ANNUAL REPORT 2005

Meeting date: June 1, 2005

Prediction of Nitride precipitation in Steel Making

Kun Xu* & Brian G. Thomas

*Ph. D. Student

Department of Mechanical & Industrial Engineering

University of Illinois at Urbana-Champaign

Introduction: Transverse cracks and location

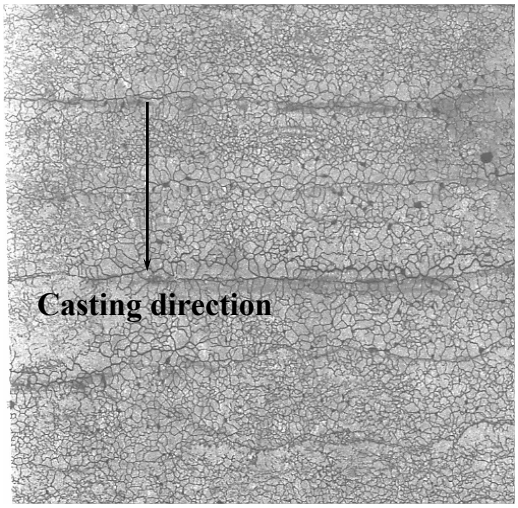
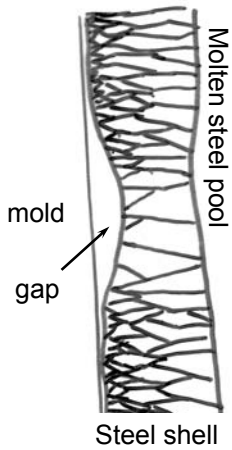


Figure 1. Widespread crazing and fine transverse cracks at oscillation marks on the as-cast surface of a line pipe steel slab (top side). Etched in hot HCl. (Note larger grains at base of oscillation marks.)

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



Larger grains beneath depressions & oscillation marks

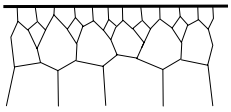
Due to:

* more heat flow resistance across gap
* higher shell temperature
* faster grain growth

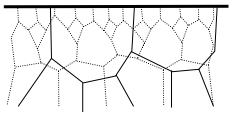
Causes:

* Tensile strain concentration area
* Make the hot grains actually align — "Secondary recrystallization"— "blown grains"
* Embrittled with large numbers of fine nitride precipitates accumulating at the weak grain boundaries —cracks open up along boundaries —transverse cracks

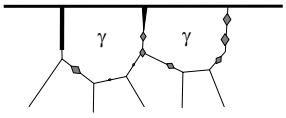
The formation of surface cracks & nitride embrittlement



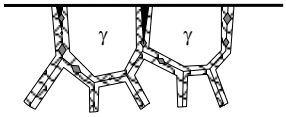
STAGE I - Normal solidification on mold wall. Surface grains are small but highly oriented.



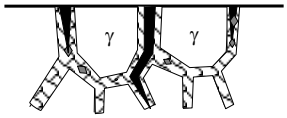
STAGE II - Surface grains "blow" locally due to high temperature (>1350°C) and strain, especially at the base of deeper oscillation marks.



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 micro-cracks grow & new ones form.



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.*

Relation between grain size and fracture

Increasing grain size decreases the strength and strain to fracture.

Hall-Petch equation

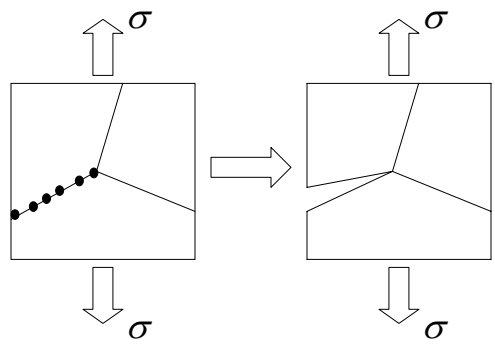
$$\sigma_y = \sigma_i + \frac{K}{\sqrt{d}}$$

