Coupled solute drag and transformation stasis during ferrite formation from austenite

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(Materials Science & Engineering, McMaster University)

We will consider 2 issues

MONASH University

<u>Can we ever hope to predict ferrite growth in Fe-C-X-Y-Z (ie. real industrial steels)</u>

Lots and lots of work on idealised Fe-C-X steels used to ‘fit’ solute drag parameters (e.g. E_b and D^{trans})

Is there any extrapolative capacity of these Fe-C-X models to real steels?

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What is the explanation for transformation stasis?

Existing solute drag based explanations for stasis have a number of issues

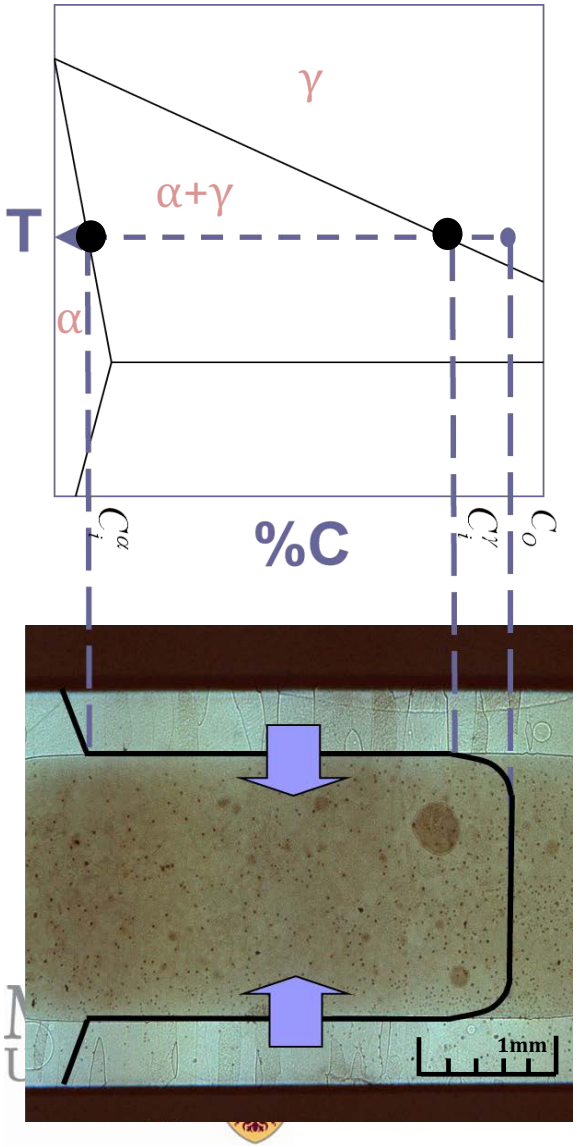
e.g. experimental measurements of negligible solute segregation (e.g. Furuhara) or our best estimated of SD magnitudes.

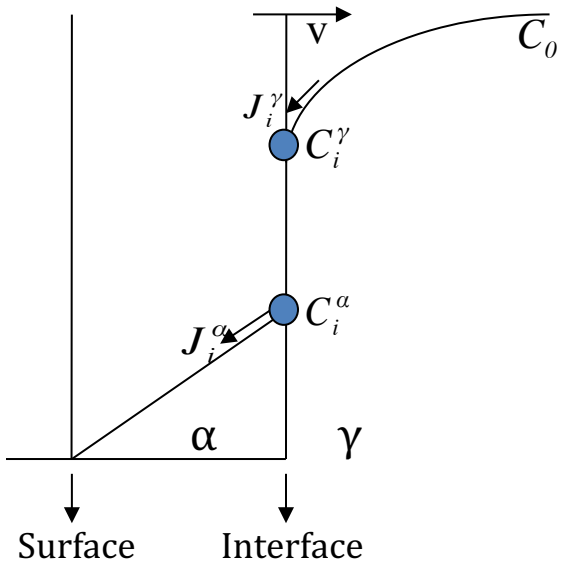
But other explanations (e.g. T_o) also have their issues

Can we find a more satisfactory explanation?

McMaster University

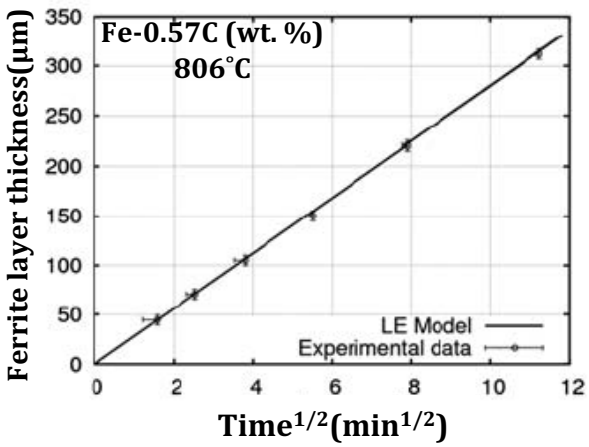
Ferrite Growth Kinetics using Decarburization





$$v_t = \frac{J_i^\alpha - J_i^\gamma}{C_i^\gamma - C_i^\alpha}$$

Local equilibrium assumption

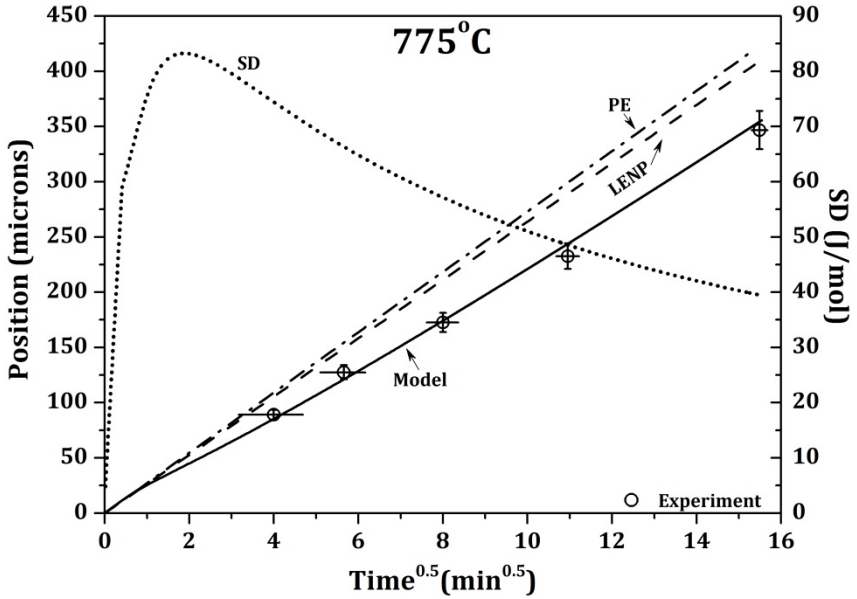


- Decarburization generates high quality data for model comparison
- The interface is stabilised to the simple planar geometry

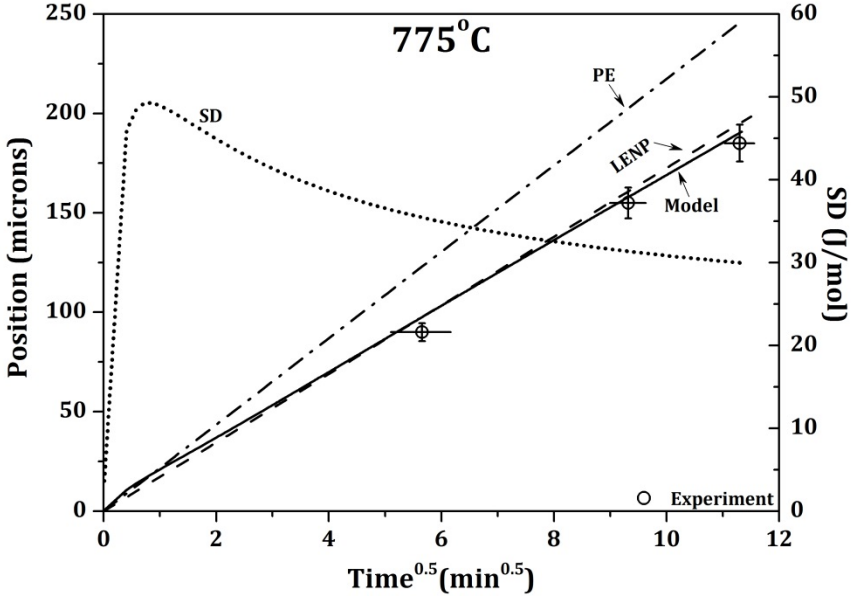
Béché A, Zurob HS, Hutchinson CR. MMTA 2007;38A:2950-55

