

Modeling of Precipitate Formation in Continuous Steel Casting

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Introduction: Transverse cracks



Widespread crazing and fine transverse cracks at oscillation marks on the as-cast surface of a line pipe steel slab (top side).

Reference:*E. S. Szekeres, A Review* of Strand Casting Factors Affecting Transverse Cracking, Proceedings of the 6th International Conference on Clean Steel, Balatonfüred, Hungary, 10-12 June 2002.



Effect of oscillation marks on grain size



The formation of surface cracks & nitride embrittlement





STAGE I - Normal solidification on mold wall. Surface grains are small but highly oriented.



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STAGE III - Nitride precipitates begin to form along the blown grain boundaries. Microcracks initiate at weak boundaries.



STAGE IV - Ferrite transformation begins and new precipitates form at boundaries. Existing microcracks grow & new ones form.

STAGE II - Surface grains "blow" locally due to high temperature (>1350°C) and strain, especially at the base of deeper oscillation marks.



STAGE V - At the straightener, microcracks propagate and become larger cracks, primarily on top surface of the strand.

Reference: E. S. Szekeres, 6th Internat. Conf. on Clean Steel, Balatonfüred, Hungary, June 2002.



Temperature & Phase fraction --- CONID
Amount of precipitates --- Equilibrium precipitation model
Size distribution and volume fraction of precipitates --- Kinetic model for precipitate growth
Grain size of steel matrix --- Grain growth model evolving with time, temperature history and precipitates constraint
Stress and strain analysis concerning effects of grain size and precipitates accumulating on the grain boundaries --- stress analysis
Final goal: Predict ductility problem and transverse cracks

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Equilibrium precipitation model

Two common methods for precipitate calculation: Free energy and solubility product.

We choose solubility product: more accurate from direct measurements

$$x[M] + y[N] \Leftrightarrow M_x N_y \text{ eg. } [Nb] + [N] \Leftrightarrow NbN$$

Define solubility product $K_{M_x N_y} = \frac{[a_M]^x [a_N]^y}{a_{M_x N_y}}$
The activity of pure $M_x N_y$ is unity. For low alloy steels, activity~concentration.
Solubility product $K_{M_x N_y} = [wt \% M(x,t)]^x [wt \% N(x,t)]^y$
Experimental measurements $\log K_{M_x N_y} = -\frac{A}{T} + B$
The criterion for precipitation formation
 $[wt \% M(x,t)]^x [wt \% N(x,t)]^y > K_{M_x N_y}$



Precipitates included in the model (oxides and sulfides)

Precipitate	$\log K_{\gamma}$	$\log K_{\alpha,\delta}$ $\log K_{i}$		Crystal Form
Composition				Lattice parameter
Al ₂ O ₃			64000 + 20 57	Hexagonal
[%A1] ² [%O] ³			T	a = 4.76 Å, c = 13.0 Å
Ti ₂ O ₃			$-\frac{56060}{+18.08}$	Hexagonal
[%Ti] ² [%O] ³			T 10.00	a = 5.16 Å, c = 13.6 Å
MgO				f.c.c
[%Mg][%O]				a = 4.21 Å
MnO			$-\frac{11749}{+4.67}$	f.c.c
[%Mn][%O]			T	a = 4.45 Å
MnS	$-\frac{9020}{+2.93}$			f.c.c
[%Mn][%S]	T T			a = 5.22 Å
MgS			$-\frac{17026}{+5.15}$	f.c.c
[%Mg][%S]			T	$a = 5.20 \text{ \AA}$
TiS	$-\frac{17640}{+8.2}$			Trigonal
[%Ti][%S]	T + 0.2			a = 3.41 Å, c = 27.7 Å
Ti ₄ C ₂ S ₂	$-\frac{15600}{+6.5}$			Hexagonal
[%Ti][%C] ^{0.5} [%S] ^{0.5}	T 10.5			$a = 3.20 \text{ \AA}, c = 11.2 \text{ \AA}$

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Precipitates included in the model (nitrides and carbides)

