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Prediction of Precipitate Formation in Steel Continuous 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 depressions on grain size





The formation of surface cracks & nitride embrittlement





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



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.



Nitrogen-related phenomena

- 1). Interstitial solid solution strengthening by free nitrogen
- 2). Nitride precipitation strengthening
- 3). Grain refinement due to presence of nitride precipitates

matrix grain size $R = \frac{4}{3} \cdot \frac{r}{f}$ (Zener equation)

r: pinning precipitate size f: fraction of precipitate

Beneath depressions & oscillation marks — higher temperature causes less precipitate amount and larger precipitate size — larger matrix grain size — the stress and strain to fracture decreases

Need to predict and control not only the nitrogen content, but also the form in which it exists



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Cracks open up at weak grain boundaries

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Crazing around a transverse crack at base of an oscillation mark on the as-cast top surface of a 0.2C steel slab. Note the larger grain size at the the base of the oscillation mark.

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

Kun Xu 5



Development and Role of Precipitation Model





Definition of solubility products of precipitates



Why choose solubility product instead of free energy?

 $2RT \cdot \ln([V][N]/[V]_{s}[N]_{s}) = \Delta G^{0}$ Consider 5% error in free energy $2[V] + N_2 \Leftrightarrow 2VN$ $\Delta G^{0}_{298 \sim 1173^{\circ}C} = -346796.37(\pm > 17340) + 241.28T$ $K_{VV} = [V][N] = 3.57 \cdot 10^4 \cdot \exp[-193825.9(\pm > 12598) / RT]$ $K_{VN} \simeq 3.15 \times 10^{-6} \sim 5.32 \times 10^{-5}$

The small error causes one order change in solubility product Experimental value ~ 4.8×10^{-5}

Measured solubility product $\log([V][N]) = -\frac{7700}{T} + 2.86$



Mutual solubility of precipitates

If two precipitates have the same crystal structures and close lattice parameters, they are mutually dissolved

For example, NbN and AlN are mutual exclusive

$$[wt\%Nb][wt\%N] = K_{NbN} \quad [wt\%Al][wt\%N] = K_{AlN}$$

NbN and TiN are mutual dissolved (increase temperature and volume fraction of precipitate)

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

Generally, solve the nonlinear equation system including the dissolved elements and the corresponding activity coefficients of each precipitate by Robust Newton method — these unknowns must satisfy definition of solubility products and the chemical reaction requirement

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Solubility for nitrides and carbides

Precipitate	Structure	Parameter $\begin{pmatrix} o \\ A \end{pmatrix}$	$\log K_{\gamma}$	$\log K_{\alpha}$	$\log K_l$
[%Al][%N]	Hexagonal	a=3.11, c=4.98	$-\frac{6770}{T}+1.03$	$-\frac{8790}{T}+2.05$	$-\frac{12950}{T}+5.58$
[%B][%N]	Hexagonal	a=2.55, c=4.17	$-\frac{13970}{T}+5.24$	$-\frac{14250}{T}+4.61$	$-\frac{10030}{T}+4.64$
[%Nb][%N]	fcc	a=4.40	$-\frac{10150}{T}+3.79$	$-\frac{12170}{T}+4.91$	
[%Nb][%C] ^{0.87}	fcc	a=4.47	$-\frac{7020}{T}+2.81$	$-\frac{9830}{T}+4.33$	
[%Ti][%N]	fcc	a=4.24	$-\frac{15790}{T}+5.40$	$-\frac{18420}{T}$ + 6.40	$-\frac{17040}{T}+6.40$
[%Ti][%C]	fcc	a=4.32	$-\frac{7000}{T}+2.75$	$-\frac{10230}{T}+4.45$	$-\frac{6160}{T}+3.25$
[%V][%N]	fcc	a=4.12	$-\frac{7700}{T}+2.86$	$-\frac{9720}{T}+3.90$	
[%V][%C] ^{0.75}	fcc	A=4.16	$-\frac{6560}{T}+4.45$	$-\frac{7050}{T}+4.24$	

Reference: E. T. Turkdogan, Fundamentals of steelmaking, The Institute of Materials, London.









Calculation for two industrial steels

Name	%C	%Mn	%Si	%V	%Nb	%Ti	%B	%N
1005	0.05	1.15	0.2	0.004	0.035	0.01	0.006	0.01
1006	0.06	1	0.2	0.004	0.015	0.015	0.006	0.01

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

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- 1) Carbides and Nitride precipitation with mutual solubility have been added to the equilibrium precipitation model
- 2) The higher temperature and precipitate formation are likely the controlling factors in susceptibility to cracks at oscillation mark roots
- 3) Many precipitates form in the mold (mainly TiN, owing to its lowest solubility product)
- 4) BN is another important nitride because of its low solubility product and lowest atomic mass of B (the same weight of B consumes much more N than other alloyed elements)
- 5) Niobium carbide and nitride are also observed because of the low ratio of carbide to nitride of Nb. NbC becomes more important if nitrogen is combined with other more stable nitrides

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sting	Future work					
1)	Add sulfides and oxides into the model					
2)	Consider kinetic model (which depends on cooling rate and undercooling) to analyze the size distribution of the precipitates					
3)	Predict accelerated grain growth, especially at oscillation mark roots					
4)	Consider the relation between the tensile stress (or strain) and the grain size, and the influence of precipitates on the intergranular fracture (transverse cracks)					
	Ductility problem					



Prof B.G.Thomas Continuous Casting Consortium

Thank you for attendance!

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Kun Xu 29