Particle-Size-Grouping Model of Precipitation Kinetics in Microalloyed Steels

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Abstract: The formation, growth, and size distribution of precipitates greatly affects the microstructure and properties of microalloyed steels. Computational Particle-Size-Grouping (PSG) kinetic models are developed to simulate precipitate particle growth due to collision and diffusion mechanisms. Firstly, the generalized PSG method for collision is clearly explained and verified. Then a new PSG method is proposed to model diffusion-controlled precipitate nucleation, growth, and coarsening with complete mass conservation and no fitting parameters. In comparison with the original population-balance models, this PSG method saves significant computation and preserves enough accuracy to model a realistic range of particle sizes. Finally the new PSG method is applied to simulate the size distribution of NbC and the precipitated fraction of AlN during isothermal aging processes, and good matches are found with experimental measurements.

1. Introduction

The demand for steels with higher strength, ductility, and toughness is always increasing. Many alloying additions act to improve these properties through the formation of precipitate particles. In addition to precipitation strengthening, the precipitates often act by pinning grain boundaries and inhibiting grain growth during steel processes. This effect arises from the disappearance of a small area of grain boundary when it intersects a second phase particle, and is widely acknowledged to depend on the volume fraction and particle size of the precipitates^[1-4]. Many small particles are more effective than a few large particles. An unfortunate side effect is a decrease in high temperature ductility and possible crack formation during processes such as casting and hot rolling due to the growth of voids around precipitate particles on the weak grain boundaries. It is therefore important to control the spatial distribution, morphological characteristics, and size distribution of precipitates during all stages of steel processing. These parameters are generally determined by the alloy composition, and temperature history. In high-deformation processes such as rolling, they also strongly depend upon strain and strain rate.

The accurate modeling of precipitate growth includes at least two analysis steps: 1) supersaturation, based on equilibrium precipitation thermodynamics, 2) kinetic effects. Many models to predict equilibrium precipitation are available in commercial packages based on minimizing Gibbs free energy, including Thermocalc^[5,6], FactSage^[7], ChemSage^[8], JMatPro^[9], other CALPHAD models^[10,11], and other thermodynamic models based on solubility products in previous literature^[12-16]. A recent equilibrium model efficiently predicts the stable formation of typical oxides, sulfides, nitrides and carbides in microalloyed steels, by solving the fully-coupled nonlinear system of solubility-product equations ^[17]. The model has been validated with analytical solutions of simple cases, results of a commercial package, and previous experimental results. A useful equilibrium model must accurately predict the occurrence and stability of precipitates, their equilibrium amounts, and compositions, for different steel compositions, phases, and temperatures, in order to calculate the supersaturation/driving force for a kinetic model.

Theoretically, precipitates start to form when the solubility limit is exceeded, but reaching equilibrium usually takes a long time. For most steel processes, especially at lower temperatures, equilibrium is seldom approached due to limited time. Thus, kinetic models of precipitate growth are a practical necessity for realistic predictions.

An early effort to predict phase transformation kinetics is the KJMA model, by Kolmogorov^[18], Johnson, Mehl^[19] and Avrami^[20], which is widely used to study precipitation processes and to generate TTT diagrams. The general isothermal KJMA equation to describe transformed fraction, f, as a function of time, t, is given by^[21]

$$f(t) = 1 - \exp(-K \cdot t^n)$$
^[1]

where K is the rate function for nucleation and growth which depends on chemical composition and temperature, and n is the Avrami exponent typically ranging from 1-4, which depends on growth dimensionality (1-D, 2-D or 3-D), nucleation index (zero, decreasing, constant or increasing nucleation rate), and growth index (interface-controlled or diffusion-controlled). The parameters K and n are determined from experimental measurements at different test temperatures and compositions, and often vary during precipitation. Although this model was successfully applied to match some precipitated fraction measurements^[22,23], its empirical nature prevents it from describing alternate thermomechanical processes without refitting the empirical parameters with further measurements. Moreover, size distributions are not predicted with this model.

Precipitates can form at different stages and locations in steelmaking, including: in the liquid steel due to collision, the mushy-zone between dendrites due to rapid diffusion during solidification, and on the grain boundaries or inside the grains due to slow solid-state diffusion. This results in different composition, morphology and size distribution of precipitates, thus greatly influences the steel product qualities. Precipitate particles grow via two major mechanisms: 1) collision in liquid

steel, 2) diffusion in both liquid and solid steel. Both mechanisms have been studied extensively, and better computational models are now available with fast improved computer power in recent decades.

Collision between particles and rapid diffusion in the liquid phase increase the number of large particles, and enhance inclusion removal by flotation. The evolution of particle concentration and size distribution due to collisions has been described by the collision frequency between particles per unit volume of liquid medium^[24], and such models have been successfully applied for various collision mechanisms, including turbulent collision^[25], Stokes collision^[26], Brownian collision^[27] and gradient collision^[28].

The entire diffusion-controlled precipitation process in solid typically includes nucleation, growth and coarsening stages. The nucleation stage includes an induction period to form stable nuclei, followed by steady-state nucleation, where the number of new particles increases linearly with time^[29]. Such a classical nucleation model^[29] has been successfully applied to predict the start of strain-induced Ti(C,N) precipitation in austenite^[30], and the results agree well with measurements inferred from stress relaxation experiments^[31].

After nucleation, particles of all sizes can grow due to the high supersaturation that defines the growth stage. After the nucleation and growth stages, precipitates of various sizes are dispersed in the matrix phase. Once the supersaturation has decreased to equilibrium (~1), the solute concentrations in the matrix and at the particle/matrix interface are comparable and capillary effects become dominant, causing coarsening or Ostwald ripening^[32]. Governed by the minimization of the total surface energy, coarsening is driven by the difference in concentration gradients near precipitate particles of different sizes. The larger particles are surrounded by low concentration, so grow by diffusion from the high concentration surrounding smaller particles, which are less stable and shrink. Thus, the net number density of all particles now decreases with time.

Each of these three stages is dominated by different mechanisms, and particle size evolution follows different laws. Coarsening increases with time according to the mean particle size cubed ^[33,34], which is slower than the square relation during the growth stage^[35]. More discussion is given elsewhere on nucleation^[36], growth^[37] and coarsening^[38] phenomena.

Although the above phenomena describing precipitation kinetics are well established, most models of nucleation, growth and coarsening are empirical curve-fits, with separate calibration parameters for each stage. Moreover, they require simplified conditions and calculate only the variation of mean precipitate size with time. Little information on the size distribution can be obtained. But, different precipitate size distributions can have very different pinning effects on grain growth, even with the same mean size. Thus a fundamental model including all possible precipitation mechanisms is needed.

Molecule-based models such as Smoluchowski^[24] for collision and Kampmann^[39] for diffusion are attractive because the particles agglomerate automatically, particles of all sizes are tracked, and the

few parameters are fundamental physical constants themselves. Unfortunately, these models encounter inevitable difficulties when they are applied to simulate practical processes, where precipitate size ranges greatly from nuclei ~ 1nm to coarsened particles larger than 100 μ m. Realistic particles range in size over at least 6 orders of magnitude, and contain from 1 to 10¹⁸ single molecules. With such an overwhelming linear scale, it is impossible to solve realistic problems using traditional models based on molecules.

Attempting to overcome this difficulty, the Particle-Size-Grouping (PSG) method has been introduced in several previous studies and has proven to be very effective in calculating the evolution of particle size distributions for collision-coagulation growth over a large size range^[40-45]. Rather than track each individual particle size, the main idea of this technique is to divide the entire possible particle size range into a set of size "groups", each with a specific mean size and size range. Careful attention is required to formulate the equations to ensure proper interaction and mass conservation^[40]. Several researchers have applied this PSG method to simulate inclusion agglomeration in liquid steel due to collisions, coagulation and removal. Such models have been applied to RH degassers^[41], continuous casting tundishes^[42,43] and ladle refining^[44,45]. To start these PSG models, an initial size distribution is still required, which can be found from either experimental measurements or assumptions.

