CCC Annual Report

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Improvements to Equilibrium Precipitation Model of Precipitate Formation

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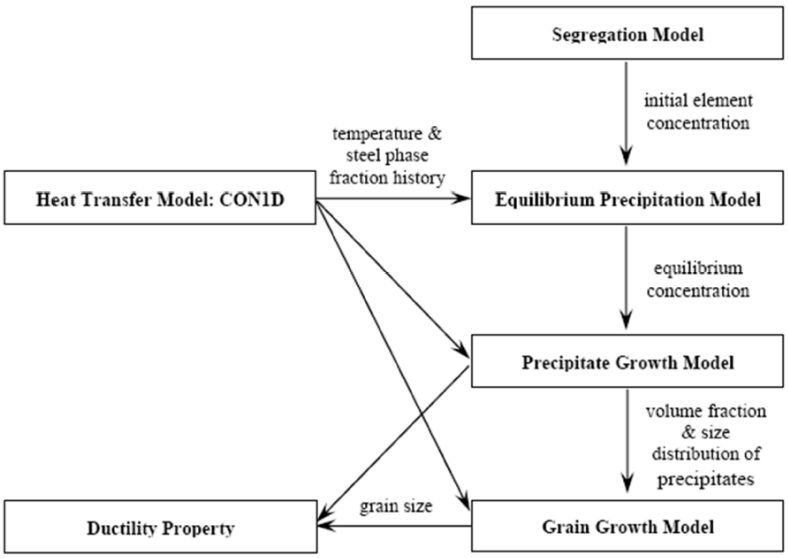
Project overview

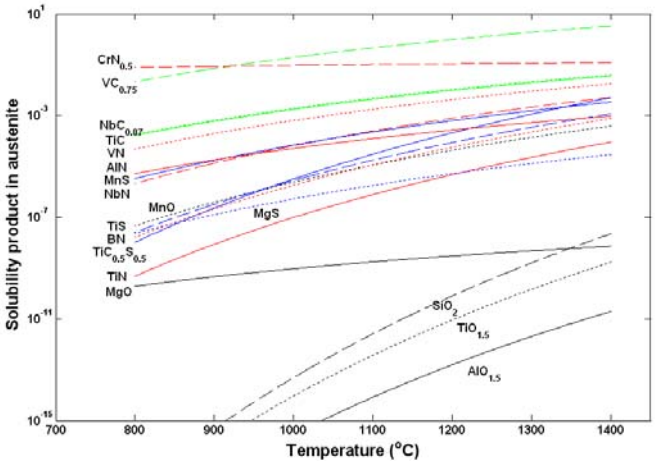


Final goal: Design casting practices to prevent transverse cracks

Equilibrium precipitation model[1]

To solve a system of nonlinear equations, which includes:

1. Solubility limits for 18 precipitates with activities from Wagner interaction between elements
2. Mass balance for 13 alloying elements during precipitation
3. Mutual solubility, e.g. (Ti,Nb,V)(C,N)

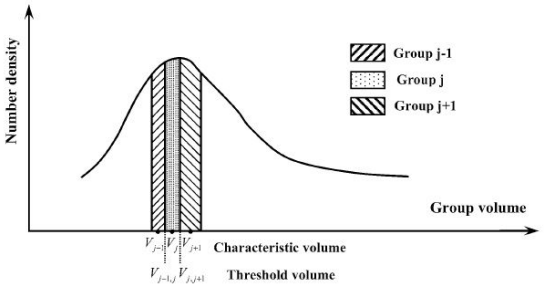


Calculate amount of stable precipitate phases and dissolved concentrations of elements at equilibrium in micro-alloyed steels for the given temperature and steel grade [1]

Kinetic Model
Particle Size Grouping (PSG) Method[2]

Features of OUR Kinetic Model-

- It simulates nucleation, growth/ dissolution and coarsening as one continuous and competing process with no explicit laws and fitting parameters
- The particles of every size are tracked, ranging from single pseudomolecule (~ 0.1nm), unstable embryos, stable nuclei to very large coarsened particles (~100μm)
- Grouping particles of Geometrically progressing size (reduces groups to <100)
- Grouping saves significant computation time but preserves accuracy



$\mathbf{m_j}$: characteristic number of pseudomolecules for size group j particle

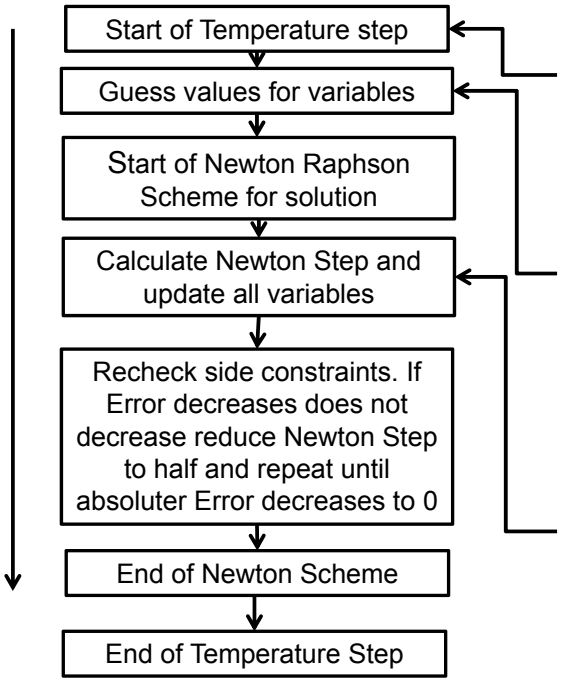
$\mathbf{m_{j,j+1}}$: Threshold number of pseudomolecules to separate j and j+1 size groups

