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Modeling Precipitate Formation during Casting and Reheating

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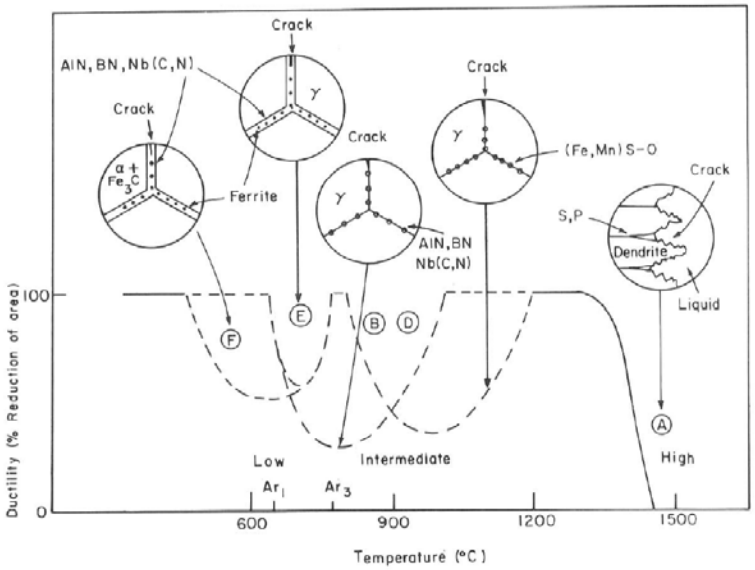
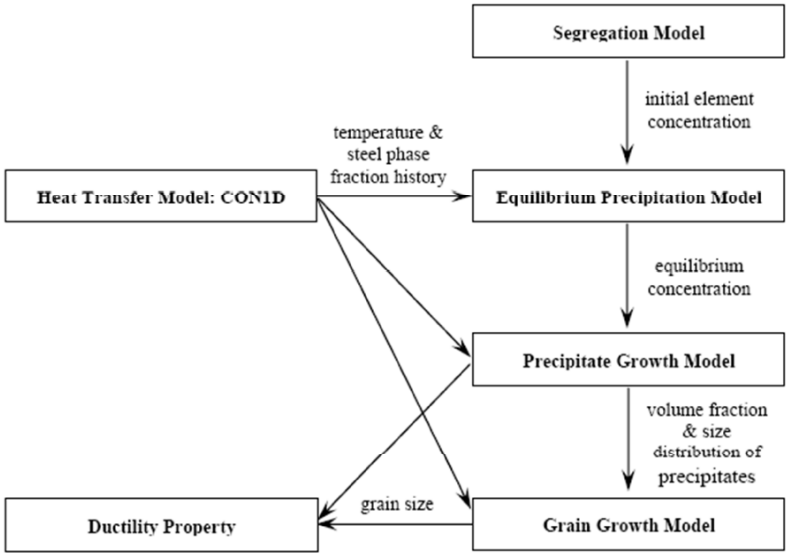
Hot ductility varies with temperature and grade due to precipitate formation



- Large grains and precipitate embrittlement are the main reasons to cause surface cracks
- Formation sequence of precipitates is determined by steel composition and solubility of precipitates
- γ→α phase transformation greatly accelerates the precipitation due to lower solubility and higher diffusion in ferrite (interphase precipitation)

B.G. Thomas, *ISS Transactions*, 1986, pp. 7.

Project Overview



Final goal: Design casting practices to predict ductility and prevent cracks

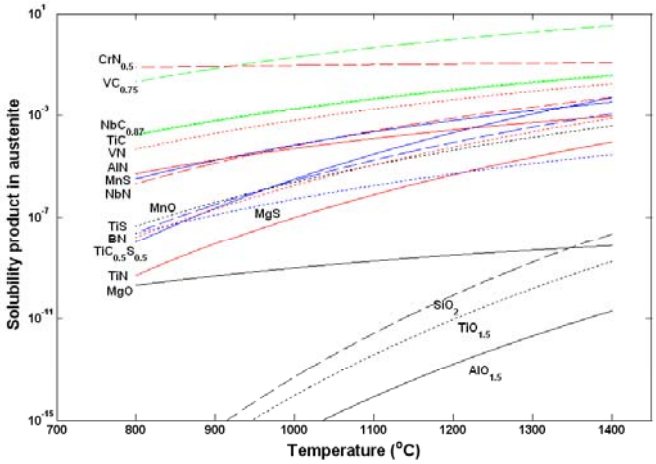
Equilibrium precipitation model

To solve system of nonlinear equations, which include:

1. Solubility limits for 18 precipitate with consideration of influence on activities from Wagner interaction between elements
2. Mass balance for 13 alloying elements during precipitation
3. Mutual solubility

Calculate the stable precipitate phases and the dissolved mass concentrations of alloying elements in microalloyed steels for the given temperature

K. Xu, B. G. Thomas and Ron O'Malley, *Metall. Mater. Trans.* A, 2011, vol. 42A, pp. 524



Classical Theory of Precipitation Kinetics

1. Nucleation (W. J. Liu, *Metall. Trans. A, 1989, pp.689*)

Steady state nucleation rate $J = \frac{\rho D X_{Ti}}{a^3} \exp\left(-\frac{\Delta G^*}{KT}\right)$ $\Delta G = V(\Delta G_{chem} + \Delta G_\varepsilon) + S\xi\sigma$

For TiC_yN_{1-y} $\Delta G_{chem} = RT/(2V_P)\left[\ln\left(X_{Ti}^e / X_{Ti}^0\right) + y\ln\left(X_C^e / X_C^0\right) + (1-y)\ln\left(X_N^e / X_N^0\right)\right]$