Fe-C-Mn and Fe-C-Si ternary systems

Fe-0.76C-0.84Si (wt. %)



Fe-0.57C-0.94Mn (wt. %)

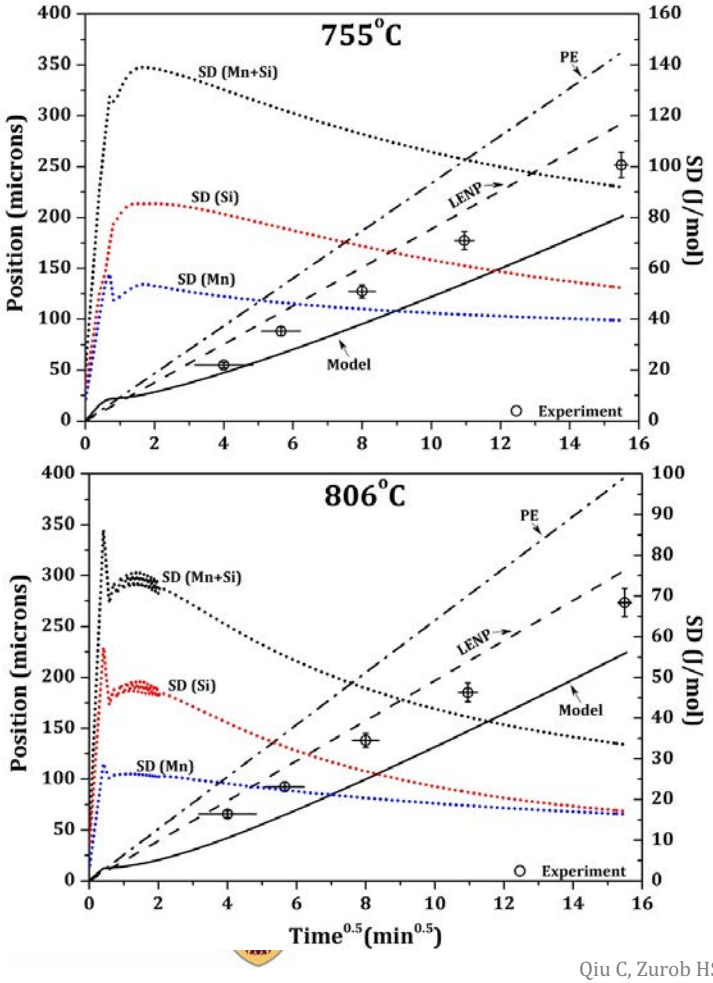


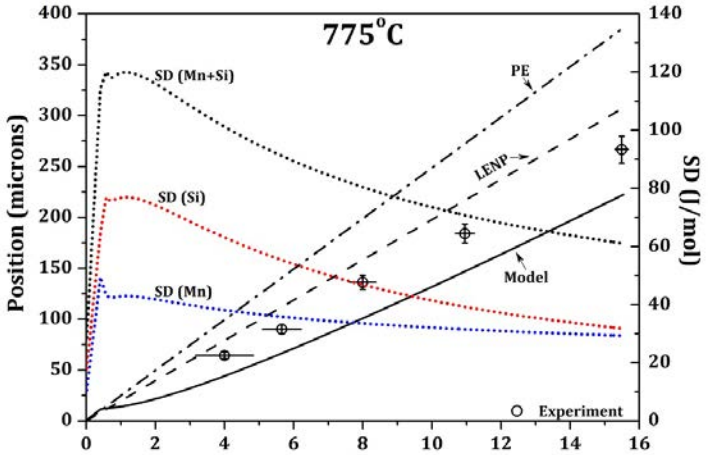
Fe-C-Mn and Fe-C-Si ternary planar ferrite growth can be quantitatively described as a function of temperature and Mn/Si content **(E_b: Si=-9kJ/mol, Mn=-2.5kJ/mol)** using trans-interface mass transfer constants closely related to the bulk diffusivities

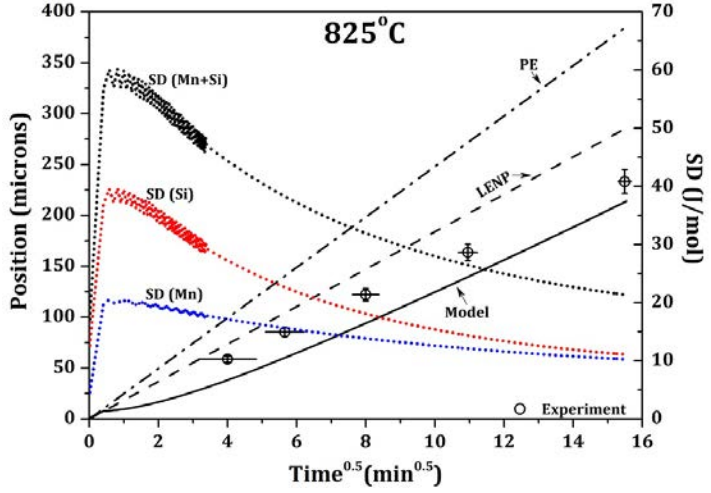
C Qiu, HS Zurob, D Panahi, Y Brechet, GR Purdy, CR Hutchinson, *MMTA*, 44, pp. 3472-3483, 2013
HS Zurob, D Panahi, CR Hutchinson, Y Brechet, GR Purdy, *MMTA*, 44, pp. 3456-3471, 2013.

But what about *predicting* Fe-C-Mn-Si?

Using the SD parameters calibrated on the Fe-C-Mn and Fe-C-Si systems, the predicted planar ferrite growth in Fe-C-Mn-Si is slower than experiments







Fe-0.66C
-1.06Mn
-0.92Si
(wt. %)

Qiu C, Zurob HS, Hutchinson CR. Acta mater, 2015, 100, pp. 333-343

Fe-C-Mn-Si – possible explanations

- SD theory may have some issues
- Thermodynamics of the interface in the quaternary system may be fundamentally different to the interface in the ternary systems
- Carbon may play a very important role (Enomoto, Acta 1999). Si has a strongly repulsive interaction with carbon and Mn is attractive.
- Perhaps there is a competition for segregation sites for the Mn and Si in the interface (this exists in Surface Science).

Experimental Design - Fe-C-Mn-Mo

Fe-0.42C-0.42Mo-0.49Mn (wt. %)
Fe-0.34C-0.42Mo-0.79Mn
Fe-0.49C-0.42Mo-1.09Mn
Fe-0.48C-0.43Mo-1.33Mn

