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. \((\text{Ti}, \text{Nb}, \text{V})(\text{C}, \text{N})\)

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]

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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
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]

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

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

- 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

Simulation Details

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial guess temperature</td>
<td>1600C</td>
</tr>
<tr>
<td>Program guess temperature</td>
<td>2801C</td>
</tr>
<tr>
<td>Temperature step size</td>
<td>0.1C</td>
</tr>
<tr>
<td>Simulation Ending temperature</td>
<td>1300C</td>
</tr>
<tr>
<td>Program crash temperature</td>
<td>1617C</td>
</tr>
</tbody>
</table>

Program guess temperature for start of precipitation is 2802C

Conclusion-
Better initial guess helps but problems at intermediate temperatures still cause problems

The program still crashes
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
   \[ s = (J)^{-1} \times Error \]
4. Enforce side constraints. If error does not decrease, half Newton step and repeat procedure until convergence

Newton-Raphson Iteration Scheme

\[ z_{\text{new}} = z_{\text{old}} + \lambda \times s \]
- \( z_{\text{new}} \) is the new value of the variable
- \( z_{\text{old}} \) is the old value of the variable
- \( s \) is the Newton Step that is taken
- \( \lambda \) 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

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

<table>
<thead>
<tr>
<th>Dissolved element</th>
<th>Initial concentration (%w/w of steel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur</td>
<td>0.0028</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.0028</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.095</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.045</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.0019</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.0036</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.081</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.0050</td>
</tr>
</tbody>
</table>

Effect of Nitride Precipitates[3]

Begona Saintillana’s[2] test case

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

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

- 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

Steel Phase details from CON1D and Simulation Details

<table>
<thead>
<tr>
<th>Steel Grade</th>
<th>Liquidus Temperature (C)</th>
<th>Solidus Temperature (C)</th>
<th>Delta to Austenite Transition Temperature (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCAK</td>
<td>1532.0</td>
<td>1511.4</td>
<td>1406.8</td>
</tr>
<tr>
<td>HSLA</td>
<td>1527.6</td>
<td>1504.1</td>
<td>1423.4</td>
</tr>
<tr>
<td>HSLA-LR</td>
<td>1526.8</td>
<td>1501.7</td>
<td>1415.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LCAK</th>
<th>HSLA</th>
<th>HSLA-LR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial input temperature from User (C)</td>
<td>1600</td>
<td>1600</td>
<td>1600</td>
</tr>
<tr>
<td>Guess temperature calculated by program (C)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Temperature step size (C)</td>
<td>1</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Simulation End temperature (C)</td>
<td>800</td>
<td>900</td>
<td>800</td>
</tr>
<tr>
<td>Simulation Time (seconds)</td>
<td>80</td>
<td>902</td>
<td>1527</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Steel Grade</th>
<th>Start Temperature for formation of Nitrides (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCAK with Sulfur</td>
<td>1269</td>
</tr>
<tr>
<td>LCAK without Sulfur</td>
<td>1269</td>
</tr>
</tbody>
</table>

Note: formation of Nitride precipitates is not affected by presence/absence of Sulfur.
HSLA – No Nitride Precipitates in Delta-Ferrite

![Graph showing precipitate formation vs temperature for HSLA steel, with a focus on VN (Vanadium Nitride) precipitation.](image)

HSLA -LR–No Nitride Precipitates in Delta-Ferrite

![Graph showing precipitate formation vs temperature for HSLA-LR steel, with a focus on VN precipitation.](image)
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]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LCAK</th>
<th>HSLA</th>
<th>HSLA-LR</th>
<th>HSLA (With Segregation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature at which Nitrides precipitates start</td>
<td>1269</td>
<td>1311</td>
<td>1343</td>
<td>1436</td>
</tr>
<tr>
<td>precipitating (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type of Nitride precipitates formed</td>
<td>TiN</td>
<td>(Ti,Nb,V)(C,N)</td>
<td>(Ti,Nb,V)(C,N)</td>
<td>(Ti,Nb,V)(C,N)</td>
</tr>
<tr>
<td>Phase in which Nitrides first form</td>
<td>Austenite</td>
<td>Austenite</td>
<td>Austenite</td>
<td>Delta Ferrite</td>
</tr>
</tbody>
</table>

- 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


Acknowledgments

• Continuous Casting Consortium Members (ABB, ArcelorMittal, Baosteel, Magnesita Refractories, Nippon Steel and Sumitomo Metal Corp., Nucor Steel, Postech/Posco, Severstal, SSAB, Tata Steel, ANSYS/Fluent)

• 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

To main program

Start of simulation for FIRST
Temperature step

Estimate if $g_{MxXy} > 1$

If $g_{MxXy} > 1$ then new precipitate forms before first temperature step

Identify precipitate with maximum value of $g_{MxXy}$ and solve for the temperature ($T_{MxXy,1}$) at which that precipitate starts to form