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AIN	6770	8790	12950	Hexagonal
[%A1][%N]	[%A1][%N] $- \frac{100}{T} + 1.03$		$-\frac{-}{T}+5.58$	$a = 3.08 \overset{0}{\mathbf{A}}, c = 4.95 \overset{0}{\mathbf{A}}$
BN	13970 5 24	14250	10030	Hexagonal
[%B][%N]	$-\frac{-}{T}+5.24$	$-\frac{-}{T}$ +4.01	$-\frac{1}{T}$ +4.04	$a = 2.55 \overset{0}{\mathbf{A}}, c = 4.17 \overset{0}{\mathbf{A}}$
NbN	10150	12170		f.c.c
[%Nb][%N]	$\frac{+3.79}{T}$	$-\frac{-}{T}$ +4.91		$a = 4.39 \overset{0}{A}$
NbC _{0.87}	7020	9830		f.c.c
[%Nb][%C] ^{0.87}	$-\frac{-}{T}+2.81$	$-\frac{1}{T}$ +4.33		$a = 4.46 \overset{0}{A}$
TiN	15790	18420	17040	f.c.c
[%Ti][%N]	$-\frac{1}{T}$ + 5.40	$-\frac{1}{T}$ + 6.40	$-\frac{1}{T}$ + 6.40	$a = 4.24 \overset{0}{A}$
TiC	7000 . 2.75	10230	6160	f.c.c
[%Ti][%C]	$-\frac{1}{T}+2.75$	$-\frac{1}{T}$ +4.45	$-\frac{1}{T}+3.25$	$a = 4.32 \overset{0}{A}$
VN	7700	9720 . 2 00		f.c.c
[%V][%N]	$-\frac{1}{T}+2.80$	$-\frac{1}{T}$ +3.90		$a = 4.12 \overset{0}{A}$
V ₄ C ₃	6560	7050		f.c.c
[%V][%C] ^{0.75}	$-\frac{-}{T}+4.45$	+4.24		$a = 4.16 \overset{0}{A}$
Cr ₂ N				Hexagonal
[%Cr] ² [%N]				$a = 4.78 \overset{0}{A}, c = 4.44 \overset{0}{A}$

Different phases have different crystal structures and thus different solubility limits. Generally, solubility product in liquid is 10 times that in austenite and 100 times that in ferrite.

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Mutual solubility of precipitates

If two precipitates have the same crystal structures and close lattice parameters, they will mutually dissolve and form mixture precipitates of uniform composition

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For example, NbN and AlN are mutually exclusive

$$[wt\%Nb][wt\%N] / x_{NbN} = K_{NbN}$$
$$[wt\%Al][wt\%N] / x_{AlN} = K_{AlN}$$
$$x_{NbN} = 1, x_{AlN} = 1$$

NbN and TiN are mutually dissolved

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 $[wt\%Nb][wt\%N] / x_{NbN} = K_{NbN}$ $[wt\%Ti][wt\%N] / x_{TiN} = K_{TiN}$ $x_{NbN} + x_{TiN} = 1$

Groups of precipitates

• TiN, TiC, NbN, NbC, VN, VC (f.c.c structure)

Experimental validation (lattice mismatch ~7.92%)

- Al₂O₃, Ti₂O₃ (hexagonal structure) lattice mismatch ~8.06%
- MgO, MnO (f.c.c structure) lattice mismatch ~5.54%
- MnS, MgS (f.c.c structure) lattice mismatch ~0.38%
- TiS (trigonal structure)
- $Ti_4C_2S_2$ (hexagonal structure)
- AlN (hexagonal structure)
- BN (hexagonal structure)
- Cr₂N (hexagonal structure)

More data about solubility products of precipitates in different phases are still needed

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To judge which element really forms precipitates and can be used to calibrate the reacted amounts of other elements

Judge dominant group of precipitates (from the maximum values of all g_i)

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Choose N as the standard to calibrate the amounts of other elements If $max(g_i)=g_{TiNbVCN}$ and $N_0=0$, $C_0\neq 0\rightarrow C$ If $max(g_i)=g_{MnMgS}$, g_{TiS} or g_{TiCS} and $S_0\neq 0\rightarrow S$ If $max(g_i)=g_{AITiO}$ or g_{mnMgO} and $O_0\neq 0\rightarrow O$