Decarburized in wet H2 at 755C, 775C and 806C

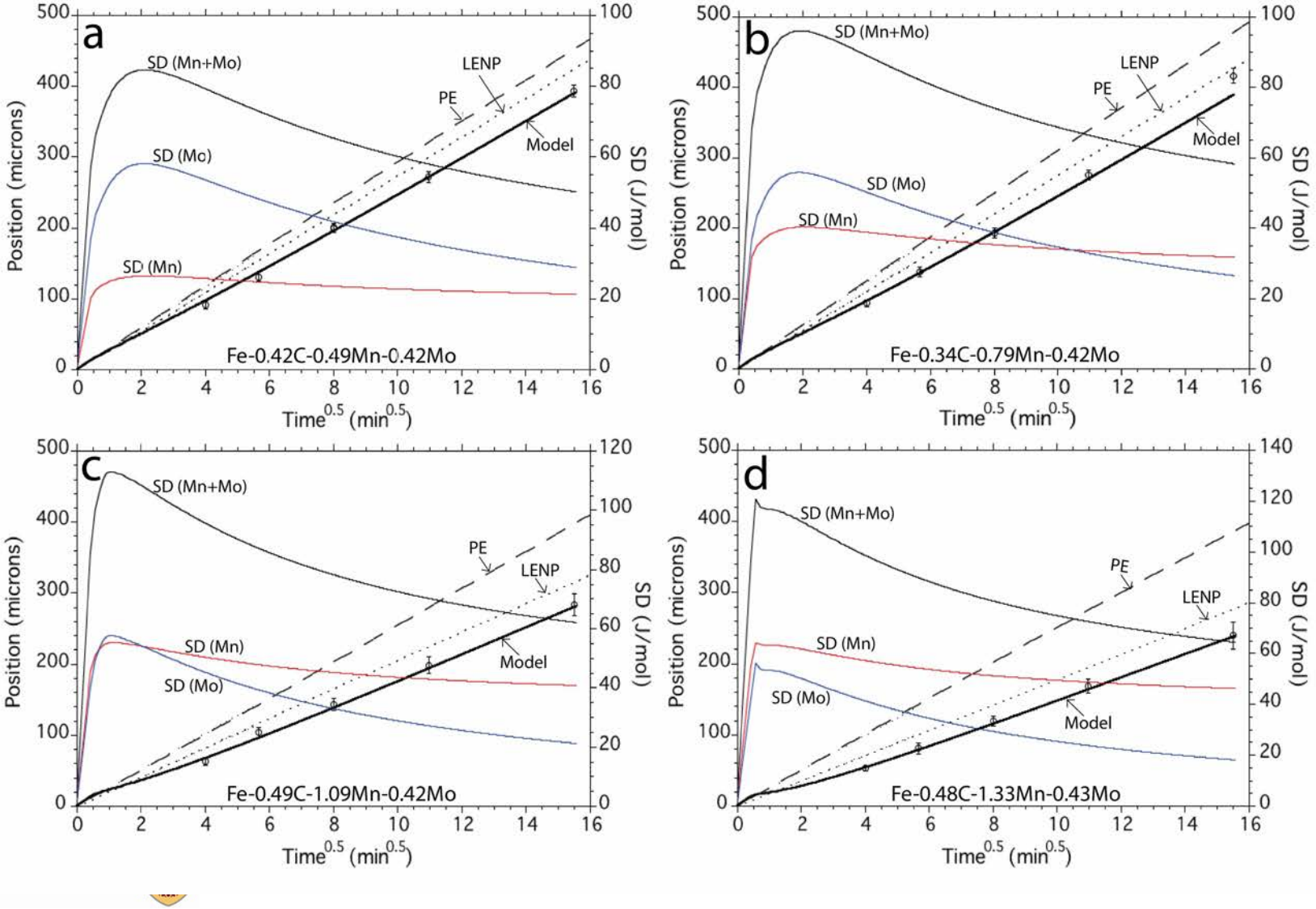
Constant Mo content and increasing Mn content

Possible Carbon effect: Mo and Mn both have an attractive interaction with carbon

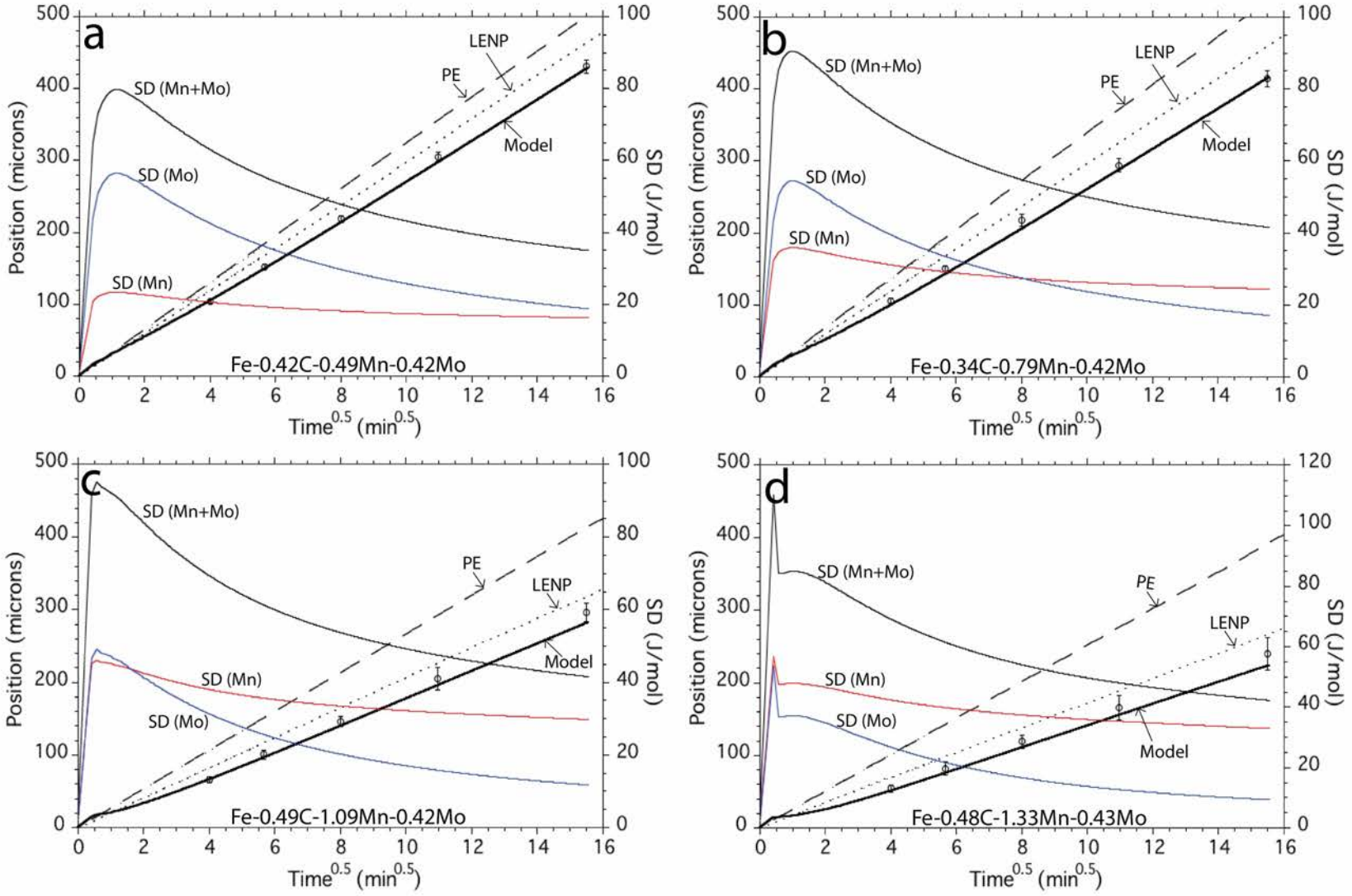
Possible Competition for sites: increasing Mn content corresponds to increasing Mn concentration

From ternary systems: E_b: Mn -2.5kJ/mol, Mo -15kJ/mol, $D^{trans}=(D_\alpha D_\gamma)^{1/2}$