ρ: Dislocation density, a: lattice parameter, D: diffusion coefficient, V_P: molar volume

Precipitation start time $P_s = N_c / J$ N_c: critical number of nuclei for precipitation

2. Precipitate growth (L. M. Cheng, *Metall. Mater. Trans. A, 2000, pp.1907*)

$$\frac{dr}{dt} = \frac{C_M - C_I}{C_P - C_I}\left[\frac{D}{r} + \left(\frac{D}{\pi t}\right)^{1/2}\right]$$ Gibbs-Thomson relation $C_I = C_e^\infty \exp\left(\frac{2\sigma V_P}{R_g T r}\right)$

Concentration: matrix C_M, matrix/precipitate interface C_I, precipitate C_P

- Diffusion growth (Zener, *J. Appl. Phys.*, 1949, pp.950)

$$\bar{r}^2 - \bar{r}_0^2 = \alpha D(t - t_0)$$

- Coarsening (Lifshitz-Slyozov-Wagner equation, 1961) $\bar{r}^3 - \bar{r}_0^3 = \frac{8\sigma D V_P C_M}{9R_g T}(t - t_0)$

Recent Development of Precipitation Kinetics

Atomic scale: kinetic Monte Carlo (diffusion through vacancy jump)

--- The largest particle size in simulation is limited by model size

Macroscopic scale

Phase filed model (minimization of free energy & interface dynamics)

Matcalc software (thermodynamic extremum principle, multi-phase precipitation in multi-component system)

Cluster Dynamics (reactions between neighboring mesoscopic clusters, or called nanoparticles, no explicit laws required)

Our developing model:

1. It includes nucleation, growth/dissolution and coarsening in one single model, and no explicit laws and fitting parameters are required

2. The particles of every size are tracked in the model, ranging from single pseudomolecule, unstable embryos, stable nuclei to very large coarsened particle

Fundamental Model for Diffusion-controlled Precipitate Growth

Particle diffusion $$\frac{dn_i}{dt} = \underbrace{-\beta_i n_1 n_i}_{\text{Diffusion growth (i→i+1)}} + \underbrace{\beta_{i-1} n_1 n_{i-1}}_{\text{Diffusion growth (i-1→i)}} \underbrace{-\alpha_i A_i n_i}_{\text{Dissolution (i→i-1)}} + \underbrace{\alpha_{i+1} A_{i+1} n_{i+1}}_{\text{Dissolution (i+1→i)}} \quad (i \geq 2)$$

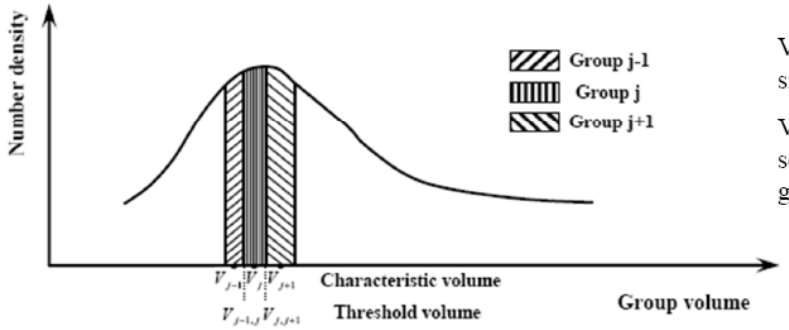
n_i: Number density of size i particle (#/m^3)
β_i: Diffusion rate constant of size i particle (m^3/s)
α_i: Dissociation rate per unit area of size i particle (m^{-2}s^{-1})

$$\beta_i = 4\pi D_1 r_i \qquad \alpha_i = \beta_i n_{1,eq} \exp\left(2\sigma V_m / RTr_i\right) / A_i$$

- The dissociation rate indicates that increasing particle radius causes the nearby solute equilibrium concentration to decrease exponentially (coarsening effect) in all stages
- Computational cost quickly becomes infeasible for realistic particle sizes
- For practical interface energy between precipitate and solid steel, calculation easily becomes unstable when the dissociation rates are too large

Introduction of Particle-Size-Grouping (PSG) Method

- The model always simulates from single pseudomolecule (~ 0.1nm) up to large coarsened particles (~100μm): particles could contain 1~10^{18} pseudomolecules
- Serious computation and memory storage issues arise with such a large size range
- Solve with PSG method: Use N_G groups (<100) of geometrically progressing size



V_j: Characteristic volume of size group j particle

$V_{j,j+1}$: Threshold volume to separate group j and j+1 size group particles

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

Average particle volume ratio

$$R_V = V_{j+1} / V_j$$

Total number density of each size group $$N_j = \sum_{V_{j,j+1} > V > V_{j-1,j}} n(V)$$

Develop New PSG Method for Diffusion

$$\frac{dN_j}{dt} = \underbrace{\frac{m_1}{m_j}\beta_j N_1 (N_j - n_j^R)}_{\text{Diffusion growth inside group j}} - \underbrace{\frac{m_1}{m_j}\alpha_j A_j (N_j - n_j^L)}_{\text{Dissolution inside group j}} + \underbrace{\frac{ceil(m_{j-1,j})}{m_j}\beta_{j-1}^R N_1 n_{j-1}^R}_{\text{Diffusion growth group j-1→j}} + \underbrace{\frac{floor(m_{j,j+1})}{m_j}\alpha_{j+1}^L A_{j+1}^L n_{j+1}^L}_{\text{Dissolution group j+1→j}}$$

$$\underbrace{-\frac{floor(m_{j,j+1})}{m_j}\beta_j^R N_1 n_j^R}_{\text{Diffusion growth group j→j+1}} \underbrace{-\frac{ceil(m_{j-1,j})}{m_j}\alpha_j^L A_j^L n_j^L}_{\text{Dissolution group j→j-1}} \quad (j \geq 2)$$

n_j^L : Number density of smallest particles in size group j, which falls into group j-1 by dissolution after losing only one single molecule