To make the PSG method more usable, Nakaoka *et al.*^[46] used different volume ratios between neighboring size groups, taking advantage of the exponential increase in sizes that accompany powers of 2. This innovation allows modeling from single molecules to realistic particle sizes with only 20-80 size groups. Particle collisions were modeled, considering both inter-group and intra-group interactions, and numerical results agreed well with experimental agglomeration curves. However, very little work has been done to apply the PSG method to diffusion, which is the dominant mechanism for precipitate growth in many processes including steel casting and rolling. One study by Zhang and Pluschkell^[47], coupled both collision and diffusion into a PSG model, but inter-group diffusion was not considered. Zhang^[48] included a discrete-sectional technique by Gelbard^[49] and Wu^[50] into the PSG model, but this weakens the efficiency of the method and the accuracy of the treatment of diffusion and the insurance of mass conservation has not been verified. No previous study has demonstrated accurate simulation of diffusion using a PSG method.

The purpose of the present study is to develop accurate PSG methods to simulate precipitate growth due to both collision and diffusion mechanisms. The standard PSG method for collision problem is developed first, and a new PSG method for diffusion is created. Both methods are verified by comparison with exact solutions of the primary population equations in test problems. The new PSG method is shown to be a very time-efficient calculation with complete mass balance and high accuracy. Finally, the new PSG method is applied to simulate several practical precipitation processes in solid steels, and compared with experimental measurements.

2. Particle collision model

The population balance model for collision first suggested by Smoluchowski^[24] is:

$$\frac{dn_i}{dt} = \frac{1}{2} \sum_{k=1}^{i-1} \Phi_{k,i-k} n_k n_{i-k} - n_i \sum_{k=1}^{\infty} \Phi_{i,k} n_k$$
[2]

where n_i is the number of size *i* particles per unit volume, or "number density", and $\Phi_{i,j}$ is the collision kernel between size *i* and size *j* particles. The first term on the right-hand side generates size *i* particles due to the collision of two smaller particles, and the second term decreases the number of size *i* particles by their collision with particles of any size to become larger particles. The generation term is halved to avoid counting collision pairs twice. However, when two particles generating size *i* particles have same size, the generation term should not be halved because the collision pair is unique. Moreover, the loss term should be doubly counted when size *i* particles collide with themselves. The number of molecules composing the largest agglomerated particle must be a finite number i_M in numerical computation. Making these appropriate changes gives the following improved expression:

$$\frac{dn_i}{dt} = \frac{1}{2} \sum_{k=1}^{i-1} (1 + \delta_{k,i-k}) \Phi_{k,i-k} n_k n_{i-k} - n_i \sum_{k=1}^{i_M} (1 + \delta_{i,k}) \Phi_{i,k} n_k$$
[3]

where $\delta_{i,k}$ is the Kronecker delta, $\delta_{i,k}=1$ for i=k and $\delta_{i,k}=0$ for i≠k.When i=1, the population balance for dissolved single molecules simplifies to:

$$\frac{dn_1}{dt} = -n_1 \sum_{k=1}^{i_M} (1 + \delta_{1,k}) \Phi_{1,k} n_k$$
[4]

Thus the number density of single molecules always decreases with collisions. Evaluating equations [3]-[4] requires summing over and tracking every possible size from 1 to i_M molecules, so is not practical for realistic particle sizes. Results from these equations, however, comprise the exact solution for collision test problems.

3. Precipitate particle diffusion model

Kampmann^[39] suggested the following diffusion-controlled model to treat the kinetics of nucleation, growth and coarsening as one continuous and simultaneous process.

$$\frac{dn_i}{dt} = -\beta_i n_1 n_i + \beta_{i-1} n_1 n_{i-1} - \alpha_i A_i n_i + \alpha_{i+1} A_{i+1} n_{i+1} \quad (i \ge 2)$$
^[5]

where β_i , α_i and A_i are the diffusion growth rate, dissociation rate and reaction sphere surface area for a size *i* particle containing *i* molecules. The first and second terms on the right-hand side account for the loss and generation of size *i* particles due to "diffusion growth" by adding single molecule to size *i* and *i*-1 particles respectively. The third and fourth terms account for the loss and generation of size *i* particles due to particle "dissociation" by losing single molecule from size *i* and i+1 particles respectively. For single molecules, i=1, the special cases of double loss when two molecules react with each other and double generation of single molecules when size 2 particles dissociate are not counted exactly in Kampmann's initial work. Thus the following revised balance equation is suggested here:

$$\frac{dn_1}{dt} = -n_1 \sum_{k=1}^{i_M} (1 + \delta_{1,k}) \beta_k n_k + \sum_{k=2}^{i_M} (1 + \delta_{2,k}) \alpha_k A_k n_k$$
[6]

Assuming a uniform spherical concentration field of single molecules with a boundary layer thickness approximated by r_i around each size *i* particle, the diffusion growth rate of size *i* particles is expressed by^[39]:

$$\beta_i = 4\pi D r_i \tag{7}$$

where D is the diffusion coefficient in the matrix phase, and r_i is the radius of size *i* particles. As precipitation reactions always involve more than one element, this coefficient is chosen for the slowest-diffusing element, which is assumed to control the diffusion rate. Because the diffusion of interstitial elements such as O, S, N, C is fast, the diffusion rate is usually determined by the diffusion coefficient of the alloying metal element in the precipitate.

The following relation is assumed for the dissociation rate, which is the number of molecules lost per unit surface area of size *i* particles per unit time, based on a mass balance of a particle in equilibrium with the surrounding matrix phase ^[39]:

$$\boldsymbol{\alpha}_{i} = \boldsymbol{\beta}_{i} \boldsymbol{n}_{1i} / \boldsymbol{A}_{i} = \boldsymbol{D} \boldsymbol{n}_{1i} / \boldsymbol{r}_{i}$$
^[8]

The concentration of single molecules, n_{1i} , in equilibrium around the surface of the size i particle is needed to evaluate this equation. This is estimated using the Gibbs-Thompson equation, and decreases with increasing particle size as follows^[51]:

$$n_{1i} = n_{1,eq} \exp\left(\frac{2\sigma V_P}{R_g T} \frac{1}{r_i}\right)$$
[9]

where $n_{l,eq}$ is the number density of dissolved single molecules in equilibrium with a plane interface of the precipitate phase, σ is the interfacial energy between the precipitate particles and the matrix phase, V_P is the molar volume of the precipitate, R_g is the gas constant, and T is the absolute temperature. This equation indicates that increasing particle radius causes the nearby solute concentration to decrease greatly, by several orders of magnitude.

Equations [5]-[9] include the effects of equilibrium, diffusion growth, dissociation, curvature effects and mass conservation, with parameters all having appropriate physical significance. Results from these equations are regarded as the exact solution for diffusion test problems.

4. Particle-Size-Grouping (PSG) method

From a theoretical point of view, these molecule-based population-balance models in the previous section are accurate and the integration of their set of governing equations is straight forward. However, the computational cost quickly becomes infeasible for realistic particle sizes. The PSG method is introduced here to overcome this difficulty. The fundamental concept of the PSG method is shown schematically in Fig. 1. In this method, the particles are divided into different size groups (size group number j) with characteristic volume V_j and characteristic radius r_j. The number density of particles of size group j is defined as

$$N_{j} = \sum_{V_{j,j+1} > V > V_{j-1,j}} n(V)$$
[10]

This summation covers all particles whose volume lies between two threshold values. The threshold volume that separates two neighboring size groups, $V_{j,j+l}$, is assumed to be the geometric average of the characteristic volumes of these two groups, instead of the arithmetic average used in previous works^[46,47].

$$V_{j,j+1} = \sqrt{V_j V_{j+1}}$$
[11]

If a newly-generated particle has its volume between $V_{j-I,j}$ and $V_{j,j+I}$, it is counted in size group *j*. The increase of number density of size group *j* particles is then adjusted according to the difference between the volume of the new particle and V_j , in order to conserve mass.