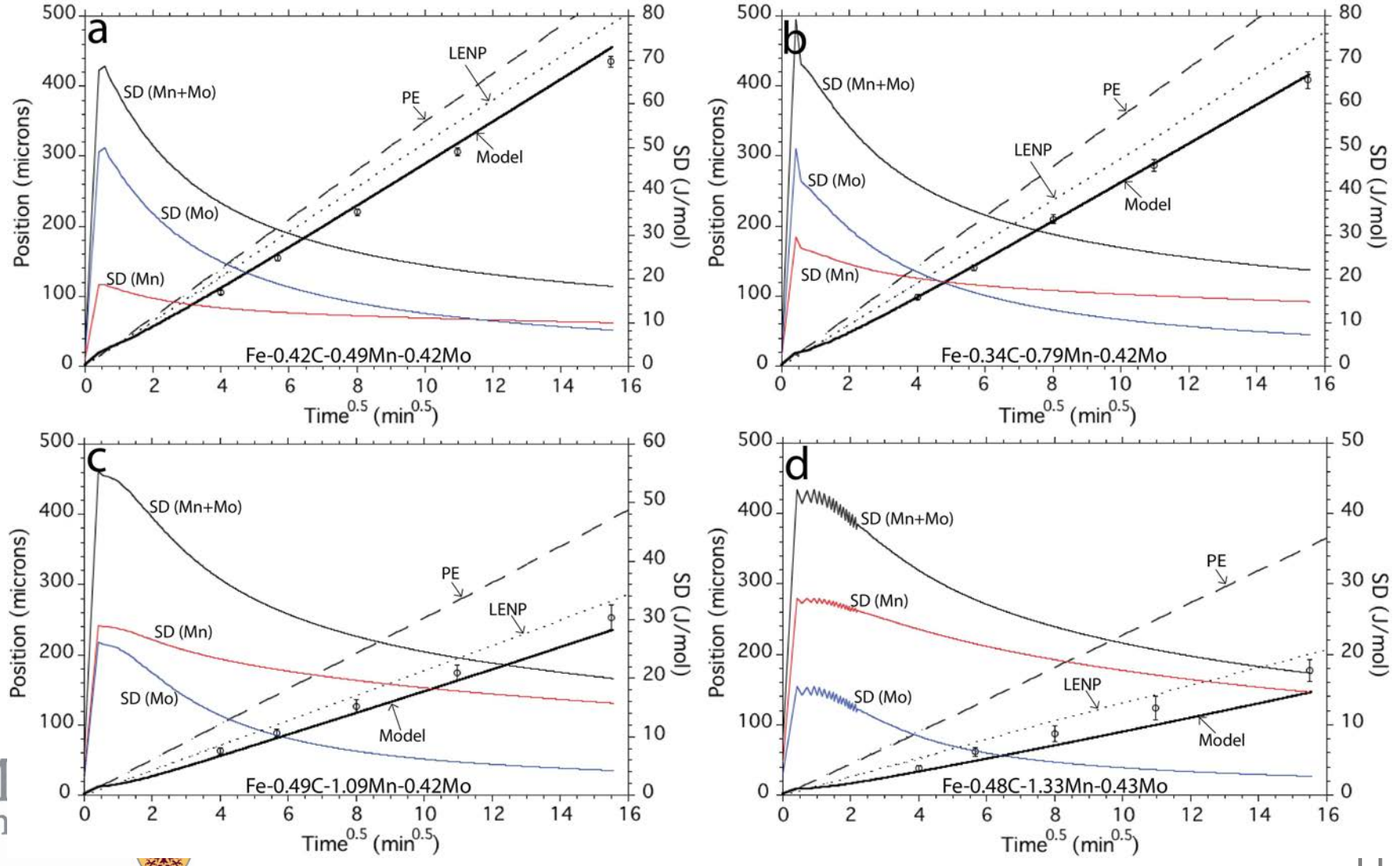
Results: Fe-C-Mn-Mo – 755C



Results: Fe-C-Mn-Mo – 775C



Results: Fe-C-Mn-Mo – 806C



Can we predict ferrite growth in real steels?

MONASH University

At the temperatures and solute contents probed in these experiments, we can predict the kinetics of ferrite growth in the Fe-C-Mn-Mo system, from SD parameters tuned on the Fe-C-Mn and Fe-C-Mo ternary systems.

Perhaps we can be optimistic about describing ferrite growth kinetics in multi-component alloys based on work in the ternary systems.

Likely, the disagreement in the Fe-C-Mn-Si system is because of the important role of carbon segregation to the interface (and its effect on Si segregation tendency).

We need to be careful in systems where the substitutional elements have opposite interactions with carbon.

McMaster University

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Is there any extrapolative capacity of these Fe-C-X models to real steels?

What is the explanation for transformation stasis?

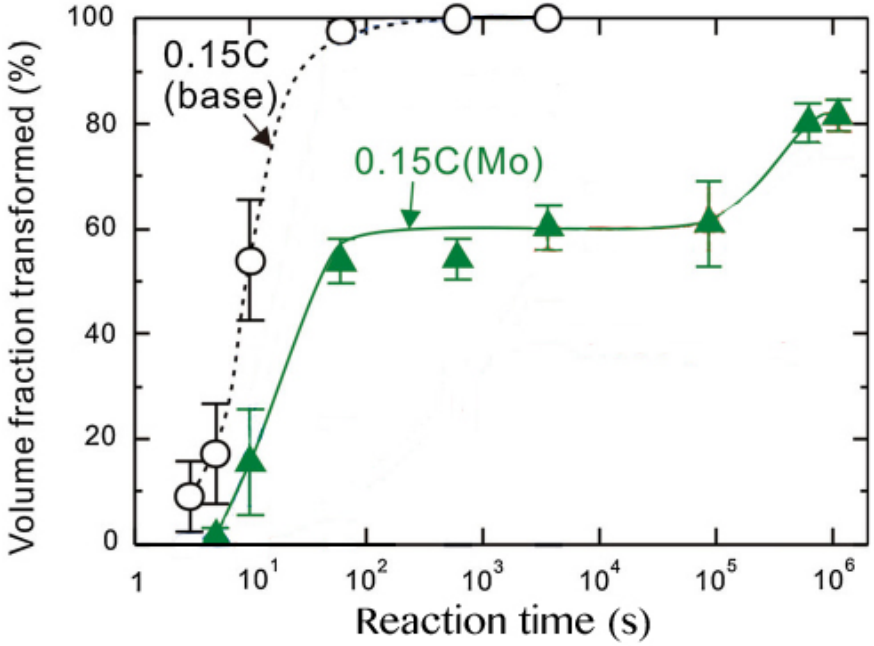
Existing solute drag based explanations (e.g. H. Chen) have a number of issues and are not consistent with experimental measurements of negligible solute segregation (e.g. Furuhara) or our best estimated of SD magnitudes

But other explanations (e.g. T_o) also have their issues

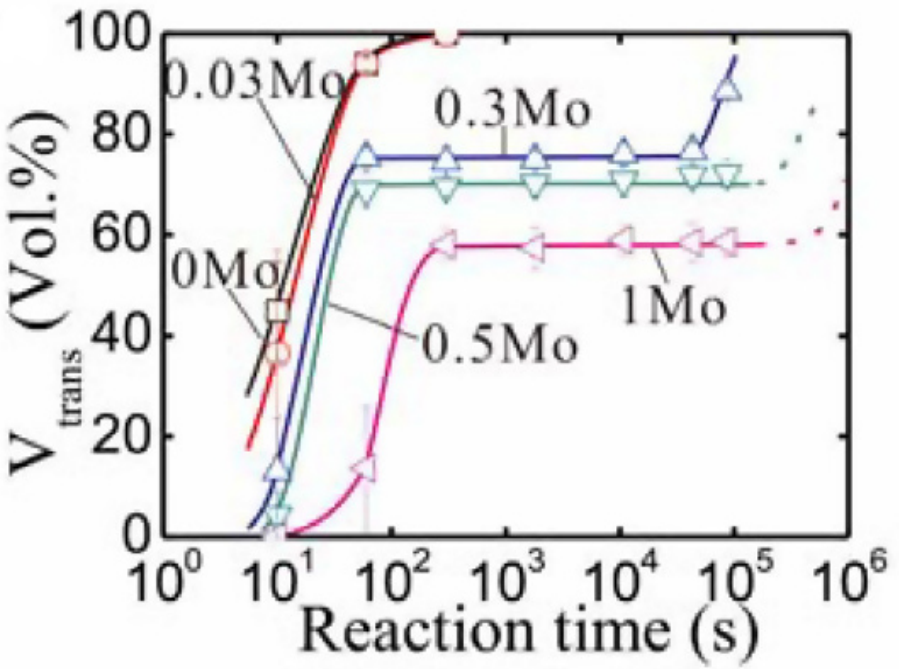
Can we find a more satisfactory explanation?