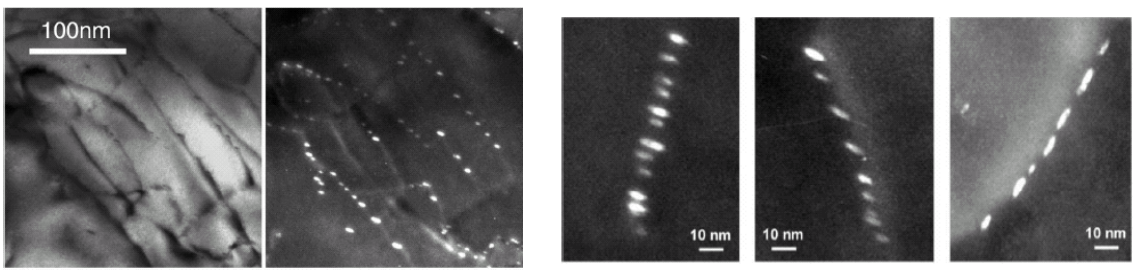
n_j^R : Number density of largest particles in size group j, which jumps into group j+1 by diffusion after gaining only one single molecule

m_j and $m_{j,j+1}$ are the containing number of molecules for the characteristic volume V_j and the threshold volume $V_{j,j+1}$. Function ceil(x) calculates the smallest integer which is not less than x, and floor(x) calculates the largest integer which is not larger than x

K. Xu and B. G. Thomas, *Accepted by Metall. Mater. Trans. A.*

Validation of volume fraction of Nb Precipitate

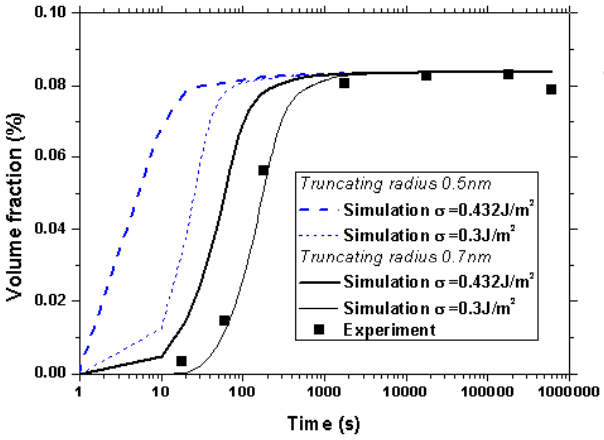
- Steel composition: 0.079%Nb, 0.011%C, 0.001%N, 0.002%Mn, 0.0023%S, 0.001%P, 0.006%Al and 0.0013%O
- Solution treated at 1350°C for 45 minutes, cooled to test temperature and held
- The precipitates are found on dislocations in ferrite
- Small-angle neutron scattering (SANS) measures the volume fraction and mean size of precipitate, TEM measures the precipitate size distribution



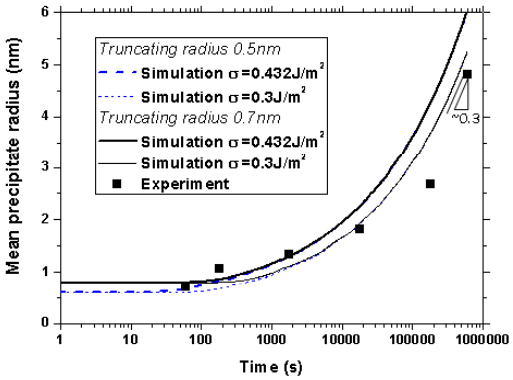
F. Perrard *et al*, *J. Appl. Crystallogr.*, 2006, pp.473

Validation of volume fraction and mean size with SANS measurement

- $D_{Nb}(m^2/s)=50.2\times10^{-4}\exp(-252000/RT)$ in ferrite
- Equilibrium calculation: Nb(C,N) forms at 1054°C, [Nb]=0.0002506wt% at 700°C, interface energy of NbC and matrix is calculated as 0.432J/m^2
- Truncating radius is introduced since we track every size (smaller than stable nuclei) and all experiments have resolution limit

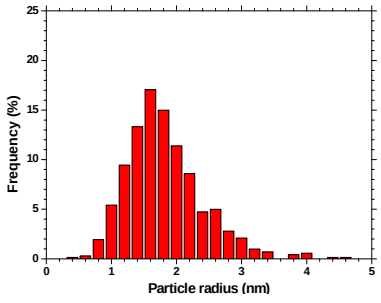


$$f_P = \frac{\sum_{j=G_T}^{G_M} m_j N_j}{n_s},\ N_P = \sum_{j=G_T}^{G_M} N_j,\ \overline{r_P} = \frac{\sum_{j=G_T}^{G_M} r_j N_j}{N_P}$$

