relative to the solubility product effects, these interaction parameters are a second order correction to precipitation in these steels. Each referenced value was determined in either the liquid melt or solid steel. They are assumed independent of steel phase and are summarized in Table II.

During phase transformations, when the steel has more than one phase (liquid,  $\delta$ -ferrite, austenite and  $\alpha$ -ferrite), the solubility product of the precipitate  $M_x X_y$  is defined with a weighted average based on the phase fractions as follows:

$$K_{M_x X_y} = f_l \cdot K_{M_x X_y}^l + f_\delta \cdot K_{M_x X_y}^\delta + f_\gamma \cdot K_{M_x X_y}^\gamma + f_\alpha \cdot K_{M_x X_y}^\alpha$$
<sup>[4]</sup>

where  $f_l$ ,  $f_{\delta}$ ,  $f_{\gamma}$  and  $f_{\alpha}$  are the phase fractions of liquid,  $\delta$ -ferrite, austenite and  $\alpha$ -ferrite in steel.

#### **B. Treatment of Mutual Solubility**

Although many different precipitates are included in the previous section, several groups are mutually soluble, as they exist as a single constituent phase. There is ample experimental evidence to show the mutual solubility of (Ti,Nb,V)(C,N) carbonitride in steels. The treatment of mutual solubility follows the ideas of Huud<sup>[18]</sup>, Gladman<sup>[19]</sup>, Speer<sup>[68]</sup> *et al*, and assumes ideal mixing (regular solution parameters are zero) for mutually soluble precipitates. The activities of precipitates which are mutually exclusive with each other remain at unity because they exist separately in the steel. On the other hand, the activities of mutually soluble precipitates are less than unity because they always appear together with other precipitates. Instead their activities are represented by their respective molar fractions in the mixed precipitates, so the sum of the activities of the precipitates that comprise a mutually soluble group is unity. The crystal structures and lattice parameters of the precipitates are given in Table I. Precipitates with the same crystal structures and similar lattice parameters (within 10%), are assumed to be mutually soluble, and this assumption could be adjusted by further experimental observations.

According to the above criterion, the 18 precipitates in the current work are separated into the following 10 groups: (Ti,Nb,V)(C,N), (Al,Ti)O, (Mn,Mg)O, (Mn,Mg)S, SiO<sub>2</sub>, TiS, Ti<sub>4</sub>C<sub>2</sub>S<sub>2</sub>, AlN, BN,

 $Cr_2N$ . Precipitates can form from the element combinations that comprise each of these groups, including those for the 4 mutually soluble groups shown in Table III. The 18 solubility limits provide the following constraint equations:

$$a_{M_x X_y} = \frac{a_M^x \cdot a_X^y}{K_{M_x X_y}}$$
[5]

The activity of precipitate  $M_x X_y$ ,  $a_{M_x X_y}$ , is determined differently for mutually soluble and exclusive precipitates. Its value is one for the 6 mutually exclusive precipitates (SiO<sub>2</sub>, TiS, Ti<sub>4</sub>C<sub>2</sub>S<sub>2</sub>, AlN, BN, Cr<sub>2</sub>N). For the 4 mutually soluble precipitate groups, the precipitate activities must satisfy:

$$a_{TiN} + a_{NbN} + a_{VN} + a_{TiC} + a_{NbC_{0.87}} + a_{V_4C_3} = 1$$
[6]

$$a_{Al_2O_3} + a_{Ti_2O_3} = 1$$
<sup>[7]</sup>

$$a_{MnO} + a_{MgO} = 1$$
<sup>[8]</sup>

$$a_{MnS} + a_{MeS} = 1$$
<sup>[9]</sup>

The y/x ratio of each precipitate  $M_x X_y$  is easily calculated from Table I, and is often a non-stoichiometric fraction, according to experimental observations. With wide uncertainties in measured solubility products<sup>[19]</sup>, further research is needed to modify these data to best match new measurements.

# C. Mass Balance on Alloying Elements

The total of the molar fractions of each group of precipitates in the steel is

$$\chi_{total} = \chi_{(Ti,Nb,V)(C,N)} + \chi_{(Al,Ti)O} + \chi_{(Mn,Mg)O} + \chi_{(Mn,Mg)S} + \chi_{SiO_2} + \chi_{TiS} + \chi_{Ti_4C_2S_2} + \chi_{AlN} + \chi_{BN} + \chi_{Cr_2N}$$
[10]

The following equations must be satisfied for the mass balance of each of the 13 alloying elements, by summing over all 18 precipitate types, as summarized in Table IV

$$\chi_{M_0} = (1 - \chi_{total})\chi_{[M]} + \sum_{i=1}^{18} \left( x \chi_{M_x X_y} \right)_i$$
[11]

$$\chi_{X_0} = (1 - \chi_{total})\chi_{[X]} + \sum_{i=1}^{18} \left(y\chi_{M_x X_y}\right)_i$$
[12]

where  $\chi_{M_0} = A_{steel} M_0 / (100 A_M)$  and  $\chi_{[M]} = A_{steel} [M] / (100 A_M)$  are the molar fractions of the total mass concentration, M<sub>0</sub> (wt%,) of the given element in the steel composition, and the dissolved concentration [M] (wt%) for the element *M*.  $A_{steel}$  and  $A_M$  are the atomic mass of the steel matrix and element *M*. A similar relation holds for element *X* in Eq. [12]. It indicates that total concentration of each alloying element is divided into that in solution and that in precipitate form. The molar fraction  $\chi_{M_x X_y}$  of precipitate  $M_x X_y$  is the product of the activity of this precipitate and its corresponding molar fraction of the precipitate group:

$$\chi_{M_x X_y} = a_{M_x X_y} \chi_g$$
[13]

where  $\chi_g$  is the molar fraction of mutually soluble precipitate group g which contains precipitate  $M_x X_y$ . For example, the group g = (Ti, Nb, V)(C, N) contains  $M_x X_y$  precipitates *TiN*, *NbN*, *VN*, *TiC*, *NbC*<sub>0.87</sub> and/or  $V_4 C_3$ .

Generally, there are **P** equations for the solubility limits of **P** precipitates, **M** equations for mass balances of **M** alloying elements, and **Q** extra constraint equations for **Q** groups of mutually soluble precipitates. The total number of equations is P+M+Q. In addition, there are **M** unknown dissolved concentrations of the **M** alloying elements, **R** molar concentrations of the **R** groups of mutually exclusive precipitates, **Q** molar concentrations of the **Q** groups of mutually-soluble precipitates, and **P-R** mutually soluble coefficients. Thus the total number of unknowns is also M+Q+P. The current study includes **P=18** precipitates, **M=13** alloying elements, and **Q=4** mutually soluble groups, giving **35** equations and **35** unknowns. With an equal number of equations and unknowns, the equation system can be solved by suitable numerical method.