σ_y : tensile yield stress

σ_i : 'intrinsic' yield stress

K : material constant

d : grain size



intergranular fracture

Cracks open up at weak grain boundaries

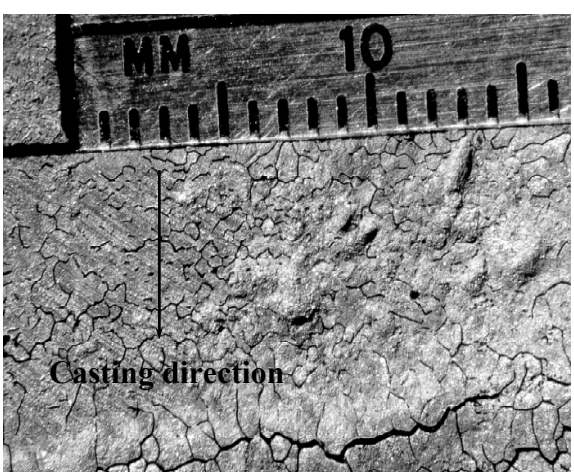


Figure 2. Crazing around a transverse crack at the base of an oscillation mark on the as-cast top surface of a 0.2C steel slab. Note the larger grain size at the the base of the oscillation mark.

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

Development and Role of Precipitation Model

CON1D —Temperature & Phase fraction

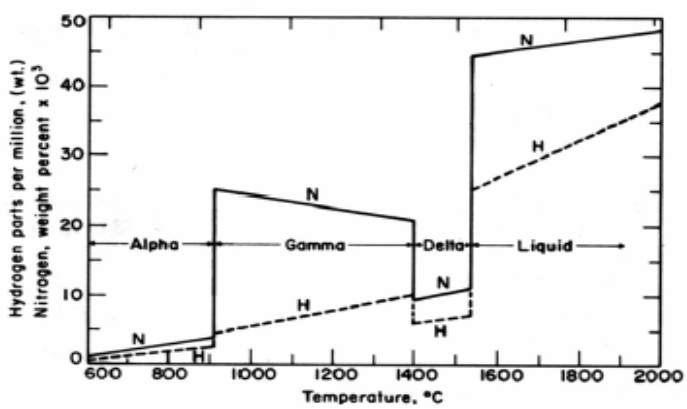
Precipitation model — Size distribution of precipitates

CON2D—Stress analysis

Final goal ⇨ Predict ductility and crack problems especially for transverse cracks

The present Model—Equilibrium content of dissolved elements and corresponding precipitates in different steels — this represents the maximum limit and driving force towards nucleation of the real amounts of precipitates considering the cooling rate

Solubility product of nitrogen in steel



Different phase has different crystal structures ⇨ Solubility product differs

Reference: *Effect of temperature on the solubility of Hydrogen and nitrogen at 1 atmosphere pressure in iron, Electric furnace steelmaking, Vol II, AIME, 1963.*

Definition of solubility products of nitride precipitations

$x[M]+y[N] \Leftrightarrow M_xN_y$ eg. $[Al]+[N] \Leftrightarrow AlN$

For low alloy steels, activity ~ concentration

Solubility product $K_{M_xN_y} = [wt\%M(x,t)]^x[wt\%N(x,t)]^y$

$$\log K_{M_xN_y} = \log[wt\%M(x,t)]^x[wt\%N(x,t)]^y = \frac{A}{T}+B$$

The precipitation takes place when

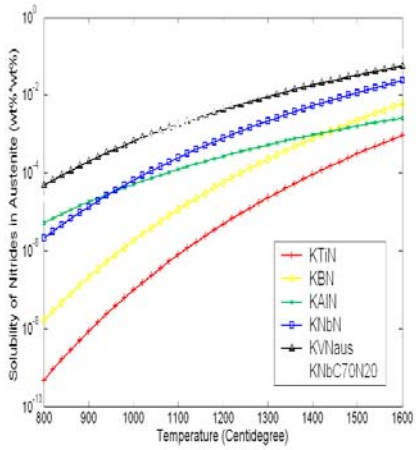
$$[wt\%M(x,t)]^x[wt\%N(x,t)]^y > K_{M_xN_y}$$