Remaining precipitation model equations

• Constraints for mutually soluble coefficients (Q)

 $x_{TiN} + x_{NbN} + x_{VN} + x_{TiC} + x_{NbC} + x_{VC} - 1 = 0$ $x_{AlO} + x_{TiO} - 1 = 0$ $x_{MnO} + x_{MgO} - 1 = 0$ $x_{MnS} + x_{MgS} - 1 = 0$

• Distribution of weight ratios among all groups of precipitates (1)

 $w_{TiNbVCN} + w_{AITiO} + w_{MnMgO} + w_{MnMgS} + w_{TiS} + w_{TiCS} + w_{AIN} + w_{BN} + w_{CrN} - 1 = 0$

Side constraints for all parameters

- $0 \le [M] \le M_0$ for all alloying element concentrations
- $0 \le x_{MX} \le 1$ for all coefficients of mutually soluble groups of precipitates
- $0 \le w_i \le 1$ for weight ratios of each group of precipitates

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Precipitate model calculation procedure

• Put the initial concentration of elements to calculate g_i⁰

If all $g_i^0 \le 1$, then there is no precipitation forming

- If any one of the $g_i^{0} > 1$, the initial guess is needed
- If there is the first place when precipitates form, use some method to give the approximate values as the initial guess
- For the below temperature, the initial guess for the current temperature is the final results of the last step at higher temperature

Loop until all equations converge to zero

- \triangleright Compute all g_i and find their maximum
- > Compute the values of functions F and its gradient A
- \blacktriangleright Calculate the Newton step $s = -A^{-1}F$ and update values of all parameters
- > Add side constraint and check if the value of norm(F,inf) decreases
- If yes, continue next iteration; if not, divide Newton step by two and repeat until norm(F,inf) decreases







Precipitates form in different stages

Different size peaks shows that precipitates form in different stages

- 1). Forming in the liquid (most possibly float into the top slag to be removed)
- 2). Forming between the dendrite arms (during solidification)
- 3). Forming in the solid (remaining precipitates)

1. If there are precipitates forming in the liquid, calculate amounts of precipitates and choose dissolved concentration at the liquidus temperature T_{liq} as the initial concentration for the next calculation during solidification

2. Calculate the amounts of precipitates forming during solidification which depends on the segregation model chosen. At solidus temperature T_{sol} , subtract the alloys mass included in the precipitates form from the initial concentration at T_{liq} to get the new initial concentration for the next calculation in the solid

3. Use the new initial concentration to calculate the precipitates in the solid, the solubility product is the combination of those in ferrite and austenite



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Validation of precipitation model during solidification

Simple case: Dissolved concentration decreases from C_0 at liquidus temperature to $C_0/2$ at solidus temperature



Differential Lever rule

$$C_{L,seg}^{i} = \frac{\left[1 + (k-1)f_{S}^{i-1}\right]}{\left[1 + (k-1)f_{S}^{i}\right]}C_{L,dis}^{i-1}$$

Differential Scheil model

$$C_{L,seg}^{i} = \frac{2 - (2 - k)f_{s}^{i-1} - kf_{s}^{i}}{2 - kf_{s}^{i-1} - (2 - k)f_{s}^{i}}C_{L,dis}^{i-1}$$



Convergence study

Lever rule

Partition coefficient	Numerical value $m_{L,pre}^{total}$	Step number (n)	Relative error	
k=1.0	0.25	10	0	
k=0.75	0.363543	100	0.137%	
k=0.5	0.501539	100	0.308%	
k=0.25	0.683078	100	0.556%	
k=0.1	0.837668	100	0.834%	
k=0.01	0.986762	100	1.526%	
k=0.0001	0.999755	10000	0.027%	

Scheil model

Partition coefficient	Numerical and a metotal	Step number (n)	Relative error
r artition coefficient	Numerical value $m_{t_{max}}$	otep namoer (n)	recimere cirer
	aspre		
k=1.0	0.25	10	0
A-1.0	0.25	10	Ŷ
k=0.75	0.439438	100	0.443%
K-0.75	0.457450	100	0.44570
k=0.5	0.632435	100	1 190%
A-0.5	0.002400	100	1.17070
k=0.25	0.834208	100	2 672%
4.0.20	0.004200	100	2.07270
k=0.1	0.980582	100	6.009%
2.0.2	0.500502	100	0.000770
k=0.01	0.997690	10000	0.523%
10.01	0.227020	10000	0.52570
k=0.0001	0 999975	100000000	0.0045%
1 0.0001	0.222213	10000000	0.001370