#### **D.** Numerical Solution Details

The above equations are solved simultaneously using a simple iterative scheme. To achieve faster

convergence, the method takes advantage of the fact that results are desired over a wide temperature range, as it runs incrementally from above the solidus temperature to below the austenite to  $\alpha$ -ferrite transformation temperature. Starting at a high temperature in liquid steel, complete solubility of every precipitate phase is assumed. Temperature is lowered at each time step, using the results from the previous step as the initial guess. The 35 equations are solved by Newton-Raphson method until the largest absolute error between left and right sides of all equations converges to less than 10<sup>-6</sup>. The (35×35) matrix of the derivatives of the equations with respect to the unknowns is calculated analytically. The solution of this system of equations F<sub>i</sub> is given as

$$z_{k+1} = z_k - \lambda J(z_k)^{-1} F(z_k)$$
[14]

The Jacobian matrix J is computed from

$$\left\{J(z)\right\}_{ij} = \frac{\partial F_i(z)}{\partial z_i}$$
[15]

The parameter  $\lambda$  is continuously halved from unity until the norm of the equations system decreases. After solving the equations, the dissolved concentrations of each alloying element and the amounts of each precipitate formed are stored at each temperature. It is worth to mention that the computational time is typically smaller than 0.1s for each temperature, so the current model gives a relatively quick prediction of the equilibrium phases for microalloyed steels. Such an efficient model is needed for coupling into a kinetic model in future work.

The molar concentration of precipitate can be transformed to the mass concentration or volume fraction in steels. For precipitate  $M_x X_y$ , its mass concentration  $w_{M_x X_y}$  (wt%), and volume fraction  $v_{M_x X_y}$  are calculated from its molar fraction  $\chi_{M_x X_y}$ , as follows:

$$w_{M_{x}X_{y}} = \frac{100A_{M_{x}X_{y}}\chi_{M_{x}X_{y}}}{A_{steel}}$$
[16]

$$\boldsymbol{v}_{M_{x}X_{y}} = \frac{\rho_{steel}A_{M_{x}X_{y}}}{\rho_{M_{x}X_{y}}A_{steel}} \chi_{M_{x}X_{y}}$$
<sup>[17]</sup>

where  $A_{steel}$  and  $A_{M_x X_y}$  are the atomic mass, and  $\rho_{steel}$  and  $\rho_{M_x X_y}$  are the density of the steel

matrix and precipitate separately. As the alloy additions are small, these properties of steel are simply taken to be constants (55.85g/mol and 7500kg/m<sup>3</sup>).

# **III. INFLUENCE OF MUTUAL SOLUBILITY ON PRECIPITATION**

#### A. Validation with Analytical Solutions of Mutually Exclusive Precipitates

For simple single-precipitate systems with y/x=1, such as NbN, Wagner interaction can be neglected and the element activities are equal to their dissolved mass concentration in the very dilute systems. The first precipitate occurs when the product of the initial concentrations, Nb<sub>0</sub> and N<sub>0</sub>, exceeds K<sub>NbN</sub>. After NbN forms, the solubility limit requires

$$[Nb][N] = K_{NbN}$$
<sup>[18]</sup>

The stoichiometry requirement for this chemical reaction is

$$\frac{Nb_0 - [Nb]}{A_{Nb}} = \frac{N_0 - [N]}{A_N}$$
[19]

The analytical solution can be summarized as

- (a). At high temperature, when Nb<sub>0</sub>\*N<sub>0</sub> $\leq$ K<sub>NbN</sub>, there are no precipitates
- (b). At lower temperature, when  $Nb_0 * N_0 > K_{NbN}$

$$[N] = \frac{(A_{Nb}N_0 - A_NNb_0) + \sqrt{(A_{Nb}N_0 - A_NNb_0)^2 + 4A_{Nb}A_NK_{NbN}}}{2A_{Nb}}$$
$$[Nb] = \frac{-(A_{Nb}N_0 - A_NNb_0) + \sqrt{(A_{Nb}N_0 - A_NNb_0)^2 + 4A_{Nb}A_NK_{NbN}}}{2A_N}$$
$$w_{NbN} = (A_{Nb} + A_N) \left( \frac{(A_{Nb}N_0 + A_NNb_0) - \sqrt{(A_{Nb}N_0 - A_NNb_0)^2 + 4A_{Nb}A_NK_{NbN}}}{2A_{Nb}A_N} \right)$$
[20]

For mutually exclusive precipitates composing with y/x=1, if these precipitates do not share any alloying elements, the analytical solution is simply two sets of equations like those for NbN. Alternatively, if they share a common element, such as with Nb-Al-N system with NbN and AlN, all of the different possible conditions, such as Nb<sub>0</sub>\*N<sub>0</sub>>K<sub>NbN</sub> and Al<sub>0</sub>\*N<sub>0</sub>>K<sub>AlN</sub>, are tested to find which

precipitate forms first. After one precipitate forms, the initial nitrogen concentration is replaced with its dissolved value to judge whether the other precipitate forms or not and the results change if both precipitates form.

If both precipitates form, the solubility limits and chemical reaction require

$$[Nb][N] = K_{NbN}$$
<sup>[21]</sup>

$$[Al][N] = K_{AlN}$$
<sup>[22]</sup>

$$\frac{Nb_0 - [Nb]}{A_{Nb}} + \frac{Al_0 - [Al]}{A_{Al}} = \frac{N_0 - [N]}{A_N}$$
[23]

The solution can be summarized as

(a). At high temperature, when  $Nb_0*N_0 \leq K_{NbN}$  and  $Al_0*N_0 \leq K_{AIN}$ , there is no precipitate

(b). At low temperature, when either  $Nb_0*N_0>K_{NbN}$  and  $Al_0*N_0>K_{AIN}$  is satisfied

(i). If Nb<sub>0</sub>\*N<sub>0</sub>>K<sub>NbN</sub>, the solution is given like a single NbN case

(ii). If  $Al_0 * N_0 > K_{AlN}$ , the solution is similar to Eq.[20], but all values of Nb are replaced with the corresponding values of Al instead.

(c). If the temperature continues to decrease so that both Nb0\*N0>KNbN and Al0\*N0>KAIN are satisfied,

 $Nb_0 {}^*N_0 / K_{NbN}$  and  $Al_0 {}^*N_0 / K_{AlN}$  are computed and compared

(i). If  $Nb_0*N_0/K_{NbN}$  is larger, the following condition is checked

$$Al_0 * [N] > K_{AIN}$$
<sup>[24]</sup>

If true, then both precipitates form. Otherwise, only NbN precipitates exist.