Values for the solubility products for nitrides

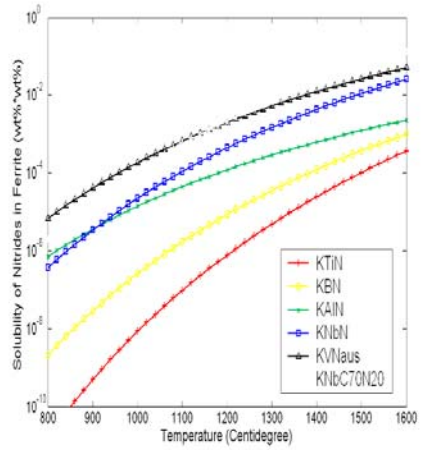
Solubility products	$\log K_\gamma$	$\log K_\alpha$	$\log K_l$
[%Al][%N]	$-\frac{6770}{T}+1.03$	$-\frac{8790}{T}+2.05$	$-\frac{12950}{T}+5.58$
[%B][%N]	$-\frac{13970}{T}+5.24$	$-\frac{14250}{T}+4.61$	$-\frac{10030}{T}+4.64$
[%Nb][%N]	$-\frac{10150}{T}+3.79$	$-\frac{12170}{T}+4.91$	
$[\%Nb][\%C]^{0.7}[\%N]^{0.2}$	$-\frac{9450}{T}+4.12$	$-\frac{12120}{T}+5.57$	
[%Ti][%N]	$-\frac{15790}{T}+5.40$	$-\frac{18420}{T}+6.40$	$-\frac{17040}{T}+6.40$
[%V][%N]	$-\frac{7700}{T}+2.86$	$-\frac{9720}{T}+3.90$	

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

Temperature dependence of the solubility products of nitrides



Austenite



Ferrite

The Solubility of AlN in Austenite

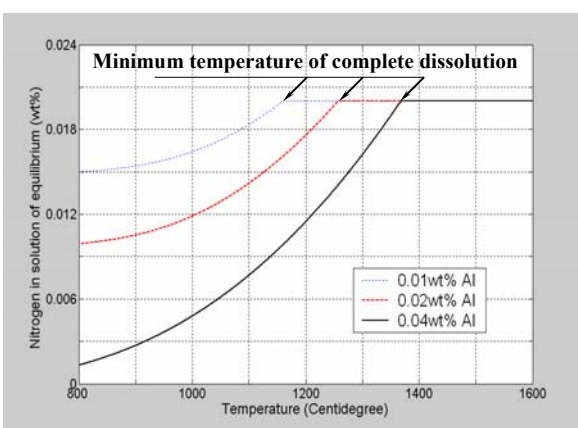


Figure 3. Effect of aluminum on solubility of nitrogen in austenite containing 0.02% nitrogen

The influence of adding different amounts of Titanium on AlN precipitation in Austenite

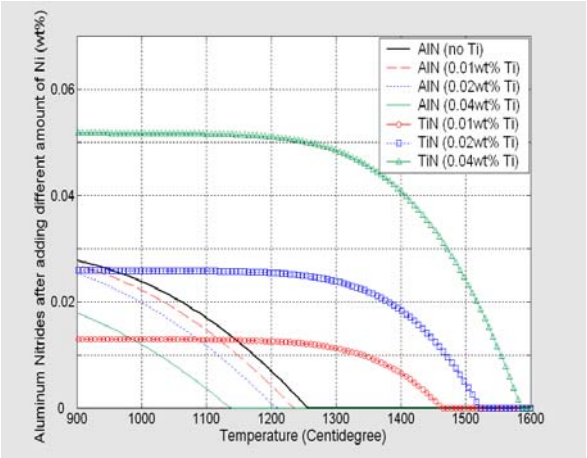


Figure 4. The influence of adding the different amount of Titanium on formation of AlN precipitate in austenite containing 0.02% nitrogen and 0.02% aluminum

The influence of adding different alloy elements on AlN precipitation in Austenite