Average particle ratio $R_v = \frac{m_{j+1}}{m_j}$

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

Average molar fraction of each phase $p_j^s = \frac{\sum_{m_{j,j+1} > m > m_{j-1,j}} m \cdot n(m) \cdot p_m^s}{\sum_{m_{j,j+1} > m > m_{j-1,j}} m \cdot n(m)}$

Outline of Improvements to Equilibrium Precipitation Program



Better start temperature for model to overcome startup issues

Check for new precipitate formation at intermediate temperatures and give a better guess value to overcome instabilities

Bound the Newton Step in Solver so as to avoid Ill-Conditioned systems

Example with convergence problems

Experimental weld steel used in commercial casting from K.Xu *et al.*[1]

Dissolved element	Initial concentration (%w/w of steel)
Carbon	0.10
Manganese	1.87
Sulfur	0.007
Vanadium	0.01
Titanium	0.005
Nitrogen	0.005
Aluminum	0.041
Niobium	0.007
Oxygen	0.030
Silicon	0.52
Boron	0.0004
Magnesium	-
Chromium	-

Example of cases where two precipitates formed quickly, problems with the next precipitate forming leading to the program crashing

Simulation Details-
Initial guess temperature from user – 1600C

Temperature step size – 1C

Simulation ending temperature – 800C

Phase - Austenite

Calculation of Initial Guess Temperature for Precipitation

Estimate which precipitates form at user input temperature

↓

Calculate the start temperature of precipitation of precipitate with largest supersaturation

↓

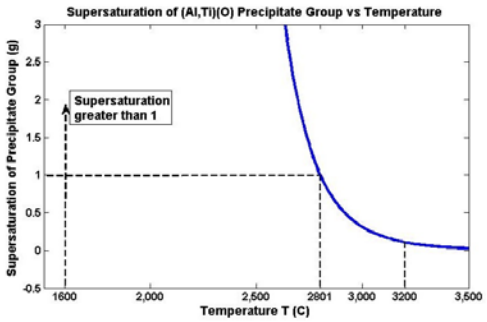
If precipitates form at new temperature then repeat procedure

$$g_{MxXy} = \frac{a_M(T) \times a_X(T)}{K_{MxXy}(T) \times a_{MxXy}(T)}$$

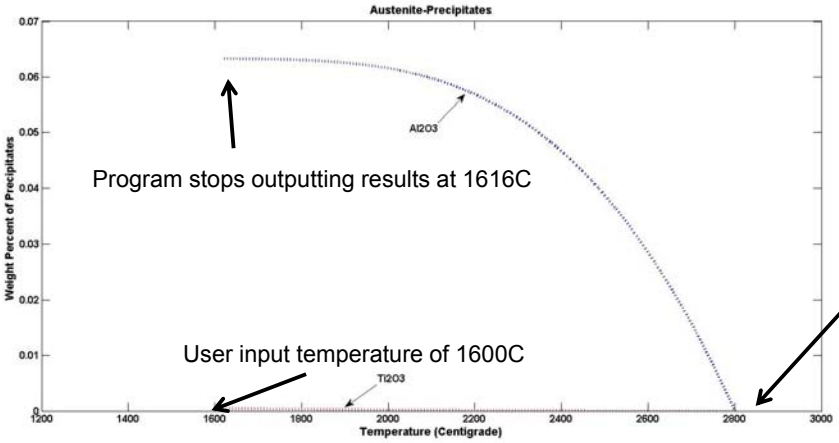
g_{MxXy} : Super-saturation
a_{MxXy} : Activity of precipitate (M_xX_y) =1
a_M : Activity of metal (M)
a_X : Activity of non-metal (X)

Precipitation occurs when $g_{MxXy}>1$

- **Program substitutes user input for start temperature as 1600C**
- **Supersaturation for mutually soluble precipitate group (Al,Ti)(O) is greater than 1 at 1600C**
- **Subroutine brackets temperature of precipitation of (Al,Ti)(O) between 1600C (g<1) and 3200C (g>1)**
- **Subroutine uses binary search within this range to obtain start temperature of precipitation as 2801C (g=1)**
- **Start of simulation is from 2802C (next temperature step)**



Results using the Initial Temperature Algorithm



Program stops outputting results at 1616C

User input temperature of 1600C

Program guess temperature for start of precipitation is 2802C

Simulation Details	
Initial guess temperature	1600C
Program guess temperature	2801C
Temperature step size	0.1C
Simulation Ending temperature	1300C
Program crash temperature	1617C

The program STILL CRASHES

↓

<u>Conclusion</u>- Better initial guess helps but <u>problems at intermediate temperatures</u> still cause problems

Modifications to Newton Raphson Scheme

Earlier Version of Scheme (A2. and A3.)