(ii). If  $Al_0 N_0/K_{AIN}$  is larger, the next condition is checked

$$Nb_0 * [N] > K_{NbN}$$
<sup>[25]</sup>

If true, then both precipitates form. Otherwise, only AlN precipitates exist.

(iii). If both precipitates form

$$[N] = \frac{[A_{Nb}A_{Al}N_0 - A_N(A_{Nb}Al_0 + A_{Al}Nb_0)]}{2A_{Nb}A_{Al}}$$

$$+\frac{\sqrt{[A_{Nb}A_{Al}N_{0} - A_{N}(A_{Nb}A_{l_{0}} + A_{Al}Nb_{0})]^{2} + 4A_{Nb}A_{Al}A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})}}{2A_{Nb}A_{Al}}}{[Nb] = \frac{-K_{NbN}[A_{Nb}A_{Al}N_{0} - A_{N}(A_{Nb}A_{l_{0}} + A_{Al}Nb_{0})]}{2A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})}} + \frac{K_{NbN}\sqrt{[A_{Nb}A_{Al}N_{0} - A_{N}(A_{Nb}A_{l_{0}} + A_{Al}Nb_{0})]^{2} + 4A_{Nb}A_{Al}A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})}}{2A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})}$$
  
$$[Al] = \frac{-K_{AlN}[A_{Nb}A_{Al}N_{0} - A_{N}(A_{Nb}A_{l_{0}} + A_{Al}Nb_{0})]^{2} + 4A_{Nb}A_{Al}A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})}}{2A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})}} + \frac{K_{AlN}\sqrt{[A_{Nb}A_{Al}N_{0} - A_{N}(A_{Nb}A_{l_{0}} + A_{Al}Nb_{0})]^{2} + 4A_{Nb}A_{Al}A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})}}{2A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})} - \frac{K_{AlN}\sqrt{[A_{Nb}A_{Al}N_{0} - A_{N}(A_{Nb}A_{l_{0}} + A_{Al}Nb_{0})]^{2} + 4A_{Nb}A_{Al}A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})}}{2A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})} - \frac{K_{NbN}\sqrt{[A_{Nb}A_{Al}N_{0} - A_{N}(A_{Nb}A_{l_{0}} + A_{Al}Nb_{0})]^{2} + 4A_{Nb}A_{Al}A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})}}{2A_{Nb}A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})} - \frac{K_{NbN}\sqrt{[A_{Nb}A_{Al}N_{0} - A_{N}(A_{Nb}A_{l_{0}} + A_{Al}(A_{Nb}b_{AlN} + A_{Al}K_{NbN})}}{2A_{Nb}A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})} - \frac{K_{AlN}\sqrt{[A_{Nb}A_{Al}N_{0} - A_{N}(A_{Nb}A_{l_{0}} + A_{N}(A_{Nb}A_{l_{0}} - A_{Al}A_{N}A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})}}{2A_{Al}A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})} - \frac{K_{AlN}\sqrt{[A_{Nb}A_{Al}N_{0} - A_{N}(A_{Nb}A_{l_{0}} + A_{N}(A_{Nb}A_{AlN} + A_{Al}K_{NbN})}}{2A_{Al}A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})} - \frac{K_{AlN}\sqrt{[A_{Nb}A_{Al}N_{0} - A_{N}(A_{Nb}A_{l_{0}} + A_{N}(A_{Nb}A_{AlN} + A_{Al}K_{NbN})}}{2A_{Al}A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})} - \frac{K_{AlN}\sqrt{[A_{Nb}A_{Al}N_{0} - A_{N}(A_{Nb}A_{l_{0}} + A_{Al}Nb_{0}]^{2} + 4A_{Nb}A_{Al}A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})}}{2A_{Al}A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})}} - \frac{K_{AlN}\sqrt{[A_{Nb}A_{Al}N_{0} - A_{N}(A_{Nb}A_{Al}A_{N} + A_{Al}K_{NbN})}}{2A_{Al}A_{N}(A_{Nb}K_{AlN} + A_{Al}K_{NbN})}} - \frac{K_{AlN}\sqrt{[A_{Nb}A$$

For mutually-exclusive precipitates which share alloying elements, the formation of the first precipitate phase changes the dissolved concentration of shared elements and delays the formation of other precipitates. The interaction parameters are all set to zero for numerical simulation of these test cases. Fig. 2 shows that the numerical results match the analytical solution very well for all three hypothetical steels. By adding 0.02%Al into steel with 0.02%Nb and 0.02%N, AlN forms first, consumes some of the dissolved nitrogen which delays the formation of NbN precipitate, and decreases the equilibrium amount of NbN. Instead, if 0.01%B is added to the 0.02%Nb and 0.02%N steel, the early precipitation of BN delays NbN to form at an even lower temperature. This is because BN has a lower solubility limit and reacts with more nitrogen in forming BN because of the

lower atomic mass of boron.

A precipitation diagram for the Nb-Al-N-Fe system at different temperatures in austenite was calculated from the current model and shown in Fig. 3. The sum of the mass concentration of elements Nb, Al and N is set as 0.05wt%. Each curve in this diagram shows the boundary between stable and unstable precipitation of AlN or NbN in these hypothetical steels. At 1573K (1300°C), AlN forms first because of its lower solubility limit. The composition region for stable AlN precipitation increases with decreasing temperature. When temperature drops below 1423K (1150°C), either AlN or NbN may exist for certain compositions. Finally, at temperatures below 1398K (1125°C), either AlN, NbN or both precipitates could coexist. Similar progressions occur in other systems.

# B. Calculation for mutual soluble precipitates

A prediction of mutually-soluble precipitation is shown in Fig. 4 for a hypothetical Ti-Nb-N steel with 0.01%Nb, 0.01%N and 0.005%Ti. The precipitates form as the single group (Ti,Nb)N, and even for this simple example of mutually-soluble system, an analytical solution could not be found. In addition to precipitate amounts, Fig. 4 shows how the precipitate composition evolves with decreasing temperature. For example, at 1573K (1300°C), the precipitate group composition is 72%Ti, 6%Nb and 22%N, which corresponds to the molar-fraction expression  $Ti_{0.48}Nb_{0.02}N_{0.50}$ . When titanium is present, TiN is the dominant precipitate at high temperature, owing to its high stability. Its molar fraction  $f_{TiN}$  decreases at lower temperature, as NbN forms from the remaining N, and increases the Nb content of the precipitate. This result is consistent with experimental findings, such as  $Strid^{[69]}$  and Craven<sup>[70]</sup>, where the core of complex carbonitrides is mainly TiN. The model suggests that precipitates generated at high temperature are Ti-rich, and the precipitate layers that form later become richer in Nb as the temperature lowers. Fig. 4(a) also shows results for the same steel without Ti. With mutual solubility, adding titanium remarkably increases the initial precipitation temperature and decreases the equilibrium activity of NbN, which allows more NbN to form. If TiN and NbN were mutually exclusive, then adding titanium would decrease NbN precipitation. This

result illustrates the importance of proper consideration of mutual solubility in the model.