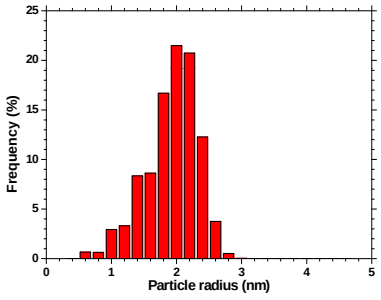


F. Perrard *et al*, *J. Appl. Crystallogr.*, 2006, pp.473

Validation of size distribution with TEM measurement at 300 minutes



Experiment

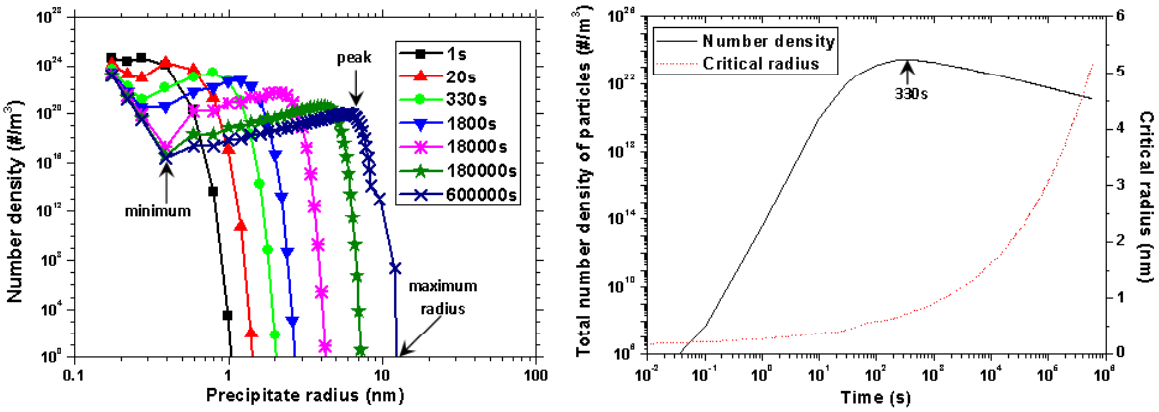


Simulation

- A reduced interface energy of 0.3J/m^2 (due to dislocation relaxing) gives good matches of volume fraction and mean size of precipitate
- The same calculation also gives reasonable agreement with precipitate size distribution of TEM measurement, mean size 1.93nm vs 1.82nm TEM
- Simulated size distribution misses the measured tail of large particle, possibly due to precipitation on grain boundaries, and the irregular aspect ratio ~2.3 in TEM imaging (spherical assumption is used in simulation)

F. Perrard *et al*, *J. Appl. Crystallogr.*, 2006, pp.473

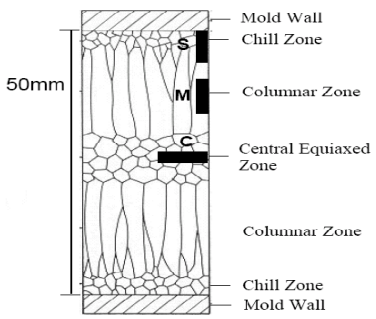
Calculation of number density and critical size of precipitate

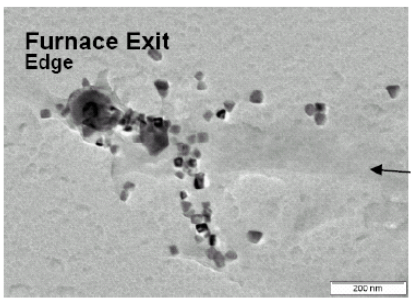


- The peak of total number density occurs at ~330s, and corresponds with the transition point of volume fraction to be flat (start of coarsening stage)
- The critical radius increases continuously with time. It starts with the radius of single pseudomolecule, and finally approaches the mean radius (the particles larger than mean size are stable and vice verse in coarsening stage)

Application: Continuous Casting and Reheating

- The effects of microalloy precipitation and (tunnel furnace) dissolution during direct strip production are explored relative to the position within the slab and alloy content.
- Niobium solute and precipitation fractions are quantified by electrochemical extraction and inductively coupled plasma, and the precipitate particle size are measured by transmission electron microscopy on carbon extraction replicas
- The extent of precipitation appears greatest with higher niobium additions. The greatest amount of alloy precipitation occurs at the slab surface, and the columnar region represents the bulk of the slab volume and exhibits the lowest precipitated amount.



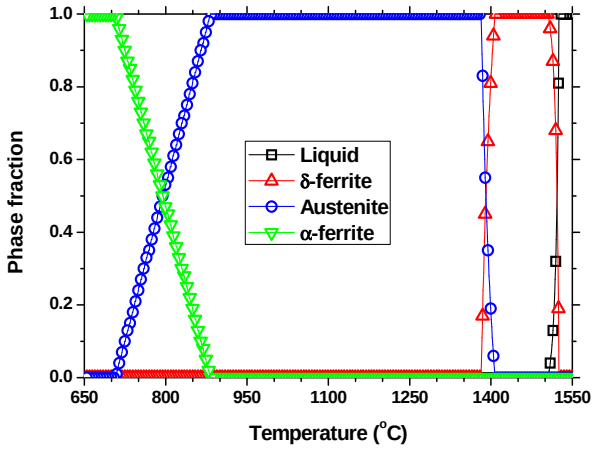


Experiment from: M. S. Dyer, *M. S. thesis*, Colorado School of Mines, 2010.