Consider transformation stasis in Fe-C-Mn-Mo

Furuhara, MMTA 2014
Fe-0.15C-1.5Mn-(0.5Mo) @ 550C



Xia, Acta 2015
Fe-0.12C-1.5Mn-(xMo) @ 550C



Classic diffusional explanation – solute drag

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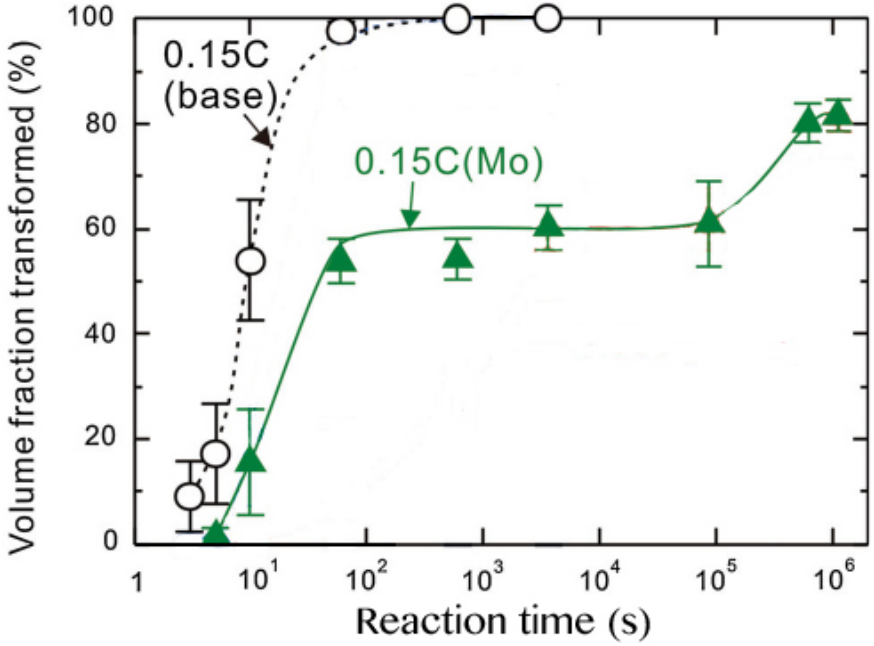
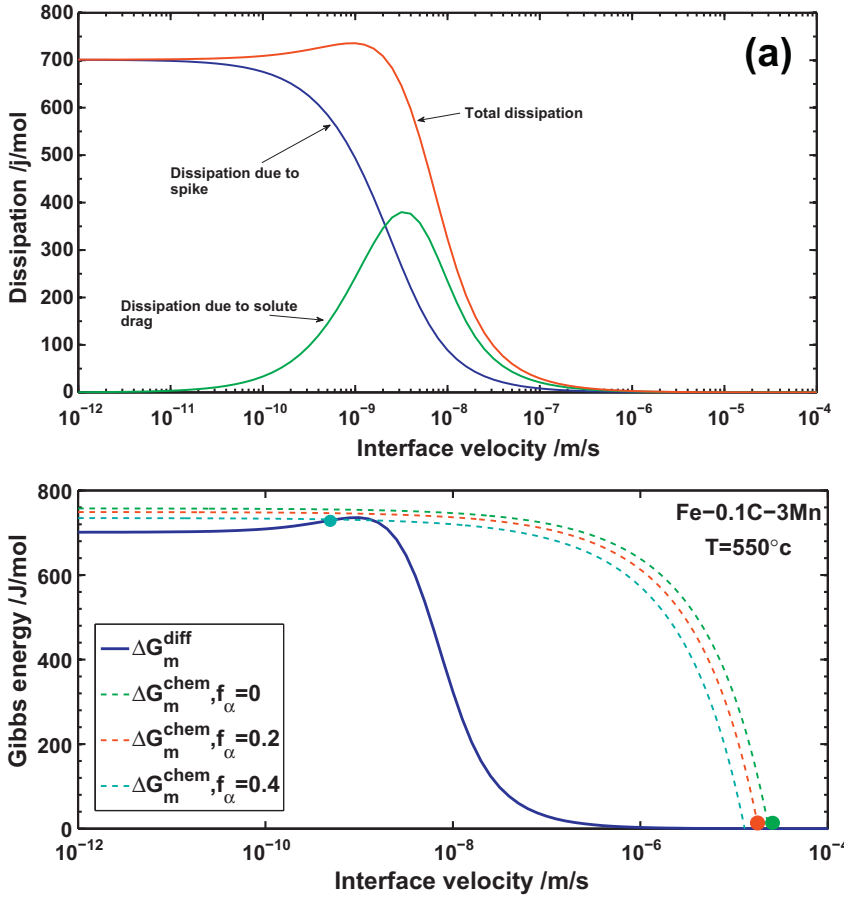


Chen, Zhu, Zhao, van der Zwaag, Acta 2013



Permissible velocities are those where $G^{chem}=G^{diss}$
This is true of all models (incl. Odqvist *et al*, Zurob *et al*) that include solute drag

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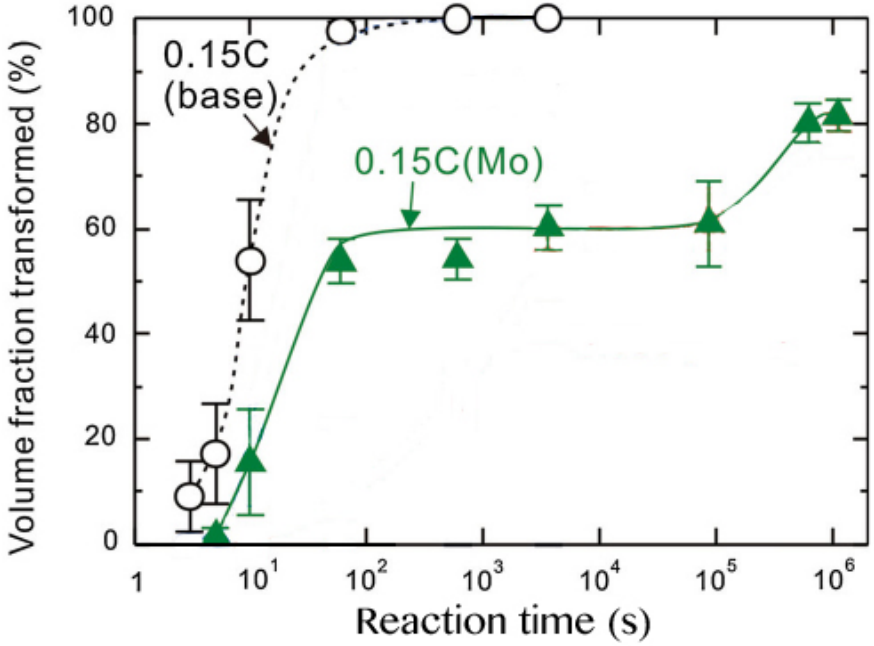

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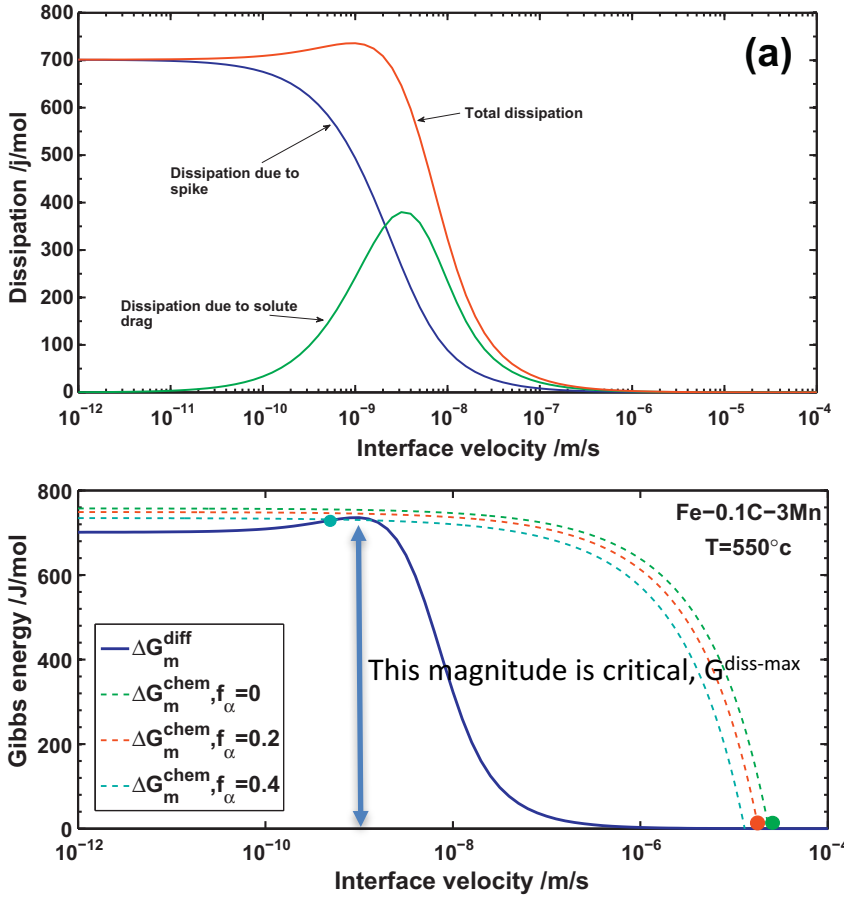