#### **IV. MODEL VALIDATION**

# A. Validation with Commercial Package

The chemical composition of the two commercial steels in this work, 1004 LCAK (low carbon aluminum killed) and 1006Nb HSLA (high strength low alloy), are given in Table V. The results from the commercial package JMat-Pro 5.0 with general steel submodule<sup>[71]</sup> and the current model are compared in Fig. 5. The JMat-Pro predicts separate precipitation of a TiN-rich "MN" phase at higher temperatures and a NbC-rich "M(C,N)" phase at lower temperatures. These are treated together as a single (Ti,Nb,V)(C,N) phase with evolving composition in the current model, as previously mentioned. The oxide M<sub>2</sub>O<sub>3</sub> predicted by JMat-Pro corresponds with the (Al,Ti)O phase in the current model.

The comparison shows qualitative agreement for the predicted precipitate types, and the amounts of (A1,Ti,)O, MnS, and (Ti,Nb,V)(C,N) between the two models are all similar. For the latter phase group, JMat-Pro predicts a double-humped curve, owing to its two precipitate groups, MN and M(C,N), which is roughly approximated by a single smooth curve with the current model. The composition of (Ti,Nb,V)(C,N) in the current model also matches reasonably with the average composition is  $Ti_{0.48}Nb_{0.02}V_{0.00}C_{0.00}N_{0.50}$  at 1577K (1304°C) and  $Ti_{0.28}Nb_{0.22}V_{0.00}C_{0.23}N_{0.27}$  at 1077K (804°C) for JMat-Pro, and  $Ti_{0.47}Nb_{0.03}V_{0.00}C_{0.02}N_{0.48}$  at 1577K (1304°C) and  $Ti_{0.29}Nb_{0.21}V_{0.02}C_{0.14}N_{0.35}$  at 1077K (804°C) for the current model. The current model predicts that (Ti,Nb,V)(C,N) and MnS first form in the  $\delta$ -ferrite phase, but dissolve after the transformation to austenite, where the solubilities are larger. This trend is missing in JMat-Pro. JMat-Pro consistently predicts more AlN than the current model, likely due to having less solubility for this precipitate in its database. Below 1073K (800°C), a jump in AlN is predicted by JMat-Pro. This is because cementite transformation is ignored in the current model. The carbon-rich Fe<sub>3</sub>C phase provides plenty of carbon to allow MN and M(C,N) to form nearly as pure carbide, which leaves more nitrogen to react with Al. In conclusion,

the differences between the two models are not considered to be significant, considering that both models neglect the important effects of kinetics.

# B. Validaiton with Measured Equilibrium-Precipitated Nb Amount

Zajac and Jansson<sup>[72]</sup> investigated equilibrium precipitation in several Nb-based industrial microalloyed steels, including the two compositions shown in Table VI. The steels were first solution treated at 1573K (1300°C) or 1623K (1350°C) for 1 hour followed by quick water quenching. Then, specimens were aged at two different temperatures isothermally for 24 to 48 hours. The precipitated amount of Nb in Nb(C,N) was measured by the inductively coupled plasma (ICP) emission method on electrolytically extracted compounds for each sample. Fig. 6 compares these experimental measurements with calculated results of precipitated niobium amount for these two steels, and shows that the current model matches well with the experimental data.

#### C. Validation with Observed Titanium Precipitate Types

Titanium sulfide and titanium carbosulfide are also observed in high-titanium steels. The equilibrium precipitation behavior of titanium stabilized interstitial free steels was studied quantitatively using dissolution experiments by Yang *et al*<sup>[41]</sup>. Several steels with different compositions were reheated at different temperatures varying from 1373K (1100°C) to 1623K (1350°C) and the holding time to reach the equilibrium state varied from 1.5 to 3 hours for different reheating temperatures. The steel compositions and the types of precipitates observed at each holding temperature in the experiments are listed in Tables VII and VIII respectively. The calculated molar fractions of the precipitates in these steels with temperature are shown in Fig. 7. The model predictions are consistent with the observed stability of these precipitates. The oxide Al<sub>2</sub>O<sub>3</sub> begins to form in the liquid steel, so was likely removed by the flux/slag, and not recorded in the experiments.

#### D. Validation with Measured Inclusion Compositions for Welding

Inclusion formation in steel welds is important to decide the final microstructure and improve

toughness in welds. It is also a good resource to validate the current model since many measurements are available in the literature. Kluken and Grong<sup>[73]</sup> measured the inclusion compositions in term of average element concentrations of aluminum, titanium, manganese, silicon, sulfur and copper in nine submerged arc welds with different steel compositions using the wavelength dispersive X-ray (EDX) intensity analysis and carbon extraction replicas method. The observed inclusions in the solidified weld pool consist of an oxide core forming due to reoxidation in the liquid state, and are covered partially by sulfides and nitrides on their surfaces. Simple empirical relations were suggested to compute the dissolved concentrations of alloying elements to match the measurements, and the order of precipitate formation was always Al<sub>2</sub>O<sub>3</sub>, Ti<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MnO, MnS and TiN regardless of the weld composition.

Hsieh<sup>[74]</sup> used Thermo-Calc software to predict inclusion development in these low-alloy-steel welds. Multi-phase equilibrium between oxides and liquid steel was assumed since the precipitation reactions are very fast at these high temperatures. The oxidation sequence was found to be sensitive to small changes in the weld composition. The calculation stopped at liquidus temperature 1800K (1527°C), so the possible formation of sulfides, nitrides and carbides after solidification was not found.

The distributions of various precipitated compounds in the inclusions are computed by the current model as functions of steel composition. Since precipitates including copper are not considered in this study, the original measured inclusion composition data were normalized to make the sum of the mass concentration of aluminum, titanium, manganese, silicon and sulfur total 100%, in order to allow for a proper comparison. The chemical compositions of the experimental welds are given in Table IX. A comparison of the calculated inclusion compositions at 1800K (1527°C) in liquid steel and 1523K (1250°C) in austenite with the measurements is shown in Fig. 8, and reasonable agreement is found especially at 1523K (1250°C), after high temperature solid-state reactions alter the normalized compositions, but before kinetics stops the diffusion (slope=0.644 and correlation coefficient=0.911 at 1800K, slope=0.988 and correlation coefficient=0.932 at 1523K). It indicates that the current model can be used as a first approximation to describe the formation of complex inclusions for different weld

metal compositions. The agreement is likely adversely affected by the lack of consideration of kinetics and segregation during solidification in the current model.