1.Make an initial guess for all variables

↓

2.Calculate the error vector (f) and Jacobian (A)

↓

3.Calculate Newton Step

$s = \{J\}^{-1} \times Error$

Update paramters along Newton Step

↓

4.Enforce side constraints. If error does not decrease, half newton step and repeat procedure until convergence

Newton-Raphson Iteration Scheme

$$z_{new} = z_{old} + lamda * s$$

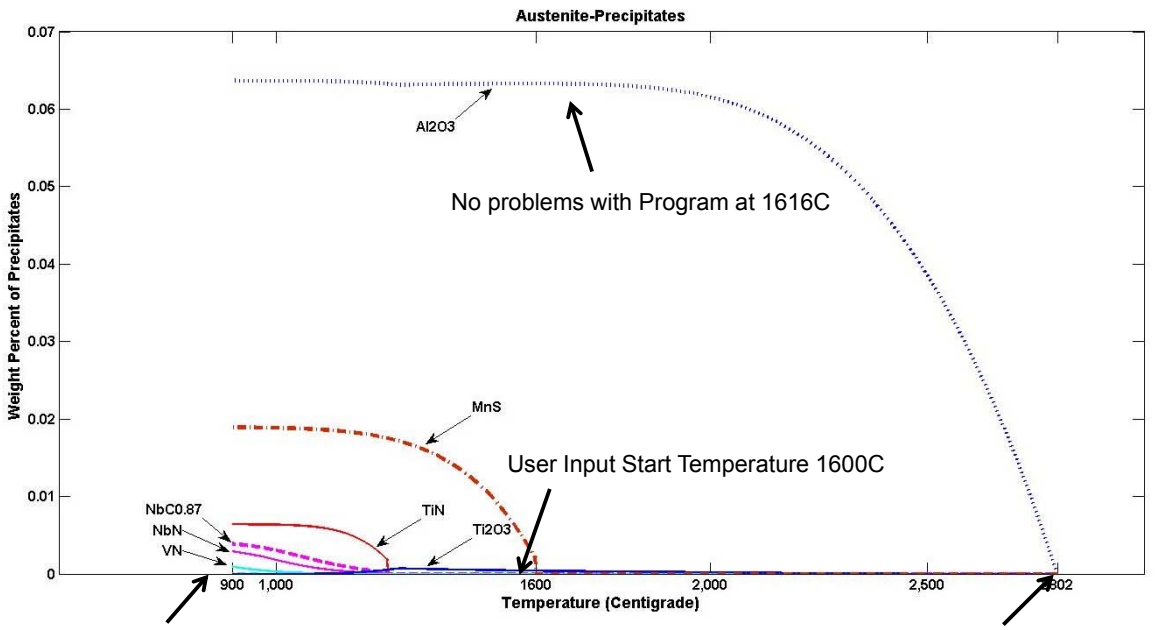
- z_{new} is the new value of the variable
- z_{old} is the old value of the variable
- s is the Newton Step that is taken
- lamda is the amount to step along Newton Step (how much to move to reduce error)

Newer Version of Scheme (A4. and A5.)

4a.Bound Newton Step

After calculating Newton Step, estimate it's lower so that the side constraints are not violated and enforce this lower bound on Newton Step

Weight Percent of Precipitates for Test Case



No problems with Program at 1616C

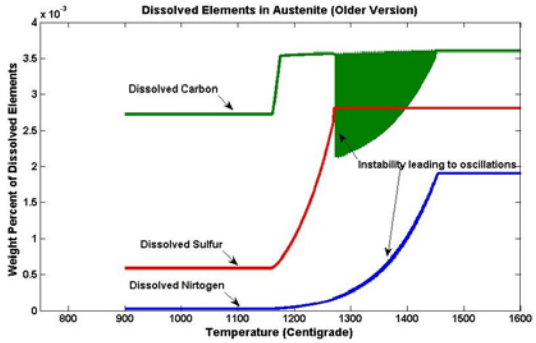
User Input Start Temperature 1600C

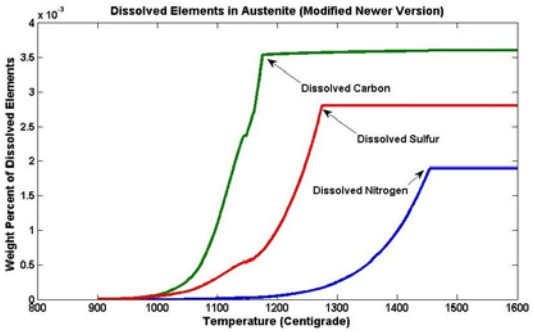
User End Temperature 900C

Program Start Temperature 2802C

Modifications to the Initial Guess at Each Temperature Step

Dissolved element	Initial concentration (%w/w of steel)
Sulfur	0.0028
Oxygen	0.0028
Titanium	0.095
Aluminum	0.045
Nitrogen	0.0019
Carbon	0.0036
Manganese	0.081
Silicon	0.0050





Changes to guess value at start of each temperature step (A6.)