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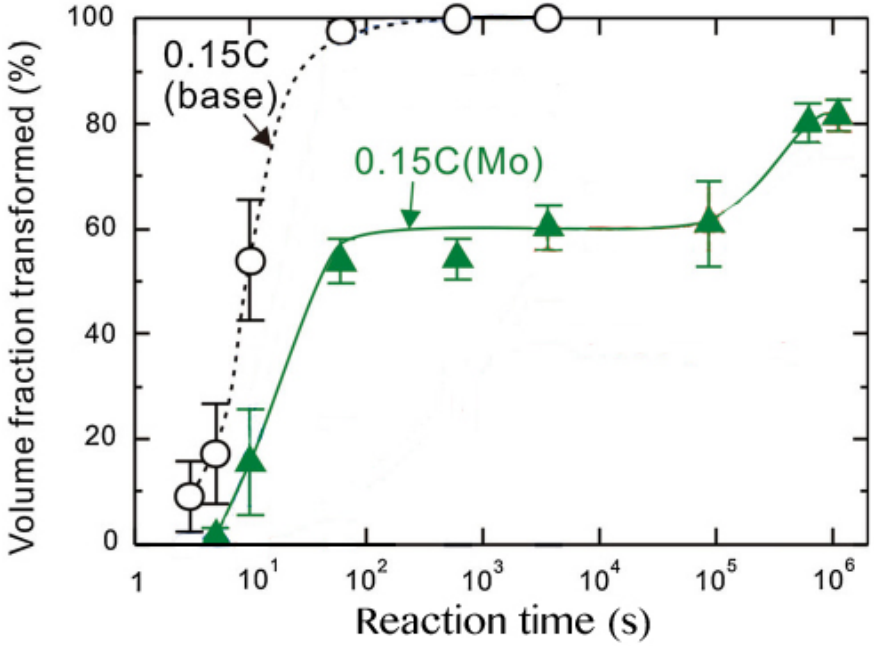

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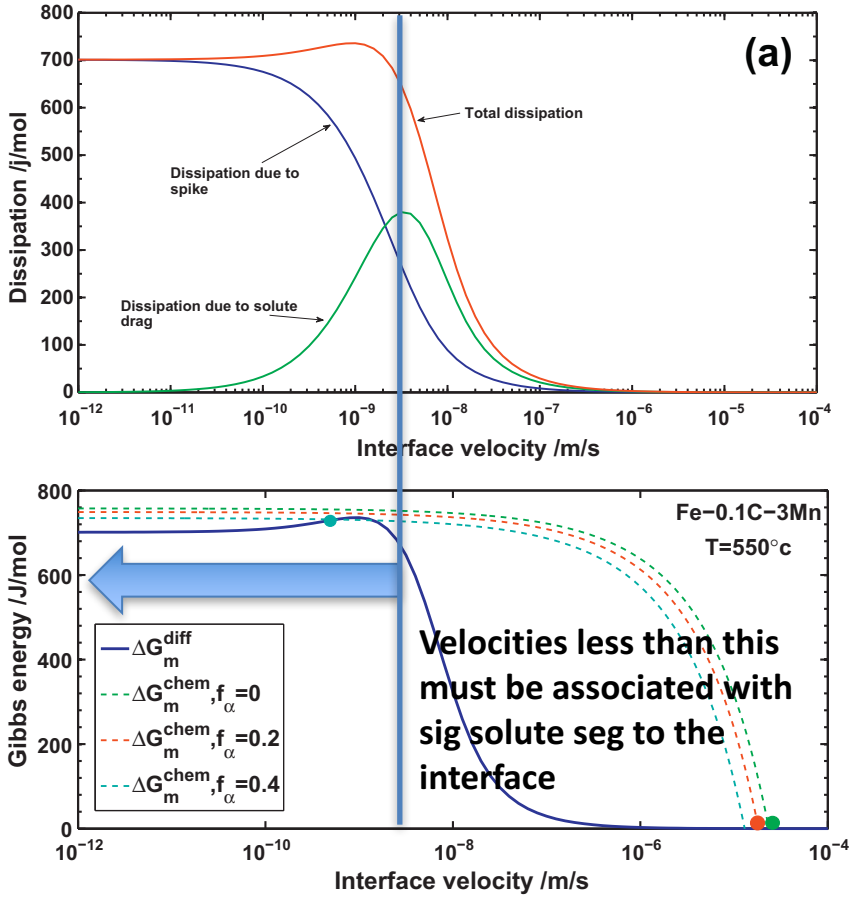

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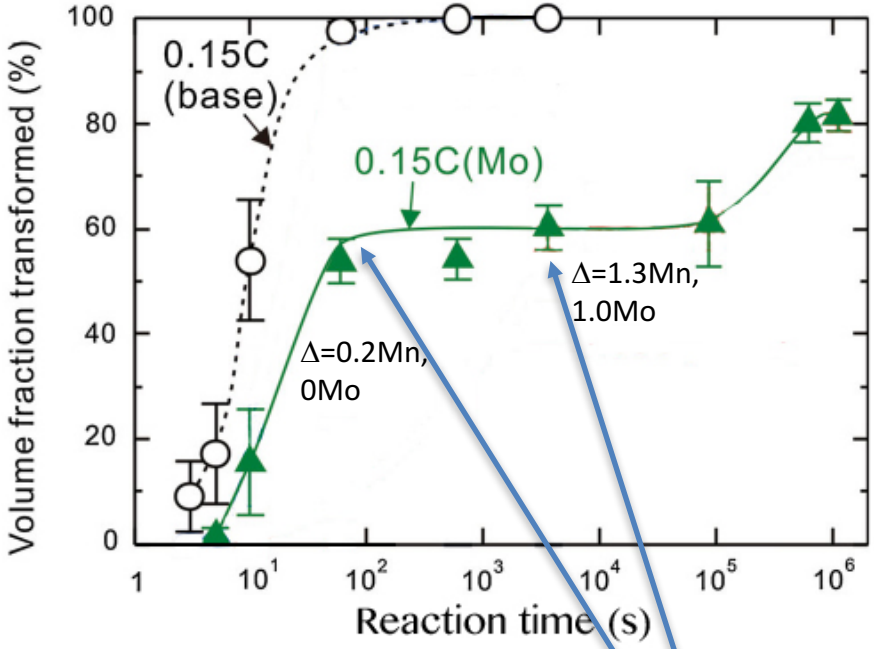

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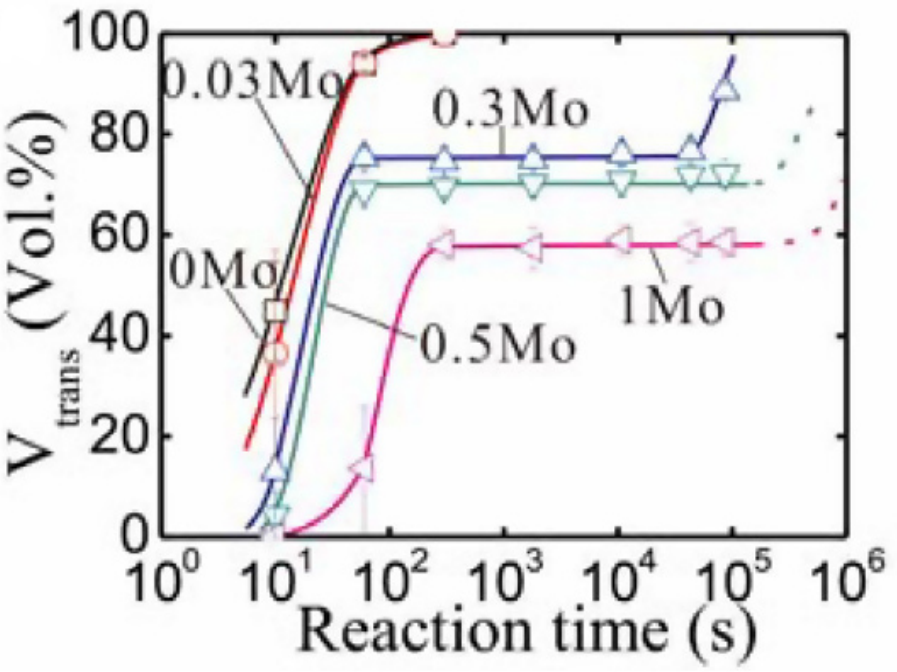
Fe-0.12C-1.5Mn-(xMo) @ 550C