# V. CALCULATION FOR COMMERCIAL STEELS IN CONTINUOUS CASTING

Temperature and phase fraction evolution during the solidification and cooling process is the first crucial step to predict microstructure and ductility. In this study, the transient heat conduction equation is solved in the mold and spray regions of a continuous steel slab caster using the CON1D program<sup>[75]</sup>. This finite-difference model calculates one-dimensional heat transfer within the solidifying steel shell coupled with two-dimensional steady-state heat transfer in the mold and a careful treatment of the interfacial gap between the shell and mold. Below the mold, the model includes the temperature and spatially-dependent heat transfer coefficients of each spray nozzle, according to the local water flow rates and the heat extraction into each support roll. A nonequilibrium microsegregation model, based on an analytical Clyne-Kurz equation developed by Won and Thomas<sup>[76]</sup>, was applied to compute the liquidus, solidus temperature and phase fractions.

The casting conditions are chosen to model two Nucor commercial low carbon steels, 1004 LCAK and 1006Nb HSLA, in a typical thin slab casting machine, with a 950-mm long parallel mold. Details of the spray zone cooling conditions are given elsewhere<sup>[77]</sup>. Simulations are run for a slab with 1396mm width and 90mm thickness. The pour temperature is 1826K (1553°C), and the casting speeds are 2.8m/min and 4.6m/min. The water spray zones extend from the end of mold to 11.25m below the meniscus. The chemical compositions of both steels are shown in Table V. The phase evolutions of 1004 LCAK and 1006Nb HSLA steels with temperature are shown in Fig. 9, and small differences are found for the two steels. The calculated temperature and phase fraction histories at the slab surface are input to the current model for computing the corresponding equilibrium precipitation behaviors.

Fig. 10(a) and 10(b) compare the predicted temperature and the predicted equilibrium precipitate phases of the two commercial steels with casting speed 2.8m/min. It is seen that only precipitates

(Ti,Nb,V)(C,N), MnS and AlN form during casting for both steels, except that a small amount of oxides (Al,Ti)O exist from the liquid state for 1004 LCAK steel. The amounts of precipitates vary significantly due to the different steel compositions.

The influence of different casting speeds 2.8m/min and 4.6m/min on the precipitation behavior of 1006Nb HSLA steel is shown in Fig. 10(b) and 10(c). The higher casting speed causes higher surface temperature, for the same spray flow rates, and correspondingly less precipitates. TiN is the main precipitate at high temperature, especially in the mold because of its lowest solubility limit. Precipitates of MnS and AIN then begin to form in succession. With the higher temperature of the high casting speed, AIN does not precipitate in the mold, and does not fully come out of solution until after exiting the caster (>15m). This is significant because surface cracks often initiate in the mold due to strain concentration at the boundaries of locally enlarged grains, especially if they are embrittled by many fine precipitate particles<sup>[78]</sup> Below the mold, thermal stresses in the spray-cooling zones and mechanical stresses from unbending can exacerbate surface cracking, if precipitates are present. The results in Fig. 10 explain why high casting speed may sometimes be beneficial in preventing these types of surface cracks.

It is important, however, to consider the kinetic effects which are neglected in this model. Precipitation is diffusion controlled and requires time to proceed, especially at lower temperature. The current model was used to simulate equilibrium precipitation on a similar thin-slab continuous caster for similar microalloyed Nb steel grades and somewhat overpredicted the measured precipitate amounts<sup>[79]</sup>, as expected, even after 15 minutes of reheating. This shows that this casting process is too fast to reach the equilibrium state shown in Fig. 10. Thus, the real precipitate amounts for these cases are expected to be lower and not to vary as much with the temperature oscillations in the spray zones. Considering the combined effects of shorter time and higher temperature, the drop in precipitation found in the 1006Nb HSLA steel, at the higher casting speed should be more pronounced than shown in Fig. 10. Much more work is needed to make realistic predictions of precipitate formation during steel processing including kinetic effects, and to further extend the models to gain insight into ductility and crack formation.

# VI. SUMMARY AND CONCLUSIONS

A thermodynamic model is established to predict equilibrium precipitation behavior in microalloyed steels. It calculates the solubility limit of 18 common precipitates including the Wagner interaction effect, mutual solubility effect and complete mass conservation of all 13 alloying elements during precipitation. The model can predict the occurrence and stability of these common oxide, sulfide, nitride, and carbide precipitates in microalloyed steels, as well as their equilibrium compositions.

The impact of mutually solubility on precipitation is demonstrated. For mutually exclusive precipitates, the formation of a second precipitate phase may delay the formation and decrease the equilibrium amount of other precipitates when they share some alloying elements. However, this result tends to reverse for mutually soluble precipitates, because the mutual solubility decreases the equilibrium activities of these precipitates.

Precipitation diagrams constructed from the model results for given temperature show how phase composition regions evolve. Starting from no precipitation at high temperature initially, precipitation begins for the most stable (least soluble) precipitates and increases with decreasing temperature, leading to overlapping phase regions where more than one precipitate can form at lower temperatures.

The model is validated with an analytical solution for simple cases involving mutually-exclusive precipitates. It is further validated by comparison with the commercial package JMat-Pro. It is then validated by comparison with the measured amounts, types, and compositions of many different experimental results from previous literature. The current model matches reasonably well in all cases.

The precipitation behavior of commercial 1004 LCAK and 1006Nb HSLA steels in continuous casting with different casting speeds is calculated. TiN is the dominating precipitate in the mold because of its lowest solubility limit. The precipitates are mainly (Ti,Nb,V)(C,N), MnS and AlN for both steels, but the amount of each precipitate varies greatly due to their steel composition differences.

With higher casting speed for 1006Nb HSLA steel, higher temperature and less precipitates are obtained under the same spray flow and AlN does not precipitate in the mold.

In conclusion, an efficient solubility-product-based model of equilibrium precipitation in microalloyed steels has been developed, which is easy to revise by adding new types of precipitates or to change the solubility data. Equilibrium models such as this one represent the first step in development of a comprehensive model of precipitate formation in steel. Future work will incorporate other important effects, such as segregation during solidification and kinetic effects that govern precipitate growth and size distribution.