The volume ratio between two neighboring size groups is defined as

$$R_V = \frac{V_{j+1}}{V_j}$$
[12]

To generate regularly-spaced threshold values, R_V is usually varied. However, for constant R_V , the PSG characteristic and threshold volumes can be expressed as:

$$V_{j} = R_{V}^{j-1}V_{1}, V_{j,j+1} = R_{V}^{(j-1/2)}V_{1}$$
[13]

where the volume of a single molecule, V_1 , is computed using the molar volume of its precipitate crystal structure, V_P :

$$V_1 = \frac{V_P}{N_A}$$
[14]

where N_A is Avogadro's number, and the small effects of temperature change and vacancies are neglected. Since the particle volume is calculated from a bulk property, V_P , consideration of the packing factor is not needed. The number of molecules contained in a given PSG volume is

$$m_j = \frac{V_j}{V_1}, \ m_{j,j+1} = \frac{V_{j,j+1}}{V_1}$$
 [15]

In the PSG method, it is easy to introduce fractal theory to consider the effect of particle morphology. The effective radius of a particle can be expressed by

$$r_j = r_1 \left(\frac{V_j}{V_1}\right)^{1/D_j}$$
[16]

where D_f is the fractal dimension, which can vary from 1 (needle-shaped precipitates) to 3 (complete coalescence into smooth spheres). Tozawa^[52] proposed $D_f=1.8$ for Al₂O₃ clusters in liquid steel, and $D_f=3$ is adopted everywhere in this work for simplicity.

After the number of single molecules composing the largest agglomerated particles i_M is determined, the corresponding total number of size groups G_M must be large enough for the second largest size group to contain the largest agglomerated particle, i_M . Thus, for constant R_V , G_M must satisfy:

$$G_M \ge ceil(\log_{R_v} i_M) + 2$$
^[17]

The largest size group is a boundary group which always has zero number density. The accuracy of the PSG method should increase with decreasing R_V , as more size groups are used. From the logarithm relation shown above, it can be seen that the PSG method is very efficient for real problems with a large range of particle sizes.

4.1 PSG method for collision

Applying the PSG method to model colliding particles involves the following rules, affecting size group j:

1). A size group *j* particle colliding with a small particle, from group 1 to $k_{c,j}$, remains in group *j*, and increases the number density, N_j .

2). A group *j* particle colliding with a relatively large particle, from a group larger than $k_{c,j}$, generates a particle in group *j*+1 or higher.

3). A group *j*-1 particle colliding with a particle from group k_{cj} to *j*-1 generates a group *j* particle.

Combining these rules gives the following equation, where the coefficients involving mean volumes are needed to conserve volume,

$$\frac{dN_{j}}{dt} = N_{j} \sum_{k=1}^{k_{c,j}} \frac{V_{k}}{V_{j}} \Phi_{j,k} N_{k} - N_{j} \sum_{k=k_{c,j}+1}^{G_{M}} \left[(1+\delta_{j,k}) \Phi_{j,k} N_{k} \right] + \sum_{k=k_{c,j}}^{j-1} \frac{V_{j-1} + V_{k}}{V_{j}} \Phi_{j-1,k} N_{j-1} N_{k} \quad (j \ge 2)$$

$$(18)$$

$$(j) + (k \le k_{c}) \rightarrow (j) \quad (j) + (k > k_{c,j}) \rightarrow (m > j) \quad (j-1) + (k \ge k_{c,j}) \rightarrow (j)$$

with
$$k_{c,j} = \begin{cases} j-1 & 4.000 > R_V > 2.148 \\ j-2 & 2.148 > R_V > 1.755 \\ j-3 & 1.755 > R_V > 1.587 \end{cases}$$
 [19]

The R_V ranges in Eq. [19] are found by solving the following equations, after inserting the Eq. [13] expressions:

$$V_{j} + V_{k_{c,j}+1} > V_{j,j+1}$$
^[20]

Finally, the number density of single molecules is calculated by

$$\frac{dN_1}{dt} = -N_1 \sum_{k=1}^{G_M} (1 + \delta_{1,k}) \Phi_{1,k} N_k$$
[21]

Equations [18], [19] and [21] are integrated over time for all size groups. The small number of size groups enables the model to simulate practical problems.

4.2 PSG method for diffusion

Applying the PSG method to solid-state diffusion processes would appear to involve fewer rules than the particle collision method just presented, because precipitate particle growth by diffusion involves gain or loss of only one individual molecule at a time. However, adding single molecule to a particle very rarely gives enough particle growth to count it in the next larger size group. In addition, size groups j-1, j and j+1 all influence the evolution of size group j number density during a given time interval. Thus, some knowledge of the particle distribution inside each size group is necessary, especially near the size group thresholds where the inter-group interaction occurs. This requires careful consideration of diffusion growth and dissociation both inside and between size groups.

All particles inside a size group *j* will still stay in group *j* even after a diffusion growth or dissociation event, except for those "border sizes" which fall on either side of the threshold sizes which define the neighboring size groups: n_j^L (closest to $V_{j,1,j}$) and n_j^R (closest to $V_{j,j+1}$). Size group *j* particles also can be generated if particles n_{j-1}^R from size group *j*-1 jump into size group *j* by diffusion growth or particles n_{j+1}^L from size group *j*+1 fall into size group *j* by dissociation. At the same time, size group *j* particles can be lost if particles n_j^R jump to size group *j*+1 by diffusion growth or particles n_j^L fall to size group *j*-1 by dissociation. These considerations are incorporated into a new PSG method, taking care to conserve mass, as follows:

$$\frac{dN_j}{dt} = \frac{m_1}{m_j} \beta_j N_1 (N_j - n_j^R) - \frac{m_1}{m_j} \alpha_j A_j (N_j - n_j^L)$$

$$+\frac{ceil(m_{j-1,j})}{m_{j}}\beta_{j-1}^{R}N_{1}n_{j-1}^{R} + \frac{floor(m_{j,j+1})}{m_{j}}\alpha_{j+1}^{L}A_{j+1}^{L}n_{j+1}^{L} - \frac{floor(m_{j,j+1})}{m_{j}}\beta_{j}^{R}N_{1}n_{j}^{R} - \frac{ceil(m_{j-1,j})}{m_{j}}\alpha_{j}^{L}A_{j}^{L}n_{j}^{L} \quad (j \ge 2)$$
[22]

where n_j^L is the number density of those particles in size group *j* which fall into size group *j*-1 by losing one molecule, and n_j^R is the number density of those particles in size group *j* which jump into size group *j*+1 by gaining one molecule. Function *ceil* calculates the smallest integer which is not less than the given real number, and *floor* for the largest integer which is not larger than the given real number. In Eq. [22], the first and second terms on the right-hand side account for the diffusion growth and dissociation inside size group *j*, and the third and fourth terms account for the generation of size group *j* particles by inter-group diffusion growth and dissociation. The last two terms are for loss of size group *j* particles due to the diffusion growth and dissociation of size group *j* particles themselves.