- **Check for change in supersaturation (g) for each temperature step**
- **If the supersaturation for a particular precipitate group becomes greater than one, use appropriate guesses for element concentrations, mutually soluble coefficients and weight ratios of precipitates**

Effect of Nitride Precipitates[3]

Begona Saintillana's[2] test case

Dissolved element	Initial conc. LCAK	Initial conc. HSLA	Initial conc. HSLA-LR	Initial conc. 99% solid segregation HSLA
Carbon (wt%)	0.045	0.045	0.045	0.0453
Manganese (wt%)	0.22	0.8	0.8	0.9022
Sulfur (wt%)	0.005	0.005	0.005	0.0059
Vanadium (wt%)	--	0.0013	0.040	0.0133
Niobium (wt%)	--	0.0013	0.013	0.0142
Nitrogen (wt%)	0.005	0.010	0.015	0.0101
Titanium (wt%) (est.)	0.003	0.003	0.003	0.0044

Parameter	LCAK	HSLA	HSLA-LR
Breakout cracks (%) (plant experience)	1.5	0.6	2.0
Critical Strain for cracks(%) (Saintillana's Model[3])	0.06	0.26 (Rare to crack)	0.02 (Easy to crack)
Crack Susceptibility	High	Low	Very high

- **Concentration of Vanadium and Nitrogen change in the three steels**
- **Addition of small amount of Titanium in the three steel types leads to lesser chance of cracks[2]**
- **However a small increase in Vanadium and Nitrogen concentration from HSLA to HSLA-LR steel causes more hot tear cracks and breakouts[2]**

Effect of Nitride Precipitates[3]

Steel Phase details from CON1D and Simulation Details

Steel Grade	Liquidus Temperature (C)	Solidus Temperature (C)	Delta to Austenite Transition Temperature (C)
LCAK	1532.0	1511.4	1406.8
HSLA	1527.6	1504.1	1423.4
HSLA-LR	1526.8	1501.7	1415.7

Parameter	LCAK	HSLA	HSLA-LR
Initial input temperature from User(C)	1600	1600	1600
Guess temperature calculated by program(C)	-	-	-
Temperature step size(C)	1	0.01	0.01
Simulation End temperature (C)	800	900	800
Simulation Time(seconds)	80	902	1527

Smaller temperature steps used in HSLA and HSLA-LR steels in order to correctly capture the presence of Niobium and Vanadium precipitates

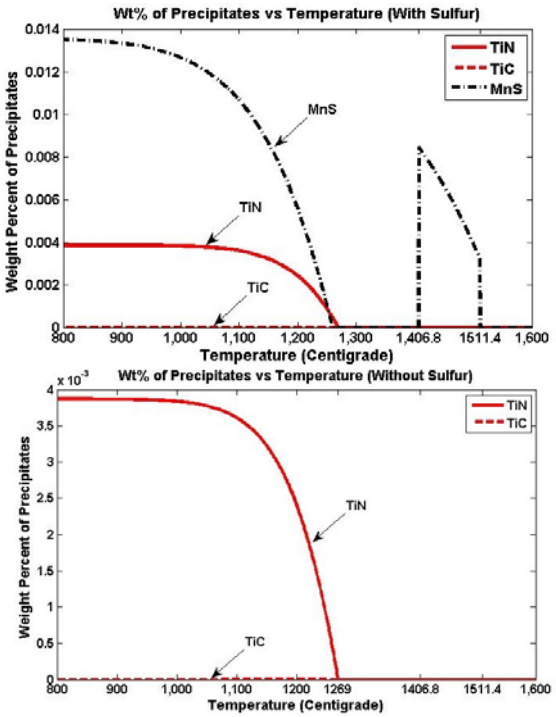
LCAK steel – Formation of Nitride Precipitates

For the LCAK steel, consider:

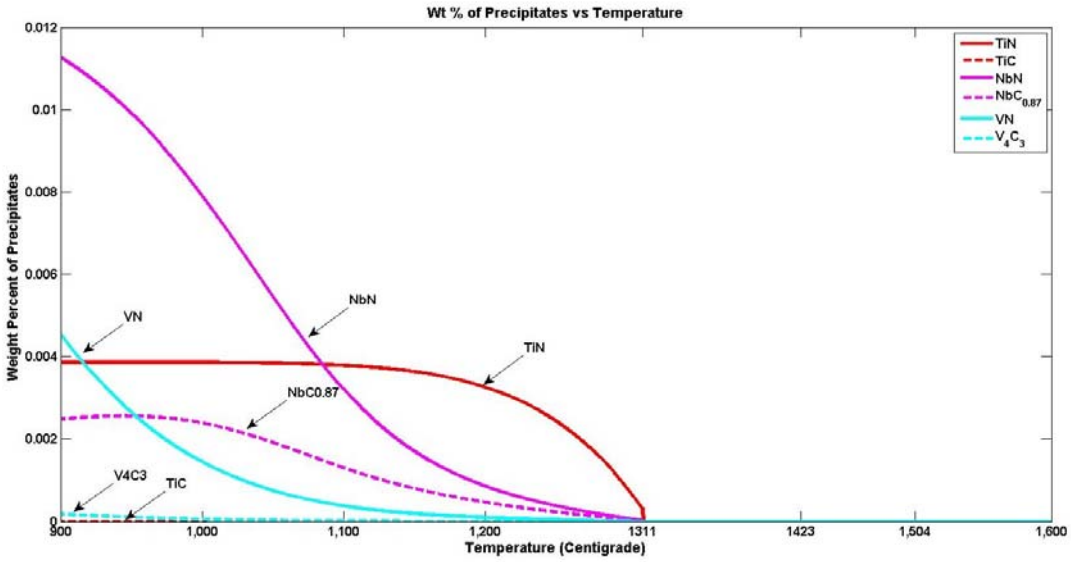
- with Sulfur
- without Sulfur

Steel Grade	Start Temperature for formation of Nitrides (C)
LCAK with Sulfur	1269
LCAK without Sulfur	1269