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Composition	Crystal form			1 V
(mass percent)	L attico paramotor	$\log_{10} \mathbf{K}_l$	$\log_{10} \Lambda_{\alpha,\delta}$	$\log_{10} \kappa_{\gamma}$
	Lattice parallet	64000	51620	51620
$AI_2O_3$	Hexagonal	$-\frac{64000}{\pi}+20.57^{[33]}$	$-\frac{51050}{\pi}+7.55^*$	$-\frac{51050}{77}+9.45^{[38]}$
[%AI] [%O]	$a = 4.76 \mathbf{A}, c = 13.0 \mathbf{A}$	Ι	Ι	Τ
Ti <sub>2</sub> O <sub>3</sub>	Hexagonal <sup>[26]</sup>	56060 18 08[34]	$56060 + 14.08^{*}$	$56060 + 15.08^{*}$
$[\% Ti]^{2}[\% O]^{3}$	$a = 5.16 \overset{0}{\mathbf{A}}, c = 13.6 \overset{0}{\mathbf{A}}$	$\frac{+10.00}{T}$	$-\frac{1}{T}$ +14.08	$-\frac{1}{T}$ +13.98
MgO	f.c.c <sup>[25]</sup>	4700 4 20[35]	4700	4700 5.22*
[%Mg][%O]	$a = 4.21 \overset{0}{\mathbf{A}}$	$-\frac{-4.28}{T}$	$-\frac{-1}{T}$ -0.28	$-\frac{-}{T}$ - 3.33
MnO	f.c.c <sup>[27]</sup>	11749	11749	11749
[%Mn][%O]	$a = 4.45 \overset{0}{\mathbf{A}}$	$-\frac{1}{T}$ + 4.000°	$-\frac{1}{T}+2.000$	$-\frac{1}{T}$ +3.010
SiO <sub>2</sub>	Trigonal <sup>[28]</sup>	30110 . 11 40[33]	30110 . 0.40*	30110 10.25*
$[\%Si][\%O]^2$	$a = 4.91 \mathbf{A}, c = 5.41 \mathbf{A}$	$-\frac{1}{T}$ +11.40 <sup>443</sup>	$-\frac{1}{T}$ +9.40	$-\frac{10.35}{T}$
MnS	f.c.c <sup>[29]</sup>	9020 2 00*	9020 1 00*	9020 . 2 02[39]
[%Mn][%S]	$a = 5.22 \overset{0}{A}$	$-\frac{1}{T}+3.98$	$-\frac{1}{T}$ +1.98	$-\frac{1}{T}+2.93^{1091}$
MgS	f.c.c <sup>[29]</sup>	9268 2.04*	9268	9268 1 01[40]
[%Mg][%S]	$a = 5.20 \overset{0}{A}$	$-\frac{1}{T}+2.06$	$-\frac{1}{T}+0.06$	$-\frac{1}{T}$ + 1.01 <sup>1.01</sup>
TiS	Trigonal <sup>[30]</sup>	13975	13975	13975
[%Ti][%S]	a = 3.30 Å, $c = 26.5$ Å	$-\frac{1}{T}$ + 6.48	+4.48	$-\frac{1}{T}$ +5.43 <sup>th</sup>
Ti <sub>4</sub> C <sub>2</sub> S <sub>2</sub> **	Hexagonal <sup>[30]</sup>	68180 . 25 9*	68180 . 27.0*	68180 . 21 ([4]]
$[\%Ti]^{4}[\%C]^{2}[\%S]^{2}$	$a = 3.30 \mathbf{A}, c = 11.2 \mathbf{A}$	$-\frac{-}{T}+35.8$	$-\frac{1}{T}+27.8$	$-\frac{1}{T}$ + 31.0°
AIN	Hexagonal <sup>[19]</sup>	12950 5 50[37]	8790 2 05[37]	6770 . 02[37]
[%Al][%N]	$a = 3.11 \mathbf{A}, c = 4.97 \mathbf{A}^{0}$	$-\frac{1}{T}$ +5.58 <sup>13/1</sup>	$-\frac{1}{T}+2.05^{15/1}$	$-\frac{1}{T}$ +1.03 <sup>1371</sup>
BN	Hexagonal <sup>[31]</sup>	10030	14250	13970
[%B][%N]	$a = 2.50 \mathbf{A}, c = 6.66 \mathbf{A}$	$-\frac{1}{T}$ +4.64 <sup>[37]</sup>	$-\frac{1}{T}$ + 4.61 <sup>(37)</sup>	$-\frac{1}{T}+5.24^{13/1}$
NbN	f.c.c <sup>[19]</sup>	12170	12170	10150 2 70[37]
[%Nb][%N]	$a = 4.39 \overset{0}{A}$	$-\frac{1}{T}$ +6.91	$-\frac{1}{T}$ + 4.91	$-\frac{1}{T} + 3.79^{13/1}$
NbCo 87	f.c.c <sup>[19]</sup>	9830	9830 4 20[37]	7020
[%Nb][%C] <sup>0.87</sup>	$a = 4.46 \overset{0}{A}$	$-\frac{1}{T}+6.33$	$-\frac{-}{T}+4.33^{13/1}$	$-\frac{1}{T}$ + 2.8 I <sup>1371</sup>
TiN	f.c.c <sup>[19]</sup>	17040	18420	15790
[%Ti][%N]	$a = 4.23 \overset{0}{A}$	$-\frac{1}{T}$ + 6.40	$-\frac{1}{T}$ +6.40 <sup>tory</sup>	$-\frac{1}{T}$ +5.40 <sup>try</sup>
TiC	f.c.c <sup>[19]</sup>	6160 2 2 5 [37]	10230	7000
[%Ti][%C]	$a = 4.31 \overset{0}{A}$	$-\frac{1}{T} + 3.25^{13/1}$	$-\frac{1}{T}$ +4.45 <sup>(3)</sup>	$-\frac{1}{T}$ + 2.75 <sup>1371</sup>
VN	f.c.c <sup>[19]</sup>	9720	9720 . 2 00[37]	7700 , 2 06[37]
[%V][%N]	$a = 4.12 \overset{0}{A}$	$-\frac{1}{T}$ + 5.90	$-\frac{1}{T} + 3.90^{-1}$	$-\frac{1}{T}+2.80$
V <sub>4</sub> C <sub>3</sub> **	f.c.c <sup>[19]</sup>	28200 24.00*	28200	26240 . 17 0[37]
$[\%V]^4[\%C]^3$	$a = 4.15 \overset{0}{A}$	$-\frac{1}{T}+24.96$	-1000000000000000000000000000000000000	$-\frac{1}{T}$ +1/.8 <sup>c/1</sup>
Cr <sub>2</sub> N	Trigonal <sup>[32]</sup>	1092 0.121*	1092 2 1 2 1*	1092 1 101[42]
$[%Cr]^{\bar{2}}[%N]$	$a = 4.76 \overset{0}{\mathbf{A}}, c = 4.44 \overset{0}{\mathbf{A}}$	-	-	$-\frac{1}{T}$