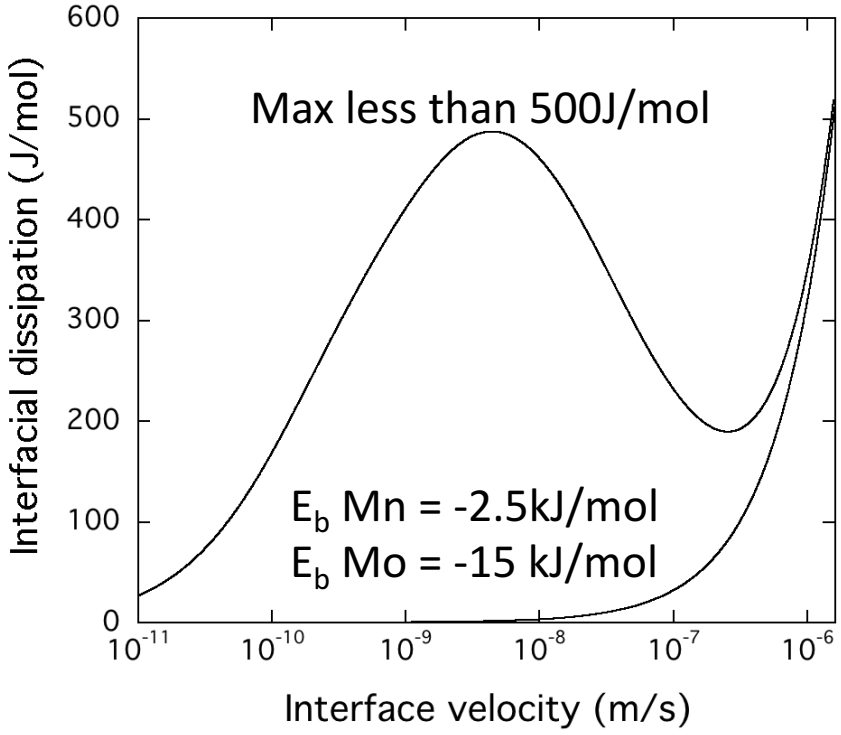


Furuhara prepared FIB-TEM samples from the interface and measured the interfacial segregation.

Sig segregation does not coincide with onset of stasis

But there are problems with the classic solute drag explanation for stasis…..

Calculated dissipation curve for
Fe-0.12C-1.5Mn-0.5Mo @ 550C



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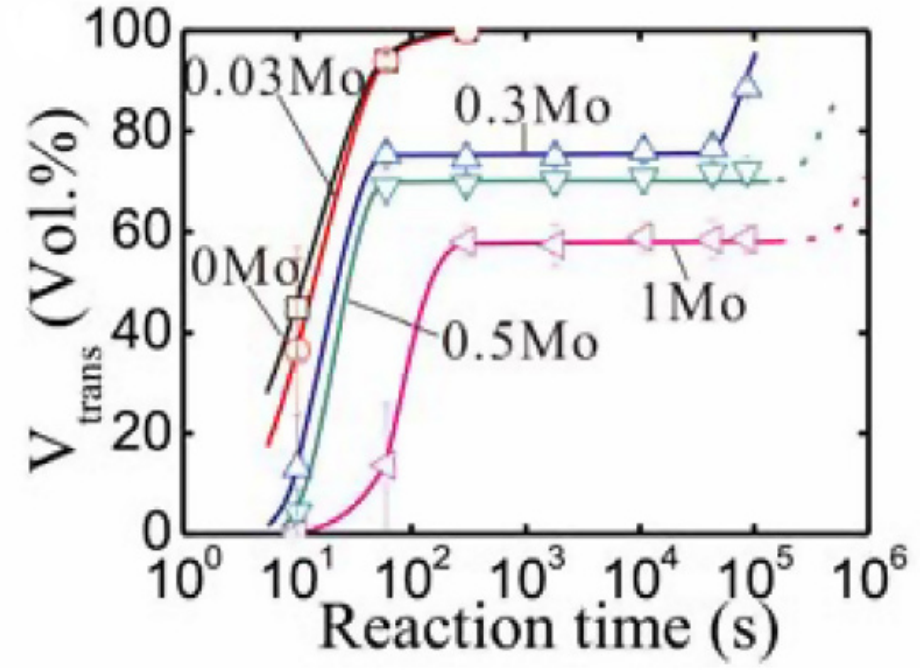

From Xia et al. for the 0.5Mo alloy at 550C, a G^{diss} of **850 J/mol** is required for stasis

Neither is the magnitude of the dissipation sufficient

But there are problems with the classic solute drag explanation for stasis…..

1. The levels of segregation to the interface corresponding to the maximum in the SD curve required for stasis are not seen experimentally. Indeed, Furuhara measures almost no segregation at the onset of stasis.

2. As we get more and more confident with the relevant binding energies, we are finding that the magnitudes of the SD are not large enough either to explain stasis.

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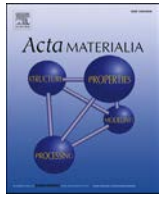

Full length article

Incomplete bainite transformation in Fe-Si-C alloys

H.-D. Wu [a, *], G. Miyamoto [b], Z.-G. Yang [a], C. Zhang [a], H. Chen [a], T. Furuhara [b]

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ABSTRACT

Bainite isothermal transformation kinetics for Fe-(1.5% and 3%)Si-0.4%C alloys (mass%) was investigated at 400–500 °C and incomplete transformation phenomenon (ICT) of bainite transformation was observed at 450 °C for the 3Si alloy and at 400 °C for the two alloys. Unlike to the ordinary ICT reported in other alloy systems, cementite precipitation with Si partitioning took place from the beginning of ICT. Carbon enrichment in austenite during ICT was measured by three-dimensional atom probe and was found to be higher than T_0 or T_0' prediction while significantly deviates from NPLE limits and PE predictions to lower carbon content. Theories for bainite transformation, such as T_0 limit, solute drag and WB_s limit, were examined based on the experimentally measured carbon content in austenite during ICT. T_0' limit theory is difficult to rationalize the much larger measured carbon content than T_0' prediction. In addition to solute drag effect and spike development in the NPLE mode, solute drag theory should incorporate dissipations caused by other sources in order to account for the estimated 1250–1700 J/mol deviation from PE predictions. In addition, WB_s limit theory gives good descriptions on the carbon enrichment in austenite during ICT stage.

But there are problems with the classic solute drag explanation for stasis…..

1. The levels of segregation to the interface corresponding to the maximum in the SD curve required for stasis are not seen experimentally. Indeed, Furuhara measures almost no segregation at the onset of stasis.

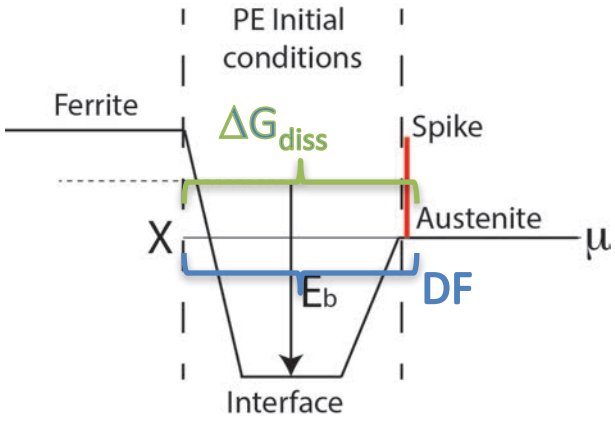
2. As we get more and more confident with the relevant binding energies, we are finding that the magnitudes of the SD are not large enough to explain stasis.