Decreasing k increases the numerical error for fixed number of steps n

Generally, for typical values of k~0.1, *n=100* gives enough accuracy

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Validation of precipitation model during solidification (AIN case)



T_{lig}=1528.1°C, T_{sol}=1501.5°C

Differential Scheil model

No AlN forming in the liquid

Weight of AlN forming during solidification is 6.86×10⁻⁴. AlN begin to form at around 1503°C

Maximum possible amount of AlN is 0.0167, and the percent of AlN during solidification is 4.1%.

Possible reasons (kinetic consideration): The remaining AlN should stay dissolved until 1060°C in the solid. At this low temperature, the nucleation and growth of new AlN particles in the solid is slow. However, the AlN particles already present (from solidification) can grow quickly. Finally, the new nuclei form in the solid at lower temperature, grow slowly from the small fraction of Al and N remaining.





Name	%C	%Mn	%Si	%Ti	%Nb	%V	%B	%N
1006	0.06	1	0.2	0.015	0.015	0.004	0.006	0.01
Partition coefficient	0.20	0.74	0.60	0.60	0.27	~1.0	0.15	0.27

Precipitates TiN, TiC, NbN, NbC, VN, VC, BN will form







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Conclusions

- 1) The higher temperature and lack of precipitate formation are likely the controlling factors in susceptibility to cracks especially at oscillation mark roots
- 2) The precipitates can form in the three stages (in the liquid, during solidification and in the solid). This causes different appearing locations (removed from liquid, between dendrites, on the grain boundary or inside the grain) and different number and size distributions. These differences have important influences on the quality of final products.
- 3) A system of nonlinear equations is established to calculate equilibrium dissolved concentration and precipitates amount for a given initial concentration and set of solubility products.
- 4) A method is suggested to calculate the amounts of precipitates in the different stages, especially these forming due to segregation during solidification.

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be introduced to validate these size measurements.

6) Among nitrides and carbides, TiN is the most stable precipitate due to its lowest solubility limit. BN is another important nitride if there are enough remaining free nitrogen available in the steel. After nitrogen is combined with other more stable nitrides and there is always plenty of free carbon, NbC will become more important because of the low ratio of solubility products of carbide to nitride of Nb and its mutual solubility with the more stable TiN and NbN particles.

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Current work for precipitates kinetics

> Add activity coefficients influence into consideration

$$K_{M_{x}N_{y}} = \frac{[a_{M}]^{x}[a_{N}]^{y}}{a_{M_{x}N_{y}}}$$

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Where $a_i = f_i[\% i]$ and $\log f_i = e_i^i[\% i] + \sum e_i^j[\% j]$

Generally, interaction coefficients of i as affected by the alloying element j are functions of concentration and temperature, so we need update the values of these coefficients during each iteration in calculation

Particle coarsening kinetics (Wagner equation)

$$r^3 - r_0^3 = \frac{8\gamma D_m C_m V_m'}{9RT}$$

Assumption: Volume fraction is almost constant. Equation is only applied when peak temperature is well below the equilibrium solvus of the precipitates.

Particles size grouping model: supersaturation effect included and no assumption of constant volume fraction

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The influence of growing precipitates on the grain growth



Update the f/r value for the growing precipitates for each step

Some parameters to fit grain size for mainly Ti-microalloyed or Nbmicroalloyed steels are given, but the influence of combined effect of many alloying elements still needs more work



Fig. 7. Predicted variation in average grain size (\overline{D}) with I_1 and *m* for $\overline{D}_{\text{Lim}}^0 = 50 \ \mu\text{m}$, n = 0.5, and $\overline{D}_0 = 0$ (growing precipitates).

Constant volume fraction f_0 for precipitate

Reference: I. Anderson, O. Grong, Acta Metall. mater. Vol. 43, No. 7, pp2673-2688, 1995.

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