Application: Steel Phase (CON1D)

CON1D program: Solve the transient heat conduction in the mold and spray regions of continuous steel slab casters using finite difference method

Steel	C	Mn	Si	Cr	Ti	Nb	V	Al	N	S	P
High-Nb	0.031	1.039	0.194	0.032	0.002	0.046	0.001	0.031	0.006	0.003	0.012

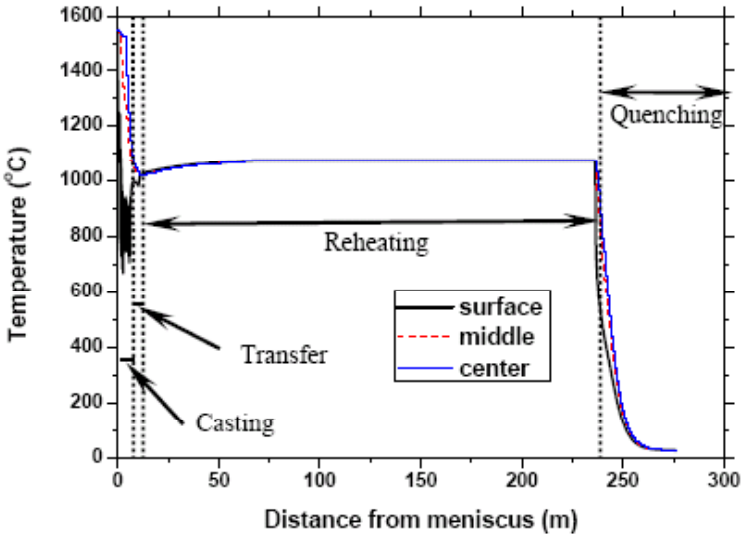


Slab size: 50mm thick, 1500mm wide
Mold exit: 0.8m below meniscus
Pouring Temperature: 1553°C
Casting speeds: 5m/min
Spray zone: 0.8-6 m

Liquidus temperature: 1524.4°C
Solidus temperature: 1504.8°C

Application : Temperature History (CON1D)

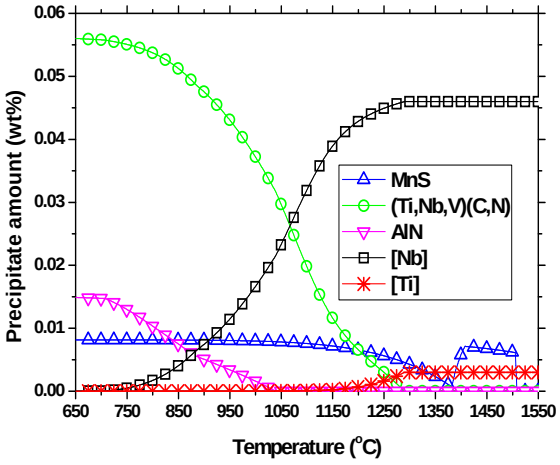
- **Casting→Transfer→Reheating→Quenching**
- **Slab is air cooled for 4m after the end of spray cooling, then heated in a 225-m long reheating furnace with reference temperature 1080°C, and finally water quenched to room temperature 25°C**



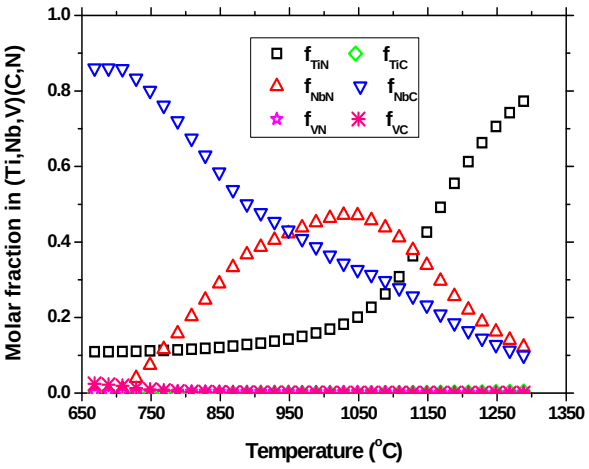
convection heat transfer coefficient of air
$h=8.7W/(m^2K)$

heat transfer coefficient of agitated water
$h=2000W/(m^2K)$

Application: Equilibrium Precipitation Calculation

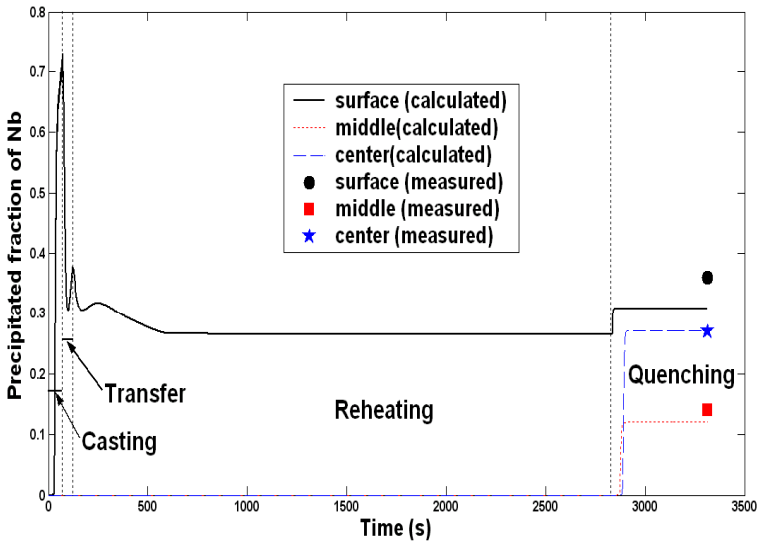


Precipitate phases



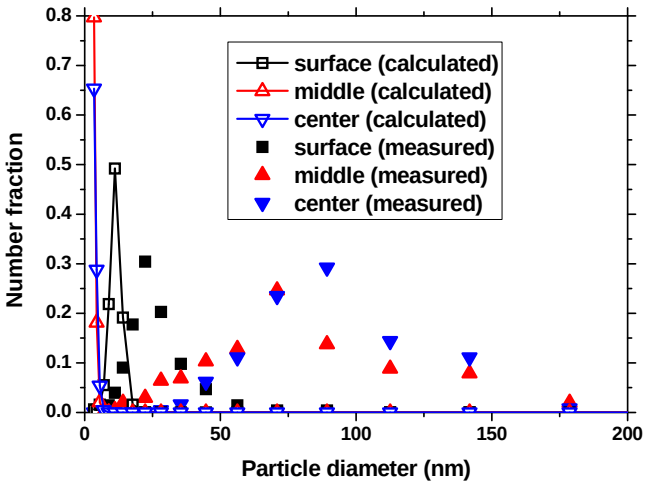
Molar fractions in (Ti,Nb,V)(C,N)