Single molecules are a special case because they comprise a group which interacts with all other size groups. Thus, the new PSG method for diffusion uses the following population balance equation for j=1:

$$\frac{dN_1}{dt} = -N_1 \sum_{k=1}^{G_M} (1 + \delta_{1,k}) \beta_k (N_k - n_k^R) + \sum_{k=2}^{G_M} \alpha_k A_k (N_k - n_k^L) -N_1 \sum_{k=1}^{G_M} (1 + \delta_{1,k}) \beta_k^R n_k^R + \sum_{k=2}^{G_M} (1 + \delta_{2,k}) \alpha_k^L A_k^L n_k^L$$
[23]

The diffusion growth rate β_j , and dissociation rate α_j of size group j particles needed to solve Eqs. [22-23] are calculated with Eqs. [7-9] using the characteristic (mean) radius given by Eq. [16]. The radius, diffusion growth rate, and dissociation rate for the border-sized particles are:

$$r_{j}^{L} = \left(ceil\left(m_{j-1,j}\right)\right)^{1/D_{f}} r_{1}, r_{j}^{R} = \left(floor\left(m_{j,j+1}\right)\right)^{1/D_{f}} r_{1}$$
[24]

$$\beta_j^L = 4\pi D r_j^L, \ \beta_j^R = 4\pi D r_j^R$$
[25]

$$\alpha_j^L = \frac{\beta_j^L N_{1,eq}}{A_j^L} \exp\left(\frac{2\sigma V_P}{R_g T} \frac{1}{r_j^L}\right), \ \alpha_j^R = \frac{\beta_j^R N_{1,eq}}{A_j^R} \exp\left(\frac{2\sigma V_P}{R_g T} \frac{1}{r_j^R}\right)$$
[26]

The particle number densities for the border sizes n_j^L and n_j^R are estimated from a geometric progression approximation

$$n_{j}^{L} = n_{j-1}^{C} \left(\frac{n_{j}^{C}}{n_{j-1}^{C}}\right)^{\frac{ceil(m_{j-1,j}) - m_{j-1}}{m_{j} - m_{j-1}}}, n_{j}^{R} = n_{j}^{C} \left(\frac{n_{j+1}^{C}}{n_{j}^{C}}\right)^{\frac{floor(m_{j,j+1}) - m_{j}}{m_{j+1} - m_{j}}}$$
[27]

In order to propagate particle growth, if $n_j^L \neq 0$ and $n_{j+1}^C = 0$, n_j^R is calculated by

$$n_{j}^{R} = n_{j}^{L} \left(\frac{n_{j}^{C}}{n_{j}^{L}}\right)^{\frac{floor(m_{j,j+1}) - m_{j}}{m_{j+1} - m_{j}}}$$
[28]

The particle number density at the center of each size group j is calculated by assuming two geometric progressions inside each size group

$$n_{j}^{C} = \frac{N_{j}}{\sum_{k=1}^{m_{j}-ceil(m_{j-1,j})} (1/q_{j}^{L})^{k} + 1 + \sum_{k=1}^{floor(m_{j,j+1})-m_{j}} (q_{j}^{R})^{k}}$$
[29]

with
$$q_j^L = \left(\frac{\overline{n}_j}{\overline{n}_{j-1}}\right)^{\frac{1}{m_j - m_{j-1}}}, q_j^R = \left(\frac{\overline{n}_{j+1}}{\overline{n}_j}\right)^{\frac{1}{m_{j+1} - m_j}}$$
 [30]

The average number density of size group *j* is calculated as

$$\overline{n}_{j} = \frac{N_{j}}{floor(m_{j,j+1}) - ceil(m_{j-1,j}) + 1}$$
[31]

Since the boundary (ceil, floor) and mean values of size groups are used directly and R_V is not explicitly found in these equations, this model is very flexible to apply. This allows arbitrary size increments between groups in a single simulation, making it easy to improve accuracy with smaller R_V in size ranges of interest and to improve computation with larger R_V in other sizes. Alternatively, the group sizes can be chosen to produce linearly-spaced particle radius intervals, needed to compare with experiments.

5. Validation of new PSG method with test problems

5.1 Collision test problem

Saffman^[25] suggested the turbulent collision frequency per unit volume of liquid medium to be:

$$\Phi_{ij} = 1.3a(\varepsilon/\nu)^{1/2}(r_i + r_j)^3$$
[32]

where ε is turbulent energy dissipation rate and ν is kinematic viscosity. The empirical coefficient a was suggested by Higashitani^[53] and is assumed constant here. This model has been often applied to study inclusion agglomeration in liquid steel^[41-45,47,48]. It is chosen here as a test problem to validate the collision model, using the complete integer-range equations in Section 2.1 as the exact solution.

Substituting into the dimensionless form of number density and time:

$$n_i^* = n_i / n_0, \ t^* = 1.3a(\varepsilon / v)^{1/2} r_1^3 n_0 t$$
 [33]

where n_0 and r_1 are the initial number density and the radius of single molecules. The initial condition is given by $n_i^*=1$ for i=1 and $n_i^*=0$ for i>1. The size of the largest agglomerated particle is $i_M=12000$, so that accuracy within 0.05% error in the total particle volume is guaranteed up to $t^*=1$. The boundary condition is always zero number density of the largest agglomerated particle (exact solution) and for the largest size group (PSG method). The Runge-Kutta-Gill method is applied for time integration with a time step of $\Delta t^*=0.0025$. Smaller time step sizes produce negligible difference.

The total dimensionless number density of molecules and particles are defined as

$$N_{M}^{*} = \sum_{i=1}^{i_{M}} i \cdot n_{i}^{*}, \ N_{T}^{*} = \sum_{i=1}^{i_{M}} n_{i}^{*} \text{ for exact solution}$$
$$N_{M}^{*} = \sum_{j=1}^{G_{M}} m_{j} \cdot N_{j}^{*}, \ N_{T}^{*} = \sum_{j=1}^{G_{M}} N_{j}^{*} \text{ for PSG method}$$
[34]

The mass balance requires N_M^* to be constant (equal to 1) through the entire calculation. Fig. 2 shows the total particle volume is conserved for both the exact solution and PSG method. There is also good agreement between both cases for $R_V=3$ and $R_V=2$ for the total particle number density, which decreases with time due to agglomeration. Fig. 3 shows that the evolution of the number densities of each size group with time from the PSG method also agrees reasonably with the exact solution for both R_V cases. With smaller R_V , accuracy of the PSG method increases as expected.

As time increases, collisions form large particles, leaving fewer smaller particles. For example, size group N_{10} in R_{I} =2 contains all particle sizes from 363 to 724 molecules, with a central size of 512 molecules. The number density of the size group increases at early times, reaches a maximum, and decreases at later times. The exact solution has limited maximum time, owing to its prohibitive computational cost. The tremendous computational efficiency of the PSG method is seen by examination of Table I.

5.2 Diffusion test problem

To validate the PSG diffusion model, a test problem is chosen where the total number density of single molecules in the system are produced by an isothermal first order reaction^[39]

$$n_s^*(t^*) = n_s(t^*) / n_{1,eq} = \sum_{i=1}^{i_M} i \cdot n_i^* = 9[1 - \exp(-0.1t^*)]$$
[35]

The number density of dissolved single molecules must be adjusted with time, to match the increase of n_s^* . This increase with time can be interpreted as an increase in supersaturation due to decreasing temperature in a practical cooling process. The dimensionless terms are defined as

$$n_i^* = n_i / n_{1,eq}, t^* = 4\pi D_1 r_1 n_{1,eq} t$$
 [36]

To calculate the dissociation rate in Eq.[9], $2\sigma V_P/(R_gTr_1)=3.488^{[39]}$. The initial condition is no particles, or $n_i^*=0$ for $i\geq 1$.

The boundary condition is always zero number density for the largest agglomerated particle (exact solution) or for the largest size group (PSG method). The maximum size of agglomerated particle is chosen as i_M =50000, to ensure that mass conservation is satisfied up to t^{*}=10000. The explicit Runge-Kutta-Gill method was used for integration with time step size of Δt^* =0.01 chosen for accuracy. The maximum time step for stability is 0.04 for both methods for this problem.