We need a new explanation more consistent with experimental results

Zurob et al. model for ferrite formation

Application to ferrite formation from austenite in Fe-C-X – Odqvist-Zurob model

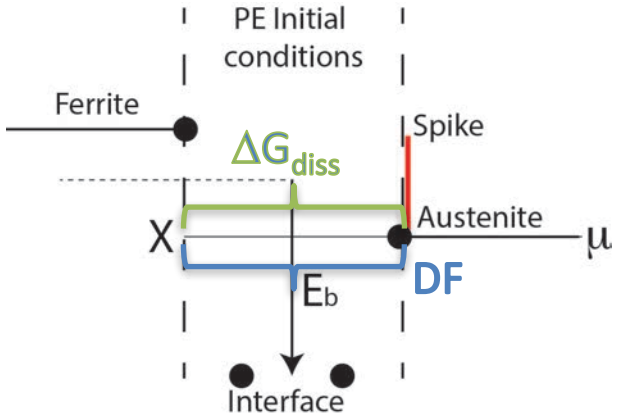
Odqvist et al. (2002)



$$\Delta G_{diss} = -\int_{-\infty}^{+\infty} (U_X - U_X^o)\frac{d(\mu_X - \mu_{Fe})}{dx}dx$$

$$D^t = D_{gb}$$

Zurob et al. (2013)



$$\Delta G_{diss} = \sum_{i=1}^{3} -\frac{V_m}{v} J_X^i \begin{bmatrix} (\mu_X^i - \mu_X^{i-1}) \\ -(\mu_{Fe}^i - \mu_{Fe}^{i-1}) \end{bmatrix}$$

$$D^t = \sqrt{D_\gamma\, D_\alpha}$$

Odqvist and Zurob interface models differ only in details and give the same results for the interface conditions, when using the same parameters

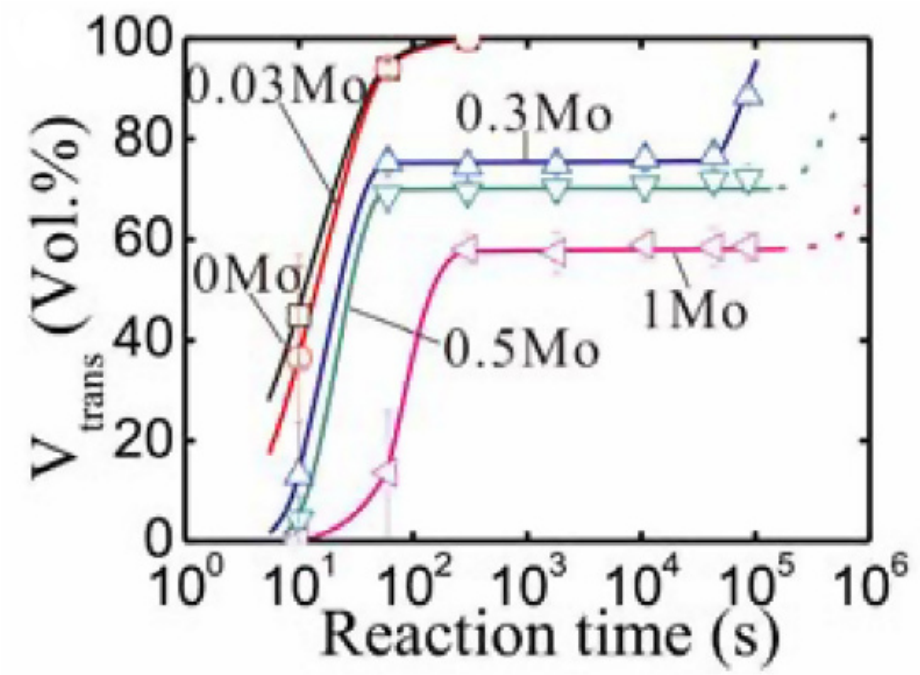
Zurob et al. model for ferrite formation

However, the Zurob et al model does differ from the Chen et al. and Odqvist et al. models in a key way – it is **fully coupled** to the carbon profiles in austenite and ferrite and their evolution during phase transformations.

HS Zurob, D Panahi, CR Hutchinson, Y Brechet, GR Purdy, "Self-Consistent Model for Planar Ferrite Growth in Fe-C-X Alloys", *Metallurgical Transactions A*, 44, pp. 3456-3471, 2013.

Ferrite formation in Fe-0.12C-1.5Mn-0.5Mo

Xia, Acta 2015
Fe-0.12C-1.5Mn-(xMo) @ 550C



Calculated dissipation curve for
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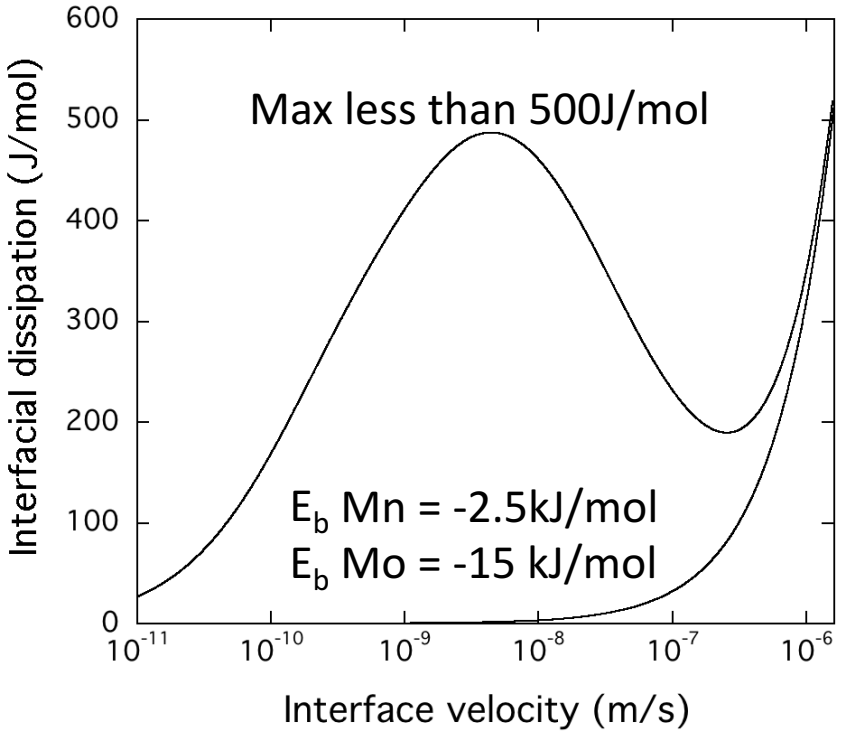

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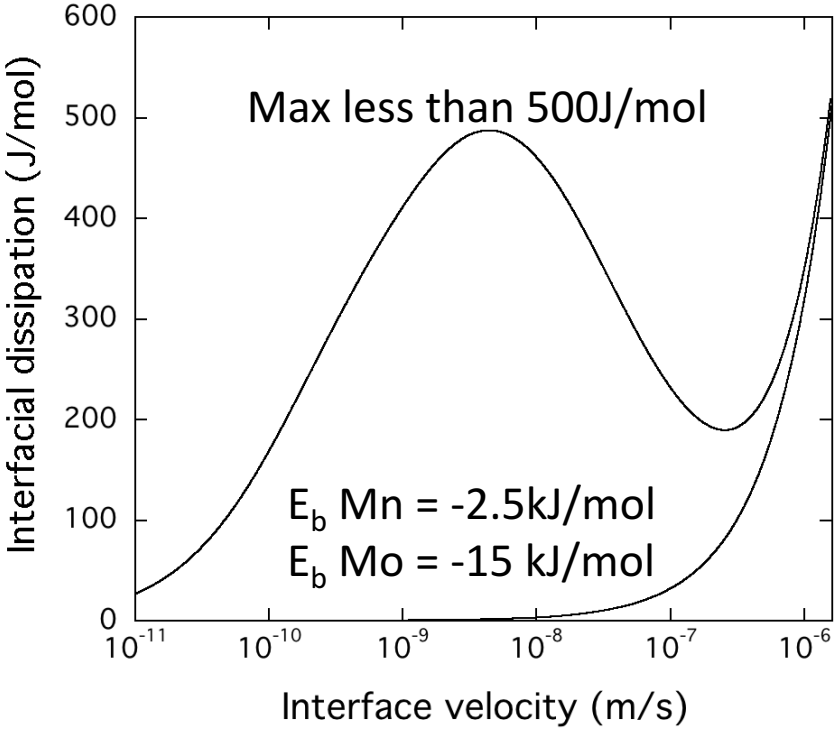