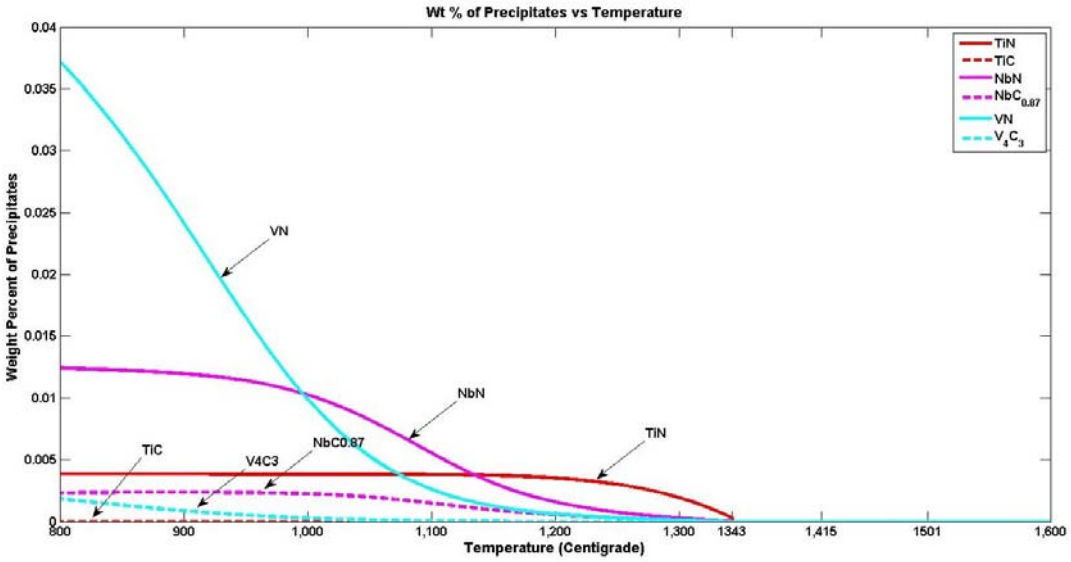
Note: formation of Nitride precipitates is not affected by presence/absence of Sulfur.



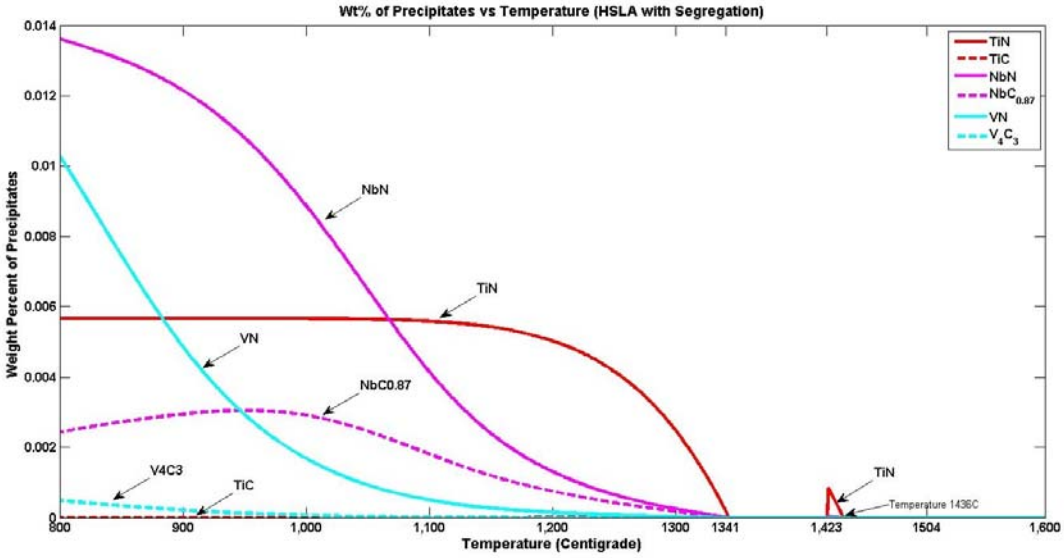
HSLA – No Nitride Precipitates in Delta-Ferrite



HSLA -LR–No Nitride Precipitates in Delta-Ferrite



HSLA (with segregation)– Formation of Nitride Precipitates in Delta Ferrite



Increased element concentration due to segregation results in formation of nitride precipitates (mainly TiN) in Delta Ferrite Phase.

Summary of results from Santillana Cases[3]

Start Temperature for Precipitation of Nitrides				
Parameter	**LCAK**	**HSLA**	**HSLA-LR**	**HSLA (With Segregation)**
Temperature at which Nitrides precipitates start precipitating (C)	**1269**	**1311**	**1343**	**1436**
Type of Nitride precipitates formed	**TiN**	**(Ti,Nb,V)C,N)**	**(Ti,Nb,V)(C,N)**	**(Ti,Nb,V)(C,N)**
Phase in which Nitrides first form	**Austenite**	**Austenite**	**Austenite**	**Delta Ferrite**

- **Use of data from segregation model and comparison with the steels, it is seen qualitatively that HSLA steel (with segregation) forms Precipitates in Delta-Ferrite Phase**
- **Presence of TiN precipitates early in Delta Ferrite helps to tie up the nitrogen**
- **This may lead to less cracks susceptibility [3]**

Conclusions and Future Work

Conclusions

1. Model startup problems have been overcome with a new method to find a good starting temperature.
2. Modifications to the model solution methodology have made it more robust: improved initial guess at each temperature step, and bounding on the Newton-Raphson solver.