As shown in Fig. 4, the total volume of particles is conserved for both the exact solution and the PSG method. This total increases with time and asymptotes at 9, according to Eq. [35]. The number density histories from all 3 cases also agree. Its behavior can be explained by examining Fig. 5.

Fig. 5 shows how the particle size distribution evolves, due to the changing concentration gradients near particles of different size groups. At early times, all size group particles grow owing to the driving force of increasing supersaturation. At later times, the results show Ostwald ripening. The large particles have low concentrations, so tend to grow at the expense of smaller particles, which have high local concentrations, and eventually shrink. For example, size group N₁ (dissolved single molecules) reaches its peak and starts to decrease in number after t^{*}=20. There is reasonable agreement for both total particle number density and number densities of each size group between the PSG method and the exact solution for both cases of $R_V=3$ and $R_V=2$. Results for $R_V=2$ naturally match the exact solution more closely.

5.3 Computation times

The computation times for both test problems are listed in Table I. All the calculations are run with Matlab on Dell OPTIPLEX GX270 with P4 3.20GHz CPU and 2GB RAM in order to enable a fair comparison. The computational cost dramatically reduces for the PSG method. It is interesting to note that the computation cost for the collision problem is proportional to i_M^2 for the exact solution or G_M^2 for the PSG method, while it is proportional to i_M or G_M respectively for the diffusion problem. Because the details of particle distribution inside the size groups must be captured to enable an accurate solution in a diffusion problem, the time saving is not as large. The savings increases exponentially with increasing maximum particle size. This is enough to make practical precipitation calculations possible, considering that less than 60 size groups covers particle sizes up to 100µm with constant $R_I=2$ for most nitrides and carbides in microalloyed steels.

6. Practical applications

When the PSG method is applied to model a real precipitation process, additional models are needed for the temperature history and corresponding mass concentrations of each element dissolved at equilibrium. The current work assumes the temperature history is given and uses a 13-element and 18-precipitate equilibrium precipitation model for microalloyed steels^[17]. This model includes solubility limits for oxide, sulfide, carbide, and nitride precipitates in liquid, ferrite and austenite, the influence of Wagner interaction on activities, and mass conservation of all elements during precipitation. Mutual solubility is incorporated for appropriate precipitates with similar crystal structures and lattice parameters.

For a given steel composition and temperature history, the first step is to use the equilibrium model to compute the dissolved molar concentrations of every element at every temperature, and to identify the critical element, which restricts the number of single molecules available to form the precipitate of interest, as a function of time. The initial condition starting from the liquid state is complete dissolution with the number density of single molecules, $N_1(t=0)$, equal to the total number density, n_s , of the precipitate of interest. For a given steel composition containing M_0 of element M, and X_0 of element X, then n_s for precipitate $M_x X_y$ is

$$n_s = \min\left(\frac{M_0}{100} \frac{\rho_{steel}}{xA_M} N_A, \frac{X_0}{100} \frac{\rho_{steel}}{yA_X} N_A\right)$$
[37]

where A_M is the atomic mass of element M, and ρ_{steel} is the density of the steel matrix (7500kg·m⁻³). All other particle sizes have zero number densities.

Sometimes, such as after a solution treatment, some of the initial processing steps from the liquid state can be ignored or replaced with a measured initial distribution. Because the current model can handle only one precipitate, the initial composition must be the dissolved concentration available for that precipitate after taking away the other precipitates that form first. For example, in the cases involving nitride AlN formation, a new Al concentration is used after subtracting the more stable oxide Al_2O_3 .

The equilibrium number density of single molecules of the precipitate in the steel, n_{1eq} , is calculated from the dissolved mass concentrations [M] and [X] at equilibrium in the same way:

$$n_{1,eq} = \min\left(\frac{[M]}{100} \frac{\rho_{steel}}{xA_M} N_A, \frac{[X]}{100} \frac{\rho_{steel}}{yA_X} N_A\right)$$
[38]

Although the current work only calculates size distributions for a single precipitate, other alloys may affect the results by forming other precipitates which change the equilibrium dissolved concentrations of the elements in the precipitate of interest. These effects are included through the equilibrium model, in addition to Wagner interactions ^[17].

The PSG kinetic model is then run, knowing the history of the equilibrium number density of single molecules of the chosen precipitate. The diffusion coefficients and dissociation rates in Eqs. [7-9] and [24-26] are updated for each time step according to the temperature history. This model calculates how the particle size distribution evolves with time.

When running the PSG model, time steps must large enough to enable reasonable computation times, while avoiding stability problems due to dissociation exceeding diffusion growth. Thus, the implicit Euler scheme is adopted here to integrate Eqs. [22-31] through time:

$$\left[1 + \Delta t \left(\frac{m_{1}}{m_{j}}\alpha_{j}A_{j} + \frac{floor(m_{j,j+1})}{m_{j}}\beta_{j}^{R}N_{1}^{i+1} + \frac{ceil(m_{j-1,j})}{m_{j}}\alpha_{j}^{L}A_{j}^{L}\right)\right]N_{j}^{i+1}$$

$$= N_{j}^{i} + \Delta t \left[\frac{m_{1}}{m_{j}}\beta_{j}N_{1}^{i+1}(N_{j}^{i+1} - n_{j}^{R}) + \frac{m_{1}}{m_{j}}\alpha_{j}A_{j}n_{j}^{L} + \frac{ceil(m_{j-1,j})}{m_{j}}\beta_{j-1}^{R}N_{1}^{i+1}n_{j-1}^{R} + \frac{floor(m_{j,j+1})}{m_{j}}\alpha_{j+1}^{L}A_{j+1}^{L}n_{j+1}^{L}\right]$$

$$+ \frac{floor(m_{j,j+1})}{m_{j}}\beta_{j}^{R}N_{1}^{i+1}(N_{j}^{i+1} - n_{j}^{R}) + \frac{ceil(m_{j-1,j})}{m_{j}}\alpha_{j}^{L}A_{j}^{L}(N_{j}^{i+1} - n_{j}^{L})\right] \quad (j \ge 2) \quad [39]$$

where i is the time-step index. This implicit scheme allows over 10^4 -fold increase in time step size comparing with the original explicit scheme, for realistic precipitate/matrix interfacial energies ~0.5J/m². The above equation system is solved with the iterative Gauss-Seidel method until the largest change of N_j^{i+1} converges to within less than 10^{-5} between two iterations. The upper limits of n_j^L and n_j^R are N_j^{i+1} , and are evaluated at each iteration. Although this scheme is stable for any time step size, its accuracy may deteriorate if the time step is too large. Thus a reasonable time step must be chosen where results stay almost the same with a smaller time step.

Having validated mass conservation with test problems, the number density of single molecules is then computed as follows, in order to save computation time relative to Eq. [23]

$$N_1^{i+1} = n_s - \sum_{j=2}^{G_M} m_j N_j^{i+1}$$
[40]

To post-process the results, the total number density of precipitate particles n_p , precipitated fraction f_P and the average precipitate particle radius $\overline{r_p}$ are computed from the number densities as follows:

$$n_P = \sum_{j=G_T}^{G_M} N_j$$
[41]

$$f_P = \frac{\sum_{j=G_T}^{G_M} m_j N_j}{n_c}$$
[42]

$$\overline{r}_{P} = \frac{\sum_{j=G_{T}}^{G_{M}} r_{j} N_{j}}{\sum_{j=G_{T}}^{G_{M}} N_{j}}$$
[43]

where size group G_T , which contains particles just larger than a "truncating" threshold radius $r_{T-1,T}$, is introduced to define the split between "dissolved" and measurable particles. This parameter must be introduced because all experimental techniques have resolution limits, while the current PSG model simulates particles of all sizes including single molecules.