Application: Prediction and Comparison of Precipitated Fraction of Nb



- Truncating radius 2nm $D=f_\gamma D_\gamma+f_\alpha D_\alpha$, $\sigma=0.5J/m^2$
- For slab surface, the precipitation occurs inside spray cooling zone, and dissolution is observed in reheating furnace
- Water quenching is not effective to "lock" precipitation at high temperature, especially for inside of slab
- The precipitation mostly occurs during γ→α phase transformation (interphase precipitation)

Comparison with Measured Precipitate Size



Compare average precipitate size

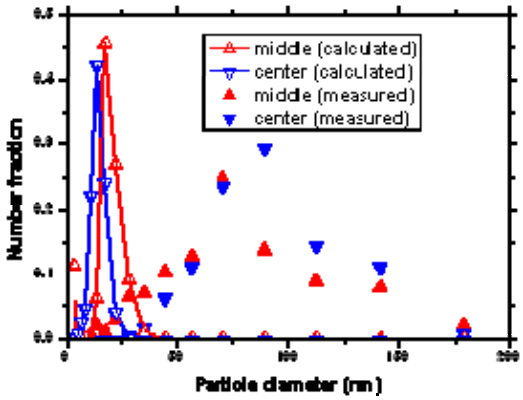
- Surface: calculated 11nm vs measured 24nm
- Middle: calculated 4nm vs measured 72nm
- Center: calculated 4nm vs measured 91nm

- Mismatch: 1). Precipitation on grain boundaries and segregated regions is ignored in the current model

2). More importantly, only Nb(C,N) is included, but experiments prove Ti is always detected in large particle (TiN is much more stable, and form at higher temperature. Ti can nearly completely precipitate in reheating furnace to form large Ti-bearing particles)

Precipitation on grain boundary and segregated rigion

- Some previous work has been done for coupling segregation model with equilibrium precipitation model and precipitate growth model (*K. Xu and B. G. Thomas et al, AISTech 2011*)



- Segregation causes precipitation to occur earlier at higher temperature

Segregation model (part backward diffusion in solid): Y. M. Won and B. G. Thomas, *Metall. Mater Trans. A*, 2001, pp. 1755.

Concentration at f_s=0.5 for middle and f_s=1.0 for center are input in calculation

$$D_{Al}^{\gamma}(m^2/s) = 2.51\times10^{-4}\exp(253400/RT)$$

$$D_{Al}^{\gamma-GB}(m^2/s) = 3.0\times10^{-4}\exp(167400/RT)$$

$$D_{Al}^{\gamma}(1000^oC) = 1\times10^{-14}m^2/s, D_{Al}^{\gamma-GB}(1000^oC) = 4\times10^{-11}m^2/s$$

Increased vacancy concentration

Special case: Modeling for multi-phase precipitation with mutually-soluble precipitates

Exact solution

$$\frac{dn_1^s}{dt} = -\beta_1^s n_1^s \sum_{k=1}^{n_o} n_1^k - n_1^s \sum_{k=1}^{n_o} \beta_1^k n_1^k - n_1^s \sum_{i=2}^{i_\omega} \beta_i^s n_i + 2\alpha_2^s A_2 p_2^s n_2 + \sum_{i=3}^{i_\omega} \alpha_i^s A_i p_i^s n_i$$

$$\frac{d(n_i p_i^s)}{dt} = (-\sum_{k=1}^{n_o} \beta_i^k n_1^k p_i^s n_i - \alpha_i^s A_i p_i^s n_i) + \sum_{k=1}^{n_o} \beta_{i-1}^k n_1^k n_{i-1} \frac{(i-1)p_{i-1}^s + \delta_{k,s}}{i}$$
$$+\alpha_{i+1}^s A_{i+1} p_{i+1}^s n_{i+1} \ (i \geq 2) \ (s=1,2,\ldots,n_p)$$

- For each size particle : average molar fraction of each precipitate (p_i^s, s=1,2,…, n_p) and number density (n_i) of variable-composition particles
- The containing number of i pseudomolecules for size i particle is determined, but the volume and size of particle vary with time (different precipitate type)
- When n_p=1, equations are simplified as exactly as 1-precipitate model
- The mass balance of each precipitate is satisfied $\sum_{i=1}^{\infty} id(n_i p_i^s)/dt = 0$
- Free pseudomolecules from all types of precipitates have influence on the diffusion growth. For dissociation: the precipitate type *k* particles in size i particles is $n_i p_i^k$, which dissolute with rate α_i^k

PSG method for multi-phase precipitation with mutually-soluble precipitates

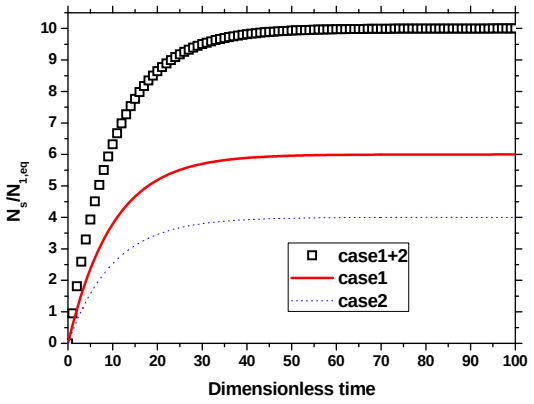
$$\frac{d(N_j p_j^s)}{dt} = \underbrace{\frac{m_1}{m_j}\beta_j^s N_1^R (N_j - n_j^R)}_{\text{Diffusion inside group j}} - \underbrace{\frac{m_1}{m_j}\alpha_j^s A_j p_j^s (N_j - n_j^L)}_{\text{Dissolution inside group j}}$$