Future Work

1. Incorporating automatic temperature stepping
2. Incorporating additional precipitates of interest
3. Kinetics program development and interfacing with other models
4. Apply model system to realistic systems, ductility, and crack prediction

References

References

1. Equilibrium model for precipitation in Micro-alloyed steel, K.Xu, B.G.Thomas and Ron O'Malley, Metallurgical Materials Transaction A, 2011, vol42A, pp524

2. Particle-Size-Grouping Model of Precipitation Kinetics in Micro-alloyed Steels**,** Kun Xu, B.G.Thomas, Metallurgical Materials Transaction A, 2012,vol43,pp1079

3. 'Effect of V and N on the microstructure evolution during continuous casting of steel', B.Santillana, D.G.Eskin,R.Boom,L.Latgerman,3rd International Conference on Advances in Solidification Processes, Rolduc, The Netherlands, June 2011

Acknowledgments

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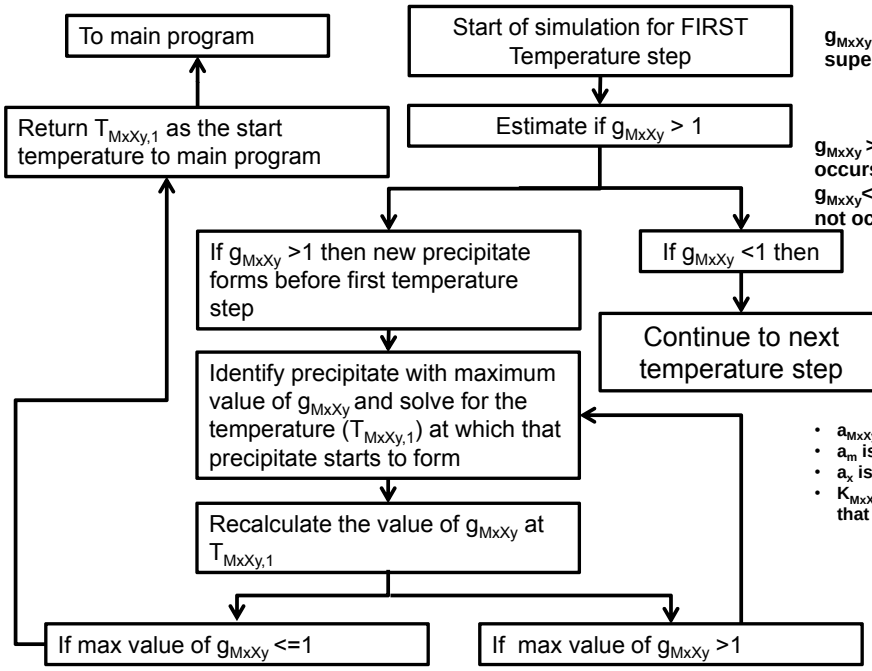
- Thanks to group members - Bryan Petrus, Lance C. Hibbeler and Matthew Zappulla for their timely inputs and advice.

Appendix

Detailed Flowcharts of Modified Program

A1.Sub-routine for Initial Guess Temperature for start of precipitation



g_{MxXy} is the degree of supersaturation of precipitate M_xX_y

$$g_{MxXy} = \frac{a_{Mx} \times a_{Xy}}{K_{MxXy} \times a_{MxXy}}$$

g_{MxXy} >1 : precipitation of MxXy occurs

g_{MxXy}<=1 : precipitation of MxXy does not occur

- **a_{MxXy} is activity of precipitate M_xX_y**
- **a_m is the activity of element m**
- **a_x is the activity of element x**
- **K_{MxXy} is solubility coefficient of M_xX_y at that temperature**

A2.Equations solved for in the Newton Raphson Scheme

General equations for the three types of equations in the error column vector (referred to as 'Error')

The first 18 rows of Error column vector represent equations for solubility constraints

The next 13 rows (row 19 to row 31) of Error column vector represent equations for mass balance constraints

$$Error_i = \begin{bmatrix} \dfrac{a_M^x . a_X^y}{K_{M_xX_y}} - a_{M_xX_y} \\ (1 - w_{total}) \times \dfrac{M \times A_{steel}}{M_0} + \dfrac{100 \times A_M}{M_0 \times A_{steel}} \sum_{i=1}^{18} (x \bullet w_{M_xX_y})_i - 1 \\ \sum_i a_{M_xX_y} - 1 \end{bmatrix}$$

A_M and A_{steel} are molecular mass of element M and steel resp.