The complete PSG model is applied here to two different example precipitate systems, where measurements were available for validation.

6.1 Size distribution for isothermal NbC precipitation

The first validation problem is to simulate the size distribution of Nb(C,N) precipitate particles in steel containing 20%Cr, 25%Ni, 0.5%Nb, 0.05%C+N, to compare with the isothermal precipitation experiments of Jones and Howell^[54]. The steel specimens were solution treated at 1350°C, quenched to the aging temperature of 930°C and held for 1800s, with no deformation. Carbon extraction replicas were used to measure particle size distributions, which can detect precipitates (nuclei) with diameters less than $2nm^{[55]}$. To compare with the measurements, a truncating radius of 0.5nm was set in the simulation. Precipitation was calculated assuming NbC precipitate formation with 0.05%C. Nitrogen was neglected because its content was not reported, the PSG model can simulate only one precipitate type, and carbon is always much more plentiful than N. The diffusion coefficient of Nb in austenite is taken as $D_{Nb}(m^2/s)=0.83\times10^{-4}exp(-266500/RT)^{[56]}$, molar volume of NbC is $V_P=13.39\times10^{-6}m^3/mol^{[57]}$, and the interfacial energy is calculated in the appendix.

The equilibrium calculation in Fig. 6 predicts that the NbC precipitates begin to become stable at 1310° C, and the equilibrium dissolved mass concentration of carbon in steel is 0.0052wt% at T=930°C. In order to compare with the experimental data, R_V was set equal 2 for particles with radius smaller than 3nm, and varied to give 1nm size groups for 3-15nm, 1.5nm size groups for 15-24nm, 3nm size groups for 24-36nm, and 6nm size groups for 36-48nm. A total of 38 size groups were used to model particle sizes up to 48nm, the largest particle observed in the experiments. The implicit time step is 0.001s with maximum of iteration 10000 for convergence. Rapid quenching from solution treatment to aging temperature and from aging to ambient is assumed, so only an isothermal simulation at 930°C is performed.

The measured particle size distribution / volume number frequency in the steel matrix is normalized and compared with simulation results in Fig. 7. The actual mean radius of NbC particles was 9.3nm in experiment and 8.13nm in simulation and the particle size distributions also match reasonably. The measured size distribution is wider than the simulation results. This is likely due to the grain boundaries, segregated regions, and dislocations present in the steel microstructure, where easier nucleation and higher diffusion rate can form locally larger precipitates, leaving smaller particles elsewhere where the concentration is lower. In addition, the uncertain presence of other alloys in the steel, such as nitrogen leading to possible Nb(C,N) precipitation, and Cr leading to Cr(C,N), could enable local heterogeneous nucleation, higher dissolved concentration (supersaturation), and changes in interfacial energy. Such precipitates could form earlier and become nucleation sites for accelerated NbC precipitation.

6.2 Precipitated fraction for isothermal AIN precipitation

The second validation problem for the PSG diffusion model was to simulate the isothermal precipitation of AlN in a 0.09%C, 0.20%Si, 0.36%Mn, 0.051%Al and 0.0073%N steel for the experimental conditions measured by Vodopivec^[58]. Specimens were solution treated at 1300°C for 2 hours, "directly" cooled to the precipitation temperature of 840°C or 700°C, aged for various times, and quenched. The AlN content in steel was measured using the Beeghly method^[59]. Because it has been suggested that Beeghly technique cannot detect fine precipitate particles which could pass through the filter^[60,61], the truncating precipitate radius is set to 2.0nm in the simulation to match the measurements.

The initial experimental measurements (zero and short aging times) report 6.4% of the total N (N₀=0.0073%) precipitated as AlN, perhaps because the cooling stages were not fast enough. The final precipitated amounts of nitrogen as AlN do not reach the predictions of the equilibrium model, even after long holding times, when the precipitated fraction becomes nearly constant. This might be due to N consumed into other types of nitrides. Thus the measurements are normalized to zero at zero aging time, and (N₀-[N])/N₀ at long times.

As shown in Fig. 6, the equilibrium model^[17] predicts AlN to start forming at 1236°C, and the equilibrium dissolved concentration of nitrogen in steel is ~0.00022wt% at 840°C (Π_N =33.2) and ~0.0000031wt% at 700°C (Π_N =2370). A sharp decrease of equilibrium dissolved aluminum concentration can be seen over the $\gamma \rightarrow \alpha$ phase transformation (865°C to 715°C) due to the lower solubility limit of AlN in ferrite predicted by the equilibrium model.

Isothermal precipitation simulations of 1 hour (700 °C) and 3 hours (840 °C) were run, neglecting the cooling histories before and after, which were not clearly reported. The molar volume V_P of AlN is $12.54 \times 10^{-6} \text{m}^3/\text{mol}^{[57]}$ and the diffusion coefficient of Al in steel $D_{Al}(\text{m}^2/\text{s})$ is taken as $2.51 \times 10^{-4} \text{exp}(-253400/\text{RT})^{[62]}$ in austenite, and $0.3 \times 10^{-2} \text{exp}(-234500/\text{RT})^{[57]}$ in ferrite. The interfacial energies for these two precipitation temperatures are calculated in the appendix, where the value is seen to be 10% higher in ferrite (700°C) than in austenite (840°C). The number densities of precipitate particles are calculated based on the nitrogen concentration, because this element is insufficient when reacting with aluminum to form AlN for this steel composition. Constant $R_r=2$ and 32 size groups are used in the simulation, which covers particle radii up to around 200nm. The time step is 0.001s with ~1000 decreasing to ~100 iterations required within each time step for convergence of the implicit method with Gauss-Siedel solver.

The predicted AlN precipitate fractions are shown and compared with experimental measurements in Fig. 8. Good matches are found at both temperatures. The calculation verifies the experimental observation of much faster precipitation in ferrite than in austenite, due to the lower solubility limit of AlN and the faster diffusion rate of aluminum in ferrite than in austenite.

The calculated evolution of the size distribution of AlN particles at each aging temperature is depicted in Fig. 9. Neglecting the numerical wiggles, each curve has the same characteristic shape, which evolves with time. The number densities decrease with increasing particle size, reach a minimum, increase to a maximum, and finally decrease to zero. With increasing time, the number density of single molecules decrease from the initial value, n_s , to the equilibrium value $n_{1,eq}$. Very small particles in the first few size groups (~<0.5nm), are unstable, as the chance of gaining molecules is less than that of losing molecules, owing to the high surface curvature. Thus, their number densities decrease with size, owing to the decreasing chance of a larger unstable "embryo" of molecules coming together. The minimum corresponds to the critical nucleus size. Particles with the critical size are expected to be the most rare. With increasing size above the critical, molecule attachment increasingly exceeds dissolution, so these stable particles grow increasingly faster and become larger. Very large particles are rare simply due to insufficient growth time.

The entire size distribution grows with time. Except for the small unstable particles which decrease in number, all other sizes increase in number during this period. For example at 840°C, the maximum particle radius increases from 10nm at 100s to 65nm at 3000s, while the peak number density increases from 2nm to 10nm.

After this growth stage, single molecules reach equilibrium concentration. Smaller particles decrease slowly in number due to dissolution, which provides single molecules for the slow growth of large particles. This is the particle coarsening or "Ostwald ripening" stage. The time for the beginning of this final precipitation stage can be found from the maximum total number of particles, shown in Fig.10 to occur at ~3000s for aging at 840°C and ~100s for aging at 700°C. These times match with the sudden changes in slope of precipitated fraction that are both predicted and measured in Fig. 8.

5.3 Discussion

The calculated size distribution of NbC particles and the precipitated amount of AlN both match well with experiments. This is significant because no fitting parameters are introduced in this model. The match is governed by the equilibrium dissolved concentration (supersaturation) calculated from the equilibrium model, and the choice of the physical parameters: diffusion rate and interfacial energy.