Recalculate the value of $g_{MxXy}$ at $T_{MxXy,1}$

If max value of $g_{MxXy} <= 1$

If max value of $g_{MxXy} > 1$

Return $T_{MxXy,1}$ as the start temperature to main program

Continue to next temperature step

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

$$ g_{MxXy} = \frac{a_{M_x} \times a_{X_y}}{K_{MxXy} \times a_{MxXy}} $$

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

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

$$Error_i = \begin{bmatrix} \frac{a_{M_x}}{K_{M_x}} d_{M_xX_y} - a_{M_xX_y} \\ (1 - W_{total}) \times \frac{M \times A_{steel}}{M_0} + \frac{100 \times A_{M}}{M_0 \times A_{steel}} \sum_{i=1}^{18} (X_{M_iX_y} \times W_{M_iX_y}) - 1 \\ \sum_{i} a_{M_iX_y} - 1 \end{bmatrix}$$

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

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

$W_{total}$ = Total weight of precipitates
$[M]$=Current dissolved element concentration
$[M_i]$=Initial dissolved element concentration at start of simulation
$W_{M_iX_y}$=Molar Weight fraction of precipitate group per mole of steel
$X_{M_iX_y}$=Precipitate weight ratio in a mutually soluble precipitate group
$a_{M_iX_y}$=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 $i^{th}$ 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

1. Guess values for variables
2. Evaluate the Error column vector and Jacobian (J) matrix
3. Calculate infinity norm of Error (a column vector)
   If infinity norm of Error > 10^-6
   Cerror = two norm of (Error) vector
4. \( s = \{J\}^{-1} \times \text{Error} \)
   \( z_{\text{new}} = z_{\text{old}} + \text{lamda} \times s \)
5. Rechecking side constraints; Re-calculate Error and J
6. Is two norm of Error > Cerror?
6(a) If 'YES' then
   \( \text{lamda} = \text{lamda}/2 \)
   \( z_{\text{new}} = z_{\text{old}} + \text{lamda} \times s \)
   re-check side constraints and recheck if two norm of Error > Cerror
   (for 200 iterations and lamda >= 0.01)
6(b) If 'NO' then
   Is infinity norm (Error) < 10^-6?
   If 'NO' then
   If 'YES' go to next temperature step
   Repeat till 200 'error'-iterations

A4. Modifications proposed for incorporating additional constraints

4. \( s = \{J\}^{-1} \times \text{Error} \)
   \( z_{\text{new}} = z_{\text{old}} + \text{lamda} \times s \)
   lamda=1 before start of 'while loop' for step 4
   -eps is the negative value of machine precision in MATLAB

5. Rechecking side constraints; Re-calculate Error and J

side constraints –
If \( (z_{\text{new}})_{j} > z_{\text{max},j} \) then
\( z_{\text{new}} = z_{\text{max},j} \)
where, \( z_{\text{max},j} \) is maximum value of the variables in NR scheme
A5. Modifications proposed for finding optimum Newton Step (relaxation parameter)

From slide 24 No.4

5. Rechecking side constraints; Re-calculate Error vector and Jacobian

If 'NO' then

6. If two-norm of Error> Error or |lamda - lamdamax| (and) lamda > eps

If 'NO' then

while \( z_{new,i} < 0 \) and lamda >= eps

\[ \text{lamda} = \frac{\text{lamda}}{10} \]

\[ z_{new,i} = z_{old,i} + \lambda \text{m} \]

If 'YES' go to next temperature step

\[ \text{If 'NO', then go to slide 4 No.4} \]

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

Earlier version of initial guess at start of each intermediate temperature step-

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.

Present version of initial guess at start of each intermediate temperature step-

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) (precipitate supersaturation flag sets off)-

For the example of \( SiO_2 \)

\[
\text{Dissolved Oxygen}_{\text{init guess}} = \min \left( \frac{K_S_{SiO_2}}{f_{Oxygen} \times S_{Oxygen_{init guess}}} \right) \times \text{Dissolved Oxygen}_{prev \text{ step}}
\]

\[
\text{Dissolved Silicon}_{\text{init guess}} = \min \left( \frac{K_{SiO_2}}{f_{Silicon} \times S_{Silicon_{init guess}}} \right) \times \text{Dissolved Silicon}_{prev \text{ step}}
\]

If \( w_{SiO_2} \) from previous temperature step=0 then,

\[
W_{SiO_2} = \frac{\text{Dissolved Oxygen}_{\text{init guess}}}{\text{A}_{Oxygen}} \times \frac{\text{A}_{Silicon}}{S_{Silicon_{init guess}}} = \frac{\text{Dissolved Silicon}_{\text{init guess}}}{\text{A}_{Silicon}}
\]

\[ \begin{align*}
K_{SiO_2} & = \text{solubility coefficient of } SiO_2 \text{ at current temperature step} \\
A_i & = \text{Molecular mass of element } i
\end{align*} \]

Oxygen is the dissolved oxygen at prev. step

\[ \text{Dissolved Oxygen}_{\text{init guess}} = \frac{\text{Dissolved Oxygen}_{\text{init guess}}}{\text{Dissolved Silicon}_{\text{init guess}}}; \text{Si is the initial dissolved silicon at prev. step.} \]