The last 3 rows of error column vector represent terms for activity constraints

i is the row index in the Error column vector

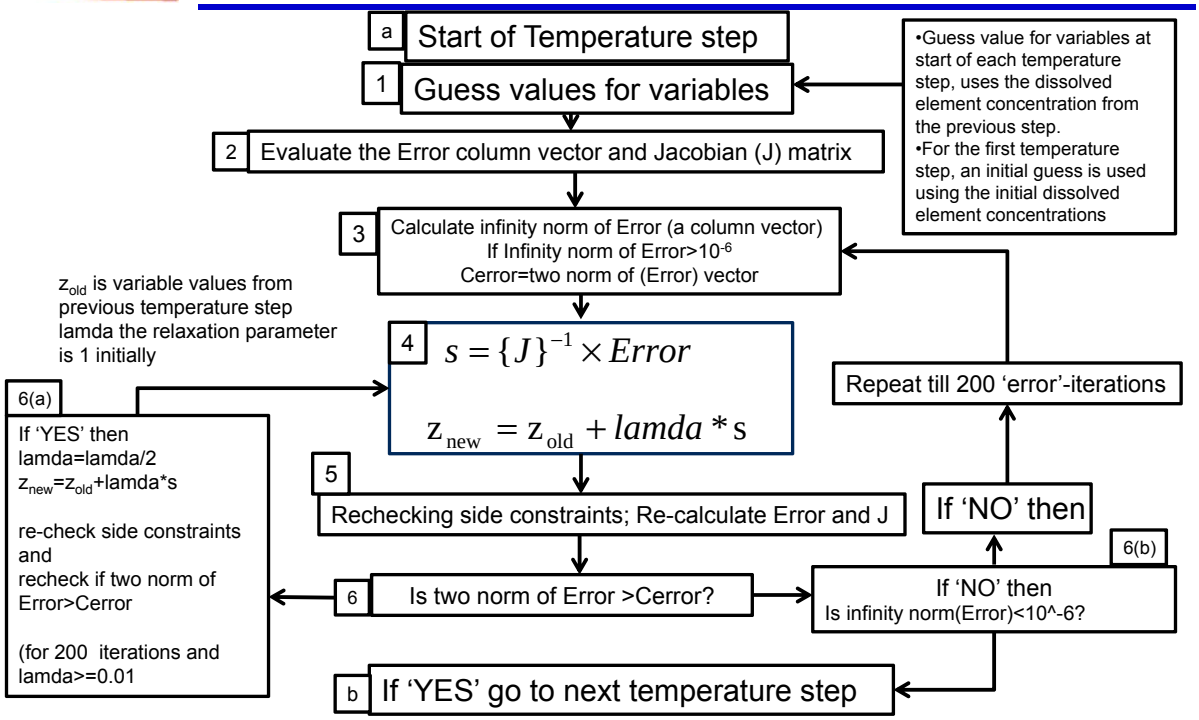
- W_{total} = Total weight of precipitates
- [M]=Current dissolved element concentration
- $[M_o]$=Initial dissolved element concentration at start of simulation
- W_{MxXy}=Molar Weight fraction of precipitate group per mole of steel
- X_{MxXy}= Precipitate weight ratio in a mutually soluble precipitate group
- a_X=activity of element X (activity)

The terms of the Jacobian matrix J are as follows-

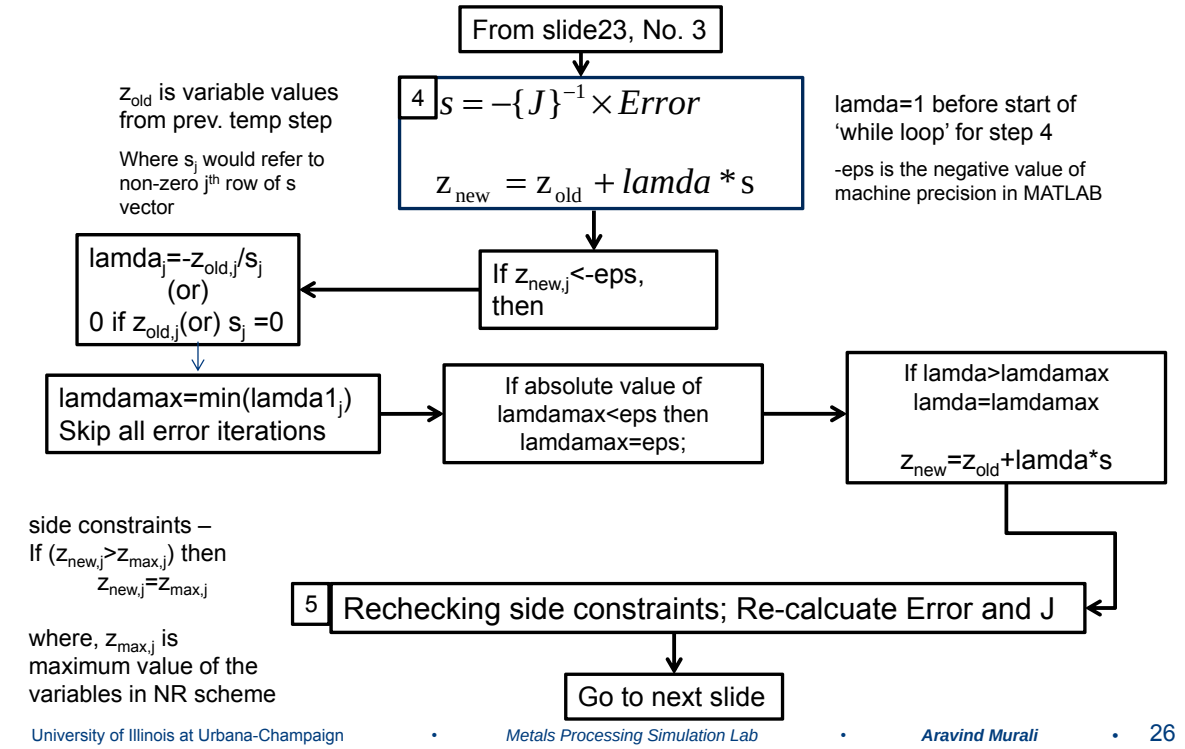
$$\{J(i,j)\} = \frac{\partial(Error_i)}{\partial z_j}$$