The model results quantify and provide new insight into the classical stages of precipitate nucleation, growth, and coarsening. For example, the minimum in the number density distributions in Fig. 9 corresponds to the critical precipitate particle size for stable nucleation. Classical nucleation

theory balances the decrease in volumetric free energy ΔG_V in forming a spherical nucleous with the energy increase to form the new interface, σ , and gives the critical minimum radius for a stable nucleus^[63] r_c of:

$$r_c = -\frac{2\sigma}{\Delta G_V}$$
[44]

where ΔG_V for a single precipitate system such as AlN is:

$$\Delta G_V = \frac{RT}{V_P} \ln \left(\frac{a_{Al} \cdot a_N}{a_{Al_0} \cdot a_{N_0}} \right)$$
[45]

where a_{Al} and a_N are the activities of Al and N respectively. Because the dissolved mass concentrations and activities of Al and N decrease with time, the critical radius decreases with time during the isothermal precipitation process, reaching equilibrium values of 0.70nm at 840°C and 0.40nm at 700°C^[17]. Both the trend of decreasing critical radius with time and these final values roughly match with the minimum of the number density distributions in Fig. 9.

It is important to mention that the results here are only approximate because only one type of precipitate is modeled of the many that actually form in steel, and only homogeneous nucleation in the matrix phase is simulated. Competition between the different precipitates for the alloy elements, such as different nitrides attracting nitrogen, causes inaccuracies that can be addressed by generalizing the current model to handle multiple precipitates. Such an enhanced multiphase precipitate model is also needed to account for previously formed precipitates which act as heterogeneous nucleation sites for new precipitates of different composition. Furthermore, microsegregation changes the alloy composition at grain boundaries, where increased vacancy concentration also increases diffusion rates. Finally, deformation influences precipitation kinetics by increasing the nucleation and growth rate, leading to a much finer particle size distribution^[54,64]. These effects on precipitation behavior will be addressed in future improvements to this model.

Conclusions:

1. The particle size group (PSG) population-balance method for modeling particle collision has been derived for an arbitrary choice of size ratio R_V and good agreement has been verified with exact solutions.

2. A new, efficient PSG population-balance method for diffusion-controlled particle growth has been developed. Results match the exact solution of Kampmann within a reasonable tolerance. The method features geometrically-based thresholds between each size group, reasonable estimates of border values in order to accurately include intra-group diffusion, corresponding accurate diffusion between size groups, and an efficient implicit solution method to integrate the equations.

3. The new PSG method can simulate particle nucleation, growth, and coalesence due to collision and diffusion over a wide size range or particles with low computational cost and reasonable accuracy. Accuracy of the method increases with decreasing R_V as more size groups are used to cover the given particle size range.

4. The new PSG method has been applied to two realistic validation problems. The computed size distributions of NbC and the precipitated fraction of AlN match reasonably with previous experimental measurements in microalloyed steel without using any fitting parameters. Precipitation in ferrite is found to be greatly accelerated due to the lower solubility limit and higher diffusion rate of these precipitates in this phase.

5. The new PSG method is available to simulate realistic nonequilibrium precipitation behavior during various steel processes, such as continuous casting, for arbitrary temperature histories. Future work will incorporate other important effects into this kinetic model, such as multi-precipitate growth and deformation-induced precipitation.

Appendix: Calculation of interfacial energy

According to Turnbull^{[65}] and Jonas^[66], the interfacial energy consists of two parts: a chemical part (σ_c) and a structural part (σ_{st}), so that

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_c + \boldsymbol{\sigma}_{st} \tag{A1}$$

The chemical interfacial energy is estimated from the difference between the energies of bonding broken in the separation process and of bonds made in forming the interface, with only the nearest neighbors considered. As given by Russell^[32]

$$\sigma_c = \frac{\Delta E_0 N_s Z_s}{N_A Z_l} (X_P - X_M)^2$$
[A2]

where ΔE_0 is the heat of solution of precipitates in a dilute solution of matrix, N_s is the number of atoms per unit area across the interface, Z_s is the number of bonds per atom across the interface, Z_l is the coordinate number of nearest neighbors within the crystal lattice, and X_P and X_M are the molar concentrations of the precipitate forming element in the precipitate (P) and matrix (M) phase respectively. ΔE_0 is estimated to equal – ΔH , the heat of formation of the precipitate.

Van Der Merwe^[67] presented a calculation of structural energy for a planar interface. When the two phases have the same structure and orientation, but different lattice spacing, the mismatch may be accommodated by a planar array of edge dislocations. Including the strain energy in both crystals, σ_{st} is given as

$$\sigma_{st} = \frac{\mu_{l}c}{4\pi^{2}} \Big\{ 1 + \beta - (1 + \beta^{2})^{1/2} - \beta \ln \Big[2\beta (1 + \beta^{2})^{1/2} - 2\beta^{2} \Big] \Big\}$$
 [A3]

with
$$\frac{2}{c} = \frac{1}{a_M^e} + \frac{1}{a_P^e}, \ \frac{2}{\mu_I} = \frac{1}{\mu_M} + \frac{1}{\mu_P}$$

$$\beta = 2\pi \delta \frac{\lambda_+}{\mu_I}, \ \delta = \frac{2|a_M^e - a_P^e|}{a_M^e + a_P^e}, \ \frac{1}{\lambda_+} = \frac{1 - \nu_M}{\mu_M} + \frac{1 - \nu_P}{\mu_P}$$
[A3]

where a_M^e and a_P^e are the effective nearest-neighbor distance across the interface, which are estimated from the lattice parameters a_M , a_P and interface orientations, c is the spacing of a reference lattice across the matrix/precipitate interface. μ_M , μ_P and μ_I are shear modulii in the matrix (M), precipitate (P) and interface (I) respectively; ν_M and ν_P are Poisson's ratios. δ is the lattice misfit across the interface.

The crystallographic relationships between the AlN (h.c.p.), NbC (f.c.c.), and steel matrix austenite phase (f.c.c.) or ferrite phase (b.c.c.) are chosen as

$$(111)_{NbC} //(111)_{\gamma-Fe} [^{32,66]}, (0001)_{AlN} //(111)_{\gamma-Fe} [^{68,69]} \text{ and } (0001)_{AlN} //(110)_{\alpha-Fe} [^{70]}$$

The physical properties in the calculation are

$$-\Delta H_{AlN} (KJ / mol) = 341.32 - 4.98 \times 10^{-2} T - 1.12 \times 10^{-6} T^2 - 2813 / T [^{71]}$$

$$-\Delta H_{NbC} (KJ / mol) = 157.76 - 4.54 \times 10^{-2} T - 3.84 \times 10^{-6} T^2 [^{72]}$$

$$\mu_{\gamma-Fe} (GPa) = 81 [1 - 0.91(T - 300) / 1810] [^{73]}, v_{\gamma-Fe} = 0.29 [^{74]}, a_{\gamma-Fe} (nm) = 0.357 [^{57]}$$

$$\mu_{\alpha-Fe} (GPa) = 69.2 [1 - 1.31(T - 300) / 1810] [^{73]}, v_{\alpha-Fe} = 0.29 [^{74]}, a_{\alpha-Fe} (nm) = 0.286 [^{57]}$$

$$\mu_{AlN} (GPa) = 127 [^{75]}, v_{AlN} = 0.23 [^{75]}, a_{AlN} (nm) = 0.311, c_{AlN} (nm) = 0.497 [^{57]}$$

$$\mu_{NbC} (GPa) = 134 [1 - 0.18(T - 300) / 3613] [^{73]}, v_{NbC} = 0.194 [^{73]}, a_{NbC} (nm) = 0.446 [^{57]}$$