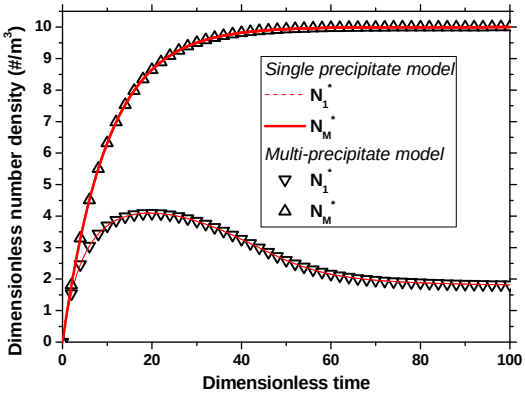
$$+\underbrace{\frac{ceil(m_{j-1,j})}{m_j}\sum_{k=1}^{n_o}(\beta_{j-1}^k)^R N_1^k n_{j-1}^R \frac{floor(m_{j-1,j})(p_{j-1}^s)^R + \delta_{k,s}}{ceil(m_{j-1,j})}}_{\text{Diffusion group j-1→j}} + \underbrace{\frac{floor(m_{j,j+1})}{m_j}(\alpha_{j+1}^s)^L A_{j+1}^L (p_{j+1}^s)^L n_{j+1}^L}_{\text{Dissolution group j+1→j}}$$

$$-\underbrace{\frac{floor(m_{j,j+1})}{m_j}\sum_{k=1}^{n_o}(\beta_j^k)^R N_1^k (p_j^s)^R n_j^R}_{\text{Diffusion group j→j+1}} - \underbrace{\frac{ceil(m_{j-1,j})}{m_j}(\alpha_j^s)^L A_j^L (p_j^s)^L n_j^L}_{\text{Dissolution group j→j-1}} \ (j \geq 2) \quad (s=1,2,\ldots,n_p)$$

- Good estimation of number densities and molar fractions of precipitate at border sizes (near threshold between neighboring size groups) are required
- Sum for all precipitate types to get N_j, and then the molar fractions of each precipitate are calcualted

Test Problem: pseudo two-precipitate case

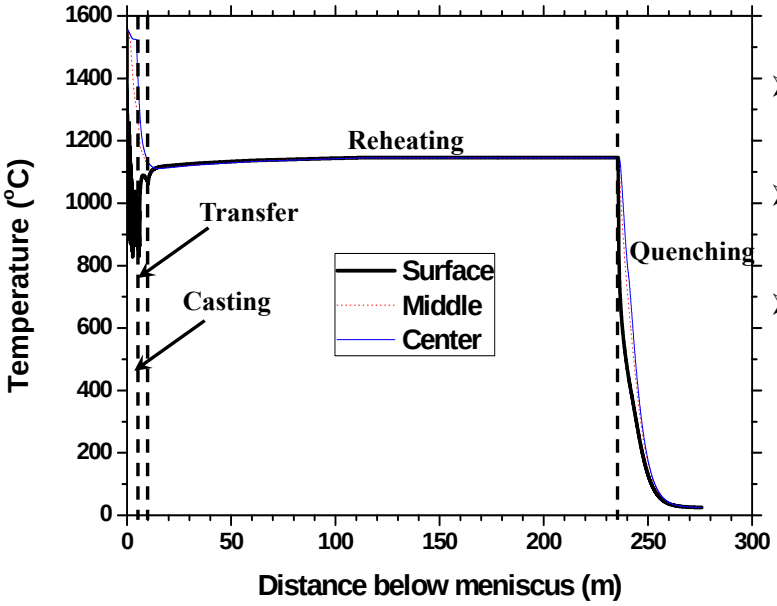




- Separate and pretend that there are two kinds of precipitates with all identical properties
- Add the released pseudomolecule number densities of two precipitates together, and run the single precipitate model
- Multi-phase precipitation model gives the same results with the single precipitate, and mass balance is guaranteed

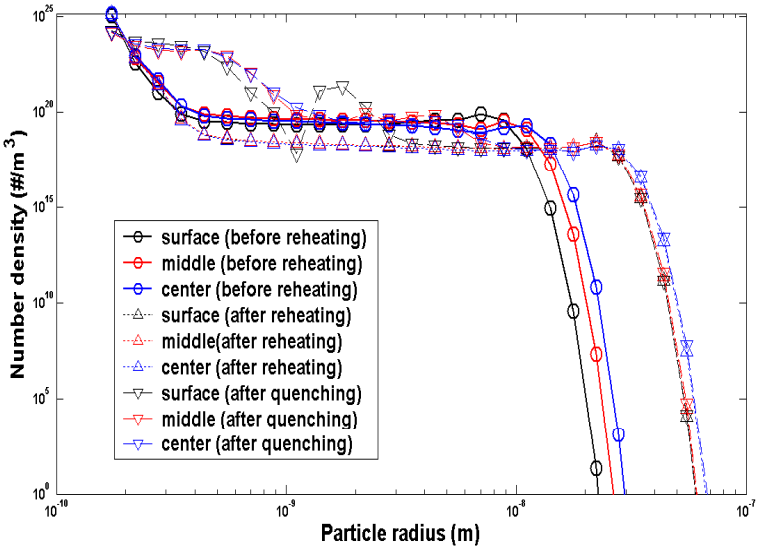
Application : Temperature History (CON1D)