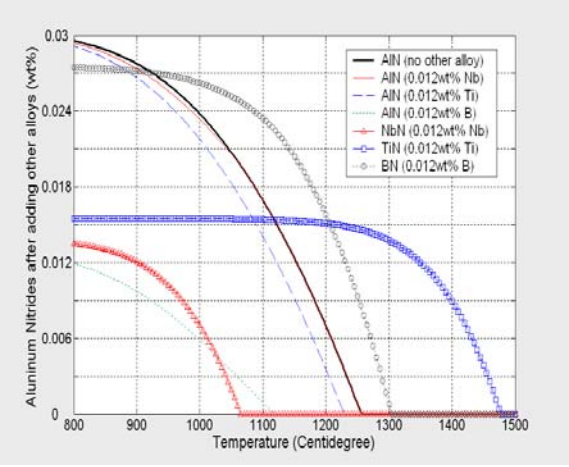


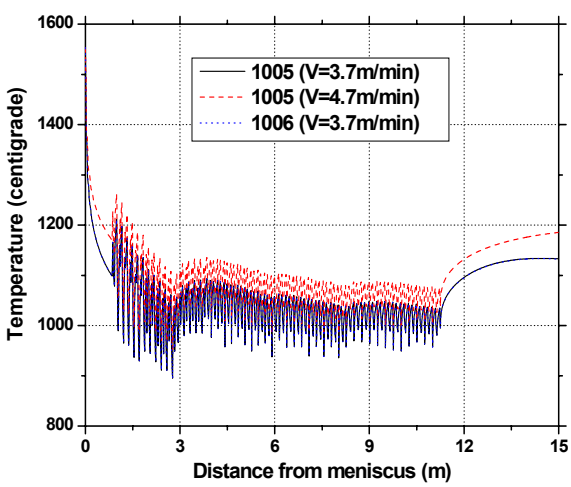
Figure 5. The influence of independently adding the same amount (0.012%) of three different alloy elements on the formation of AlN precipitates in austenite containing 0.02% nitrogen and 0.02% aluminum

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

Nitride precipitates TiN, BN, $NbC_{0.7}N_{0.2}$ will form

Temperature files from CON1D (Shell surface)