Table I. Lattice parameters and solubility products of precipitates

\* Estimated values used in the present work; temperature is in Kelvin

\*\* For consistency, these solubility products are rewritten in the form  $M_x X_y$ , according to  $\log_{10} K_{M_x X_y} = x \log_{10} K_{M X_{y/x}}$ 

Element j	$e_{\scriptscriptstyle N}^{j}$	$e_C^j$	$e_{\scriptscriptstyle S}^{j}$	$e_O^j$	$e_{Ti}^{j}$	$e^{j}_{\scriptscriptstyle Nb}$
N	6294/T <sup>[43]</sup>	5790/T <sup>[46]</sup>	$0.007^{[37]}$	$0.057^{[50]}$	-19500/T+8.37 <sup>[47]</sup>	-
C	$0.06^{[37]}$	8890/T <sup>[44]</sup>	$0.11^{[37]}$	-0.42 <sup>[33]</sup>	-221/T-0.072 <sup>[33]</sup>	-
S	$0.007^{[37]}$	0.046 <sup>[37]</sup>	-8740/T-0.394 <sup>[45]</sup>	-0. 133 <sup>[50]</sup>	-0.27 <sup>[33]</sup>	-
0	$0.05^{[37]}$	-0.34 <sup>[37]</sup>	-0.27 <sup>[37]</sup>	-1750/T+0.76 <sup>[33]</sup>	-3.4 <sup>[33]</sup>	-
Ti	-5700/T+2.45 <sup>[47]</sup>	-55/T-0.015 <sup>[33]</sup>	$-0.072^{[50]}$	$-1.12^{[33]}$	$0.042^{[33]}$	
Nb	-235/T+0.055 <sup>[48]</sup>	-66257/T <sup>[54]</sup>		-	-	$-2^{[46]}$
V	-356/T+0.0973 <sup>[49]</sup>	-	-	-	-	-
Al	-0.028 <sup>[50]</sup>	0.043 <sup>[37]</sup>	0.035 <sup>[50]</sup>	$-1.17^{[33]}$	0.93 <sup>[58]</sup>	-
Mn	-8336/T-27.8	-5070/T <sup>[55]</sup>	-0.026 <sup>[37]</sup>	$-0.021^{[33]}$	-0.043 <sup>[33]</sup>	-
	$+3.652 \ln T^{[51]}$					
Mg	-	$-0.07^{[50]}$	-	-1.98 <sup>[33]</sup>	$-1.01^{[59]}$	-
Si	-286/T+0.202 <sup>[52]</sup>	162/T-0.008 <sup>[50]</sup>	0.063 <sup>[37]</sup>	-0.066 <sup>[33]</sup>	177.5/T-0.12 <sup>[52]</sup>	77265/T-44.9 <sup>[54]</sup>
В	1000/T-0.437 <sup>[53]</sup>	-	-	-	-	-
Cr	-65150/T+24.1 <sup>[51]</sup>	-21880/T+7.02 <sup>[56]</sup>	-0.011 <sup>[50]</sup>	-0.046 <sup>[57]</sup>	-0.016 <sup>[57]</sup>	-216135/T+140.8 <sup>[54]</sup>

Table II. Selected interaction coefficients in dilute solutions of microalloyed steel

Element	$e_V^j$	$e^{j}_{Al}$	$e^{j}_{Mn}$	$e_{Mg}^{j}$	$e_{Si}^{j}$	$e_B^j$	$e_{Cr}^{j}$
J		1201					
Ν		$-0.058^{[50]}$	-	-	-	-	-
С	-	0.091 <sup>[33]</sup>	-0.0538 <sup>[33]</sup>	-0.25 <sup>[59]</sup>	$0.18^{[33]}$	-	-0.12 <sup>[50]</sup>
S	-	0.035 <sup>[33]</sup>	-28418/T+12.8 <sup>[39]</sup>	-	0.066 <sup>[33]</sup>	-	-153/T+0.062 <sup>[50]</sup>
0	-	-1.98 <sup>[33]</sup>	-0.083 <sup>[33]</sup>	-3 <sup>[33]</sup>	-0.119 <sup>[33]</sup>	-	$-0.14^{[50]}$
Ti	-	$0.004^{[58]}$	-0.05 <sup>[33]</sup>	-0.51 <sup>[59]</sup>	$1.23^{[33]}$	-	$0.059^{[50]}$
Nb	-	-	-	-	-	-	-
V	470/T-0.22 <sup>[60]</sup>	-	-	-	-	-	-
Al	-	0.043 <sup>[33]</sup>	$0.027^{[61]}$	$-0.12^{[59]}$	0.058 <sup>[33]</sup>	-	0.023 <sup>[57]</sup>
Mn	-	0.035 <sup>[61]</sup>	-175.6/T+2.406 <sup>[43]</sup>	-	-0.0146 <sup>[33]</sup>	-	0.0039 <sup>[33]</sup>
Mg	-	-0.13 <sup>[59]</sup>	-	-	-	-	$0.042^{[62]}$
Si	-	0.056 <sup>[33]</sup>	-0.0327 <sup>[33]</sup>	-0.088 <sup>[33]</sup>	0.103 <sup>[33]</sup>	-	-0.0043 <sup>[50]</sup>
В	-	-	-	-	_	0.038 <sup>[53]</sup>	-
Cr	_	0.012 <sup>[57]</sup>	0.0039 <sup>[33]</sup>	0.047 <sup>[59]</sup>	-0.0003 <sup>[33]</sup>	-	-0.0003 <sup>[50]</sup>

-.: not found value in literature, they are assumed to be zero in current calculation; temperature is in Kelvin

Table III. Mutually-soluble precipitate groups and their precipitates

Mutually-soluble precipitate group	Precipitate types involved
(Ti,Nb,V)(C,N)	$TiN, NbN, VN, TiC, NbC_{0.87}, V_4C_3,$
(Al,Ti)O	$Al_2O_3, Ti_2O_3$
(Mn,Mg)O	MnO, MgO
(Mn,Mg)S	MnS, MgS