For γ -Fe (111) plane, $Z_s^{\gamma-Fe} = 3$ and $N_s^{\gamma-Fe} = 4/(\sqrt{3}a_{\gamma-Fe}^2)$. For α -Fe (110) plane,

 $Z_s^{\alpha-Fe} = 4$ and $N_s^{\alpha-Fe} = \sqrt{2} / a_{\alpha-Fe}^2$. For both f.c.c. and h.c.p. precipitate structures, $Z_l = 12$. The calculated interfacial energy decreases slightly as temperature increases, and also decreases for NbC (relative to AlN) because its crystal structure matches the austenite matrix. The values used in the current simulations are:

$$\sigma_{NbC}^{\gamma-Fe}(930^{\circ}C) = 0.540J/m^{2}$$

$$\sigma_{AlN}^{\gamma-Fe}(840^{\circ}C) = 0.908J/m^{2}, \ \sigma_{AlN}^{\alpha-Fe}(700^{\circ}C) = 0.997J/m^{2}$$

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Nomenclatures:

- *a* : Empirical coefficient for turbulence collision
- a_M, a_P : Lattice parameter of the steel matrix and precipitate phase (m)
- c: Spacing of a reference lattice across the interface (m)
- f: Transformed fraction in phase transformation
- f_P : Precipitated fraction in precipitation process
- i_M : Number of molecules for the largest agglomerated particle in simulation
- n : Avrami exponent in KJMA model
- n_0 : Initial total number density of single molecules for collision problem (#·m⁻³)
- $n_{1,eq}$: Equilibrium concentration of dissolved single molecules for diffusion problem (#·m⁻³)
- n_i : Number density of size *i* particles ($\# \cdot m^{-3}$)
- n_p : Total number density of precipitate particles (#·m⁻³)
- n_s : Released number density of single molecules for diffusion problem (#·m⁻³)

- n_j^C : Number density of particles at the center of size group $j (\# \cdot m^{-3})$
- n_i^L : Number density of border particles, representing the smallest particles in size group $j \ (\# \cdot m^{-3})$
- n_j^R : Number density of border particles, representing the largest particles in size group $j \ (\# \cdot m^{-3})$
- $r_i(r_i)$: Characteristic radius of size *i* particles (or size group *j* particles) (m)
- $r_{j-1,j}$: Threshold radius to separate size group j-1 and size group j particles in PSG method (m)
- r_c : The critical radius for nucleation (m)
- $\overline{r_p}$: Average precipitate particle size (m)

t : Time (s)

- Δt : Time step size in numerical computation (s)
- $A_i(A_i)$: The surface area of size *i* particles (or size group *j* particles) (m²)

 A_M : Atomic mass unit of element M (g·mol⁻¹)

- D: Diffusion coefficient of the precipitation in the parent phase (m²·s⁻¹)
- D_f : Fractal dimension for precipitate morphology
- G_M : Number of size groups for the largest agglomerated particle in PSG method
- G_T : Truncating size group in PSG method to match experimental resolution
- K: Rate function for nucleation and growth in KJMA model
- M_0 : Total mass concentration of alloying element M in the steel composition (wt%)
- [M]: Equilibrium mass concentration of alloying element M (wt%)
- N_i : Total number density of size group *j* particles in PSG method ($\#\cdot m^{-3}$)
- N_A : Avogadro number (6.022×10²³ #·mol⁻¹)
- N_M : Total number density of molecules (#·m⁻³)
- N_s : Number of atoms per unit area across the interface ($\#\cdot m^{-2}$)
- N_T : Total number density of all particles (#·m⁻³)
- R_{σ} : Gas constant (8.314 J·K⁻¹·mol⁻¹)
- R_{V} : Particle volume ratio between two neighboring particle size groups
- T: Absolute temperature (K)
- $V_i(V_i)$: Characteristic volume of size *i* particles (or size group *j* particles) (m³)

 $V_{j-1,j}$: Threshold volume to separate size group *j*-*I* and size group *j* particles in PSG method (m³) V_p : Molar volume of precipitated phase (m³·mol⁻¹)

 X_M , X_P : Molar concentration of precipitate-forming element in matrix and precipitate phases

- Z_s : Number of bonds per atom across the interface
- Z_1 : Coordinate number of nearest neighbors within the crystal lattice
- α_i : Dissociation rate of size *i* particles (#⁻¹·m⁻²·s⁻¹)
- β_i : Diffusion growth rate of size *i* particles (m³·#⁻¹·s⁻¹)
- δ : Relative lattice misfit across the interface between pairs of precipitate and matrix atoms

 $\delta_{i,k}$: Kronecker's delta function ($\delta_{i,k}=1$ for i=k, $\delta_{i,k}=0$ for i $\neq k$)

- \mathcal{E} : Turbulent energy dissipation rate (m²·s⁻³)
- μ_M, μ_P, μ_I : Shear modulus of the steel matrix, precipitate phase and interface (Pa)
- V: Kinematic viscosity (m²·s⁻¹)
- V_M, V_P : Poisson's ratio of the steel matrix and precipitate phases
- ρ_{steel} : Density of steel (kg·m⁻³)
- ρ_p : Density of precipitates (kg·m⁻³)
- σ : Interfacial energy between precipitated particle/steel matrix (J·m⁻²)
- σ_c : Chemical interfacial energy between precipitated particle/steel matrix (J·m⁻²)
- σ_{st} : Structural interfacial energy between precipitated particle/steel matrix (J·m⁻²)
- Φ_{ik} : Collision kernel between size *i* and size *k* particles (m³·#⁻¹·s⁻¹)
- ΔE_0 : Heat of solution of precipitate in a dilute solution of matrix (J·mol⁻¹)
- ΔG_V : Change of Gibbs free energy per unit volume between matrix solution and precipitate (J·m⁻³)
- ΔH : Heat of formation of precipitate (J·mol⁻¹)

Superscripts:

- * : Dimensionless value
- -: Average value
- L, R: Left and right border-size particles in each size group

Functions:

ceil(x): The smallest integer which is not less than real number x

floor(x): The largest integer which is not larger than real number x

	Collision $(t^*=1)$			Diffusion ($t^*=10000$)		
	Exact	$PSG(R_V=2)$	$PSG(R_V=3)$	Exact	$PSG(R_V=2)$	$PSG(R_V=3)$
Storage	n _M =12000	N _G =16	N _G =11	n _M =50000	N _G =18	N _G =13
Computational time	~225 hours	~0.8s	~0.4s	~27 hours	~560s	~390s

Table I. Comparison of computational cost for test problems



Fig.1-The schematic of particle size distribution in PSG method



Fig.2–Comparison of collision curve calculated by PSG method with exact solution for different R_V



Fig.3–Comparison of collision curve of each size group calculated by PSG method with exact solution for different R_V



Fig.4–Comparison of diffusion curves calculated by PSG method with exact solution for different R_V



Fig.5–Comparison of evolving numbers of each size group calculated by PSG diffusion method with exact solution for different R_V



Fig.6–Calculated equilibrium dissolved mass concentration of C for Jones case^[54] and N for Vodopivec case^[58] showing aging test temperatures



Fig.7– Size distribution frequency of particles calculated in undeformed steel matrix compared with measurements from Jones at 930°C^[54]



Fig.8–Calculated and measured precipitated fraction of AlN in 0.051wt%Al-0.0073wt%N steel during isothermal aging at 840°C and 700°C (experimental data from Vodopivec^[58])



(a). 840°C



Fig.9–Calculated size distributions of AlN particles for 0.051wt%Al-0.0073wt%N steel during isothermal aging at 840°C and 700°C



Fig.10–Calculated total number density of AlN particles for 0.051wt%Al-0.0073wt%N steel during isothermal aging at 840°C and 700°C