- **Updated information: Surface temperature 900°C at the base of caster, reheating furnace has reference temperature 1150°C for 20 minutes**



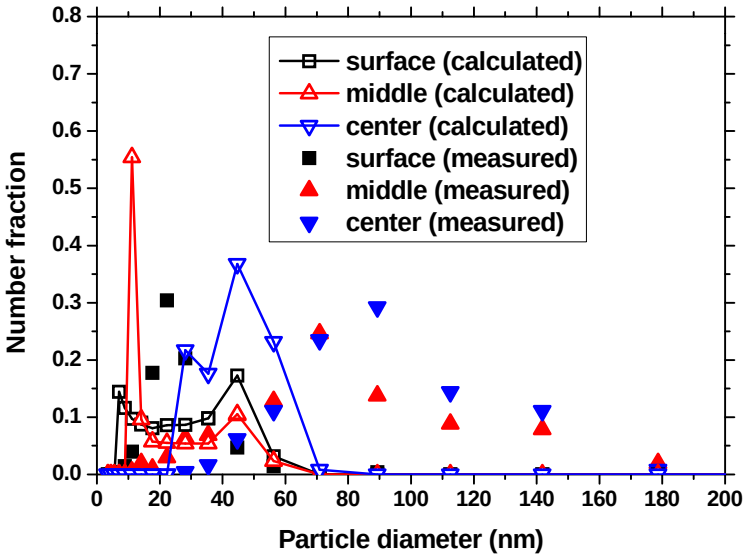
- **Slab surface temperature is around 900°C at the base of caster (plant: 900°C)**
- **Slab surface temperature is 1060°C entering furnace (plant: 900-1100°C)**
- **Reheating at 1150°C for 20 minutes (transfer speed is changed to 11.2m/min)**

Application: Calculated particle size distribution



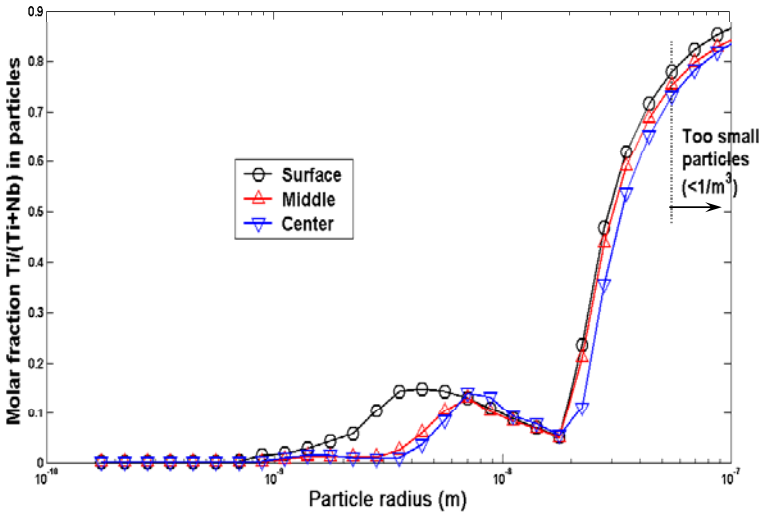
- $D=f_\gamma D_\gamma+f_\alpha D_\alpha$, $\sigma=0.8J/m^2$ for Ti(C,N) and $\sigma=0.5J/m^2$ for Nb(C,N)
- The precipitation happens before reheating, and the surface has smaller size due to lower temperature, higher supersaturation
- During reheating stage, precipitate get enough time for growth
- During quenching, not enough time for large particle to grow, but more finer particles form

Application : Prediction and comparison for multi-phase (Ti,Nb)(C,N) precipitation



- Multi-phase model greatly increases the calculated particle size
- The calculated particle diameter is around 40-50nm, which is still less than measurements for middle and center
- More accurate match: need precipitation on grain boundaries and segregation

Application : Molar fraction of Ti/(Ti+Nb) for different particle size



- Steel composition: 0.003% Ti and 0.046%Nb
- High stability of TiN causes precipitation at high temperature, and other precipitates can accumulate on surface of TiN particles due to mutual solubility
- The molar fraction Ti/(Ti+Nb) is larger for larger particles. It shows the Ti precipitation is the cause to form large particles

Conclusions

1. A fundamentally-based model of precipitate formation in practical steel processes has been developed, which includes

- heat transfer model to predict temperature and steel phase histories
- equilibrium precipitation model to predict equilibrium precipitate phases and amounts
- kinetic model for predicting the evolution of the precipitate size distribution, including smooth transitions between the nucleation, growth, and coarsening stages

2. The single Nb(C,N) model predictions of precipitate fraction and amounts agree with measurements conducted on continuous-cast HSLA steel samples taken from a thin-slab caster, but it underpredicts the measured size distributions for all edge, columnar, and centerline regions. The predicted trend of decreasing precipitate size from edge to centerline is also contrary to the measurements.
3. The potential importance of precipitation during specimen acquisition (associated with quenching) is highlighted by the model predictions, especially for slab interior
4. Multi-phase (Ti,Nb)(C,N) model shows potential ability to match both measured precipitate particle size distributions, and composition variation with size.

Future work

1. The multi-phase precipitate growth model is being developed
   - ➢ Better estimations of number densities and molar fractions at border size
   - ➢ Need to be verified with exact solution and experimental measurements
2. The model will be used to simulate precipitation in segregated region and on grain boundaries, where larger precipitate particles are observed
3. The precipitation model will be coupled with grain growth model to predict the grain size, and possibly explain the larger grains under oscillation marks and near slab corner where high temperature is expected and transverse cracks mostly occur

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