- i and j refer to the row and column indices of the matrix elements
- Error(i) refers to the i^{th} row of the Error column vector
- z_j refers to the j^{th} variable present in the j^{th} row in z column vector which is a vector of the variables being solved for in the Newton Raphson scheme

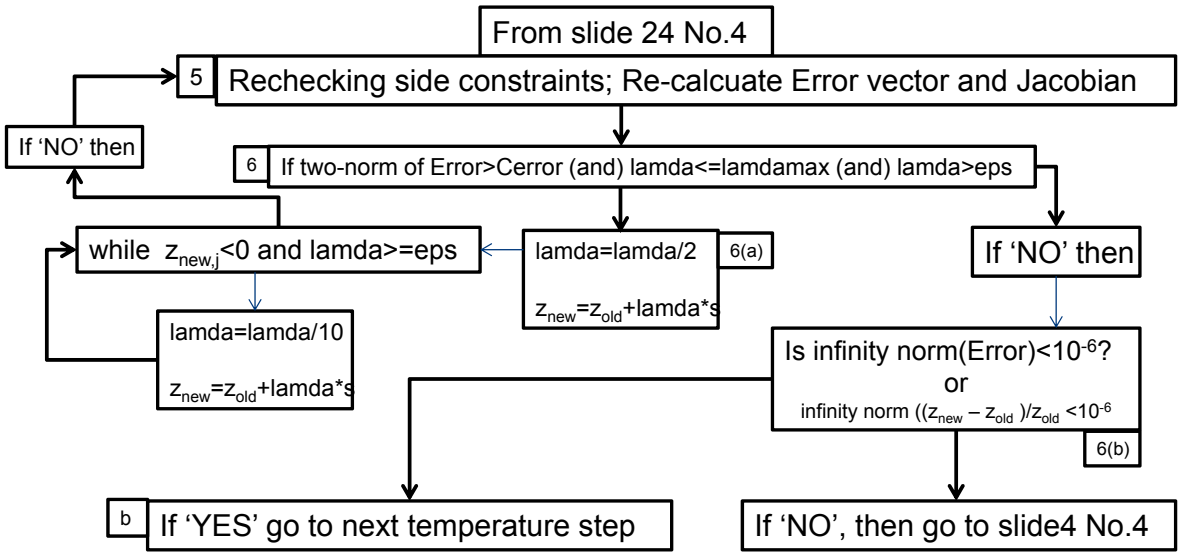
A3.Original Newton Raphson Scheme Used in the Temperature Solver



A4.Modifications proposed for incorporating additional constraints



A5.Modifications proposed for finding optimum Newton Step (relaxation parameter)



A6.Modifications to initial guess at start of each temperature step of NR scheme

<u>Earlier version of initial guess at start of each intermediate temperature step-</u>

Initial guess for variable = Value of variable at the end of previous temperature step

For eg.

Initial guess for $Si_d(current\_step) = Si_d(end\_of\_previous\_step)$

where, Si_d is the dissolved silicon concentration in steel.

<u>Present version of initial guess at start of each intermediate temperature step-</u>

When new precipitate is not forming, the initial guess value for each variable is same as previous version.

When a new precipitate starts forming (for eg. SiO_2 starts forming) (precipiate supersaturation flag sets off)-

For the example of SiO_2

$$DissolvedOxygen_{initialguess} = \min[\frac{K_{SiO_2}}{(f_{si} \times Si_0)^{\frac{1}{2}} \times f_{Oxy}}, DissolvedOxygen_{prev.tempstep}]$$

$$DissolvedSilicon_{initialguess} = \min[\frac{K_{SiO_2}}{(f_{Oxygen} \times Oxygen_O)^2 \times f_{Si}}, DissolvedSilicon_{prev.tempstep}]$$

If w_{Si02} from previous temperature step=0 then,

$$w_{SiO2} = \left(\frac{Oxygen_0 - Oxygen_{initialguess}}{100}\right) \times \frac{A_{steel}}{A_{Oxygen}} + \left(\frac{Si_0 - Si_{initialguess}}{100}\right) \times \frac{A_{steel}}{A_{Si}}$$

- $K_{SiO2}$is solubility coefficient of SiO_2 at current temperature step
- $f_{Si}$is the activity coefficient of Silicon at the current temperature step
- Si_j is the initial concentration of Silicon at start of first temperature step
- f_{Oxygen} is the activity coefficient of Silicon at the current temperature step
- $Oxygen_j$ is the initial concentration of Silicon at start of first temperature step
- A_i=Molecular mass of element I

$Oxygen_j$is the dissolved oxygen at prev. step

$Oxygen_{initialguess}$=$DissolvedOxygen_{initialguess}$

$Si_j$is the initial dissolved silicon at prev. step.

$Si_{initialguess}$=$DissolvedSilicon_{initialguess}$