1	
Groups of precipitates	Types of precipitates
$(Ti, Nb, V)(C, N), AlN, BN, Cr_2N$	TiN, NbN, VN, AlN, BN, Cr <sub>2</sub> N
$(Ti,Nb,V)(C,N), Ti_4C_2S_2$	$TiC, NbC_{0.87}, V_4C_3, Ti_4C_2S_2$
$(Mn, Mg)S, TiS, Ti_4C_2S_2$	$MnS, MgS, TiS, Ti_4C_2S_2$
$(Al,Ti)O, (Mn,Mg)O, SiO_2$	$Al_2O_3$ , $Ti_2O_3$ , $MnO$ , $MgO$ , $SiO_2$
$(Ti,Nb,V)(C,N), (Al,Ti)O, TiS, Ti_4C_2S_2$	$TiN, TiC, Ti_2O_3, TiS, Ti_4C_2S_2$
(Ti,Nb,V)(C,N)	$NbN, NbC_{0.87}$
(Ti,Nb,V)(C,N)	$VN, V_4C_3$
(Al,Ti)O, AlN	$Al_2O_3, AlN$
(Mn,Mg)O, (Mn,Mg)S	MnO, MnS
(Mn,Mg)O, (Mn,Mg)S	MgO, MgS
SiO <sub>2</sub>	SiO <sub>2</sub>
BN	BN
$Cr_2N$	$Cr_2N$
	Groups of precipitates $(Ti,Nb,V)(C,N), AlN, BN, Cr_2N$ $(Ti,Nb,V)(C,N), Ti_4C_2S_2$ $(Mn,Mg)S, TiS, Ti_4C_2S_2$ $(Al,Ti)O, (Mn,Mg)O, SiO_2$ $(Ti,Nb,V)(C,N), (Al,Ti)O, TiS, Ti_4C_2S_2$ $(Ti,Nb,V)(C,N), (Al,Ti)O, TiS, Ti_4C_2S_2$ $(Ti,Nb,V)(C,N)$ $(Ti,Nb,V)(C,N)$ $(Al,Ti)O, AlN$ $(Mn,Mg)O, (Mn,Mg)S$ $SiO_2$ BN $Cr_2N$

Table IV. Precipitates considered for each alloying-element mass balance

Table V. Compositions of 1004 LCAK and 1006Nb HSLA steels (weight percent)

Steel	Al	С	Cr	Mn	Mo	Ν	Nb	S	Si	Ti	V	0
1004 LCAK	0.040	0.025	0.025	0.141	0.007	0.006	0.002	0.0028	0.028	0.0013	0.001	0.00015
1006Nb HSLA	0.0223	0.0472	0.0354	0.9737	0.0085	0.0083	0.0123	0.0013	0.2006	0.0084	0.0027	0

Table VI. Compositions of Nb-based microalloyed steels (weight percent)

Steel	С	Si	Mn	Р	S	Nb	Al	N	V	Ti
Nb4	0.158	0.28	1.48	0.008	0.002	0.010	0.016	0.005	0.013	0.003
Nb8	0.081	0.31	1.44	0.010	0.002	0.033	0.017	0.004	0.011	0.003

Table VII. Compositions of Ti-based microalloyed steels (weight percent)

Steel	С	Si	Mn	Р	S	Al	Ti	Ν	Ο
В	0.0036	0.0050	0.081	0.011	0.0028	0.045	0.095	0.0019	0.0028
С	0.0033	0.0040	0.081	0.011	0.0115	0.037	0.050	0.0022	0.0036

Table VIII. Precipitates observed in two steels after holding several hours at different temperatures

Steel	1300°C	1250°C	1200°C	1150°C	1100°C
В	TiN	TiN,TiS*	TiN,TiS	TiN, Ti <sub>4</sub> C <sub>2</sub> S <sub>2</sub>	TiN, Ti <sub>4</sub> C <sub>2</sub> S <sub>2</sub>
С	TiN,TiS	TiN,TiS	TiN,TiS	TiN,TiS	TiN, <tis>,Ti<sub>4</sub>C<sub>2</sub>S<sub>2</sub></tis>

Note: \* means very scarce and <> means minor amount

Weld	С	0	Si	Mn	Р	S	Ν	Nb	V	Cu	В	Al	Ti
1	0.09	0.034	0.48	1.86	0.010	0.010	0.005	0.004	0.02	0.02	0.0005	0.018	0.005
2	0.09	0.037	0.55	1.84	0.010	0.009	0.005	0.005	0.02	0.03	0.0006	0.020	0.025
3	0.10	0.035	0.69	1.88	0.012	0.010	0.008	0.004	0.02	0.03	0.0008	0.028	0.063
4	0.10	0.030	0.52	1.87	0.010	0.007	0.005	0.007	0.01	0.06	0.0004	0.041	0.005
5	0.09	0.039	0.58	1.95	0.009	0.009	0.005	0.005	0.02	0.03	0.0006	0.037	0.022
6	0.09	0.040	0.69	1.97	0.009	0.009	0.006	0.007	0.02	0.03	0.0006	0.044	0.058
7	0.09	0.032	0.53	1.90	0.009	0.008	0.005	0.006	0.02	0.03	0.0004	0.062	0.008
8	0.10	0.031	0.62	1.92	0.010	0.010	0.005	0.005	0.02	0.03	0.0006	0.062	0.032
9	0.09	0.031	0.62	1.78	0.011	0.007	0.006	0.004	0.01	0.08	0.0006	0.053	0.053

Table IX. Compositions of experimental weld steels (weight percent)



Fig. 1—Example precipitates in microalloyed steels: (a).Fine spherical AlN<sup>[2]</sup>, (b).Cruciform (Ti,V)N after equalization at 1373K (1100°C)<sup>[3]</sup>, (c).(Ti,Nb)C on grain boundaries<sup>[4]</sup>, (d). Cubic TiN on grain boundaries<sup>[5]</sup>, (e),(f).Coarse complex multiple precipitates by heterogeneous nucleation<sup>[6]</sup>



Fig. 2—Comparison of mutually-exclusive precipitation model predictions with analytical solution in austenite for 3 Fe alloys containing 0.02%N and 0.02%Nb, and either 0.02% Al or

0.01% B



Fig. 3—Calculated precipitation phase diagram for quaternary Nb-Al-N system with 99.95%Fe



(a). Precipitate amount



(b). Molar fraction of (Ti,Nb)N precipitates

Fig. 4—Model calculation of mutually-soluble precipitation in austenite for 2 Fe alloys containing 0.01%N and 0.01%Nb, with and without 0.005%Ti



(b). 1006Nb HSLA steel





Fig. 6—Comparison of predicted amounts of Nb precipitation with experimental measurements at different temperatures (Table V steels<sup>[71]</sup>)



(a). Steel B



(b). Steel C

Fig. 7-Calculated molar fractions of precipitates for Ti-steels in Table VI



Fig. 8—Comparison of calculated and measured inclusion compositions for welding metals<sup>[72]</sup>



Fig. 9-Evolution of phase fractions with temperature for 1004 LCAK and 1006Nb HSLA steels



(a). 1004 LCAK steel with 2.8m/min casting speed



(b). 1006Nb HSLA steel with 2.8m/min casting speed



(c). 1006Nb HSLA steel with 4.6m/min casting speed

Fig. 10—Equilibrium precipitation behaviors of 1004 LCAK and 1006Nb HSLA steels in continuous casting with two different casting speeds