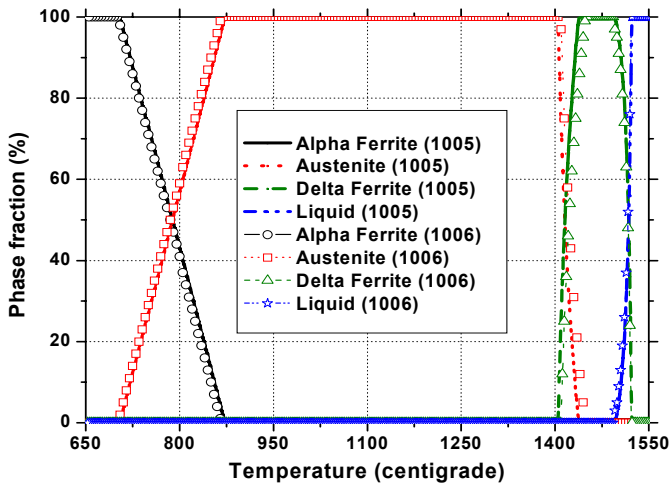


Mold length: 0.95m

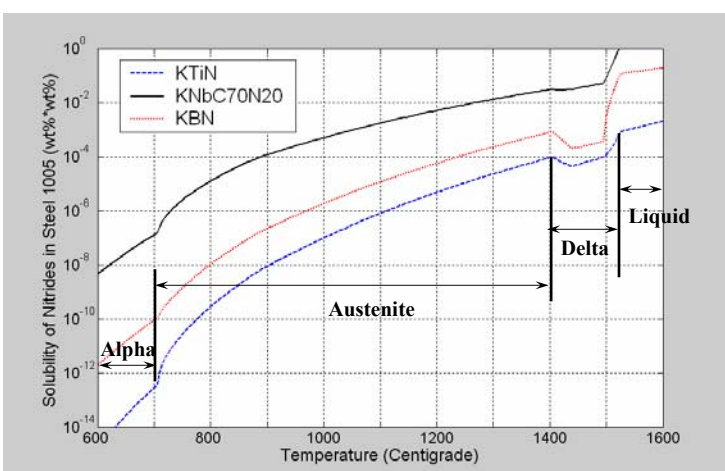
Start of first spray zone: 0.85m

End of last spray zone: 11.25m

Phase fraction files from CON1D

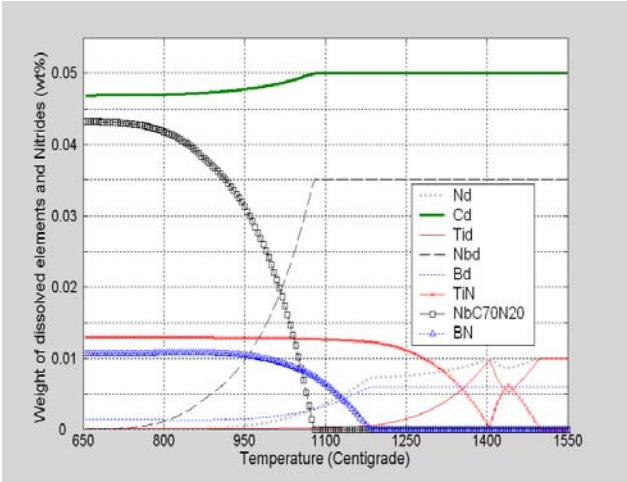


Solubility product of Steel 1005



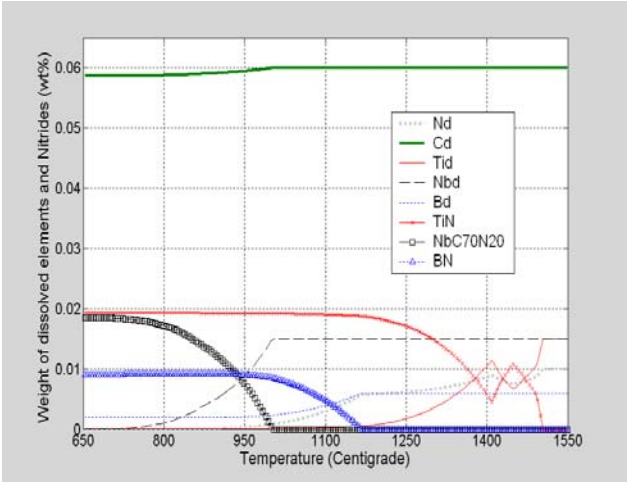
$$K(T) = f_{aus}(T)K_{aus}(T) + f_{fer}(T)K_{fer}(T) + f_{liq}(T)K_{liq}(T)$$

Precipitate Calculation for 1005 steel



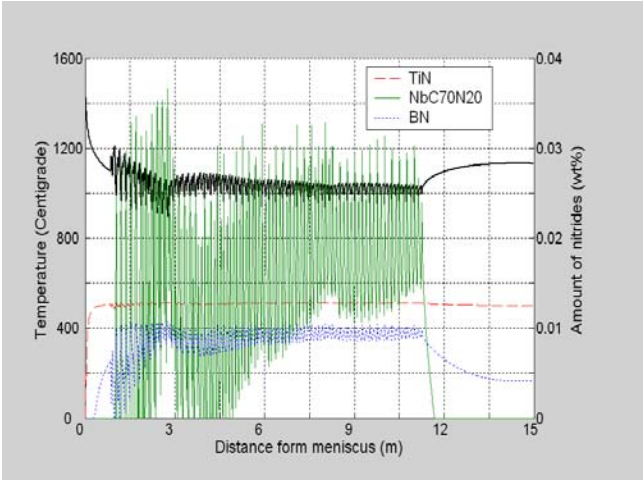
$$C_0 = 0.05; N_0 = 0.01; Ti_0 = 0.01; Nb_0 = 0.035; V_0 = 0.004; B_0 = 0.006$$

Precipitate Calculation for 1006 steel



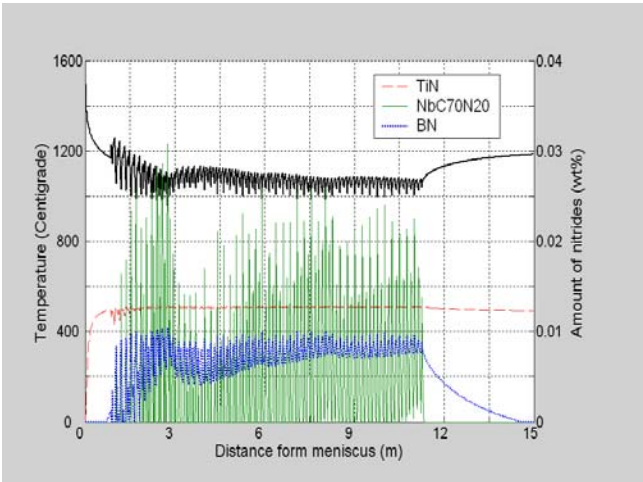
$$C_0 = 0.06; N_0 = 0.01; Ti_0 = 0.015; Nb_0 = 0.015; V_0 = 0.004; B_0 = 0.006$$

Precipitates for 1005 steel (3.7m/min)



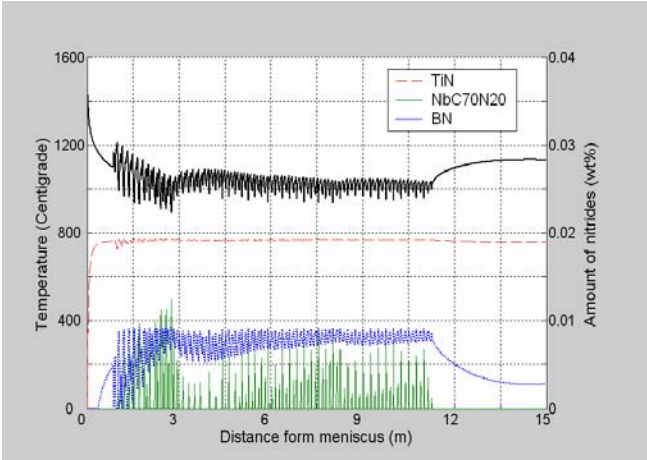
$$C_0 = 0.05; N_0 = 0.01; Ti_0 = 0.01; Nb_0 = 0.035; V_0 = 0.004; B_0 = 0.006$$

Precipitates for 1005 steel (4.7m/min)



$$C_0 = 0.05; N_0 = 0.01; Ti_0 = 0.01; Nb_0 = 0.035; V_0 = 0.004; B_0 = 0.006$$

Precipitates for 1006 steel (3.7m/min)



$$C_0 = 0.06; N_0 = 0.01; Ti_0 = 0.015; Nb_0 = 0.015; V_0 = 0.004; B_0 = 0.006$$

Conclusions

1) Very little nitride precipitates in the mold (just a few TiN)
2) Precipitate formation appears not to be a controlling factor in the susceptibility to cracks at oscillation mark roots: thus, the higher temperature there causes other phenomena (eg. accelerated grain growth or tensile strain concentration) leading to transverse cracks
3) Precipitation contributes to embrittlement in the spray zones prior to unbending:
4) Tremendous variation in nitride solubility occurs due to thermal cycling

Conclusions

5) Adding Ti combines with N to delay and lower other nitride precipitates because TiN has the least solubility product

6) Adding B combines with N to maybe heavily delay and lower Al, Nb nitride precipitates because B has the lowest atomic mass and the same amount of B consumes much more N

7) The $NbC_{0.7}N_{0.2}$ is very sensitive in the temperature range of the spray zones in our cases and needs to be considered carefully

Future work

1) Predict accelerated grain growth, especially at oscillation mark roots
2) Consider kinetic model (which depends on cooling rate and undercooling) to analyze the size distribution of the precipitates
3) 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

Acknowledge

Prof B.G.Thomas

CCC group

Thank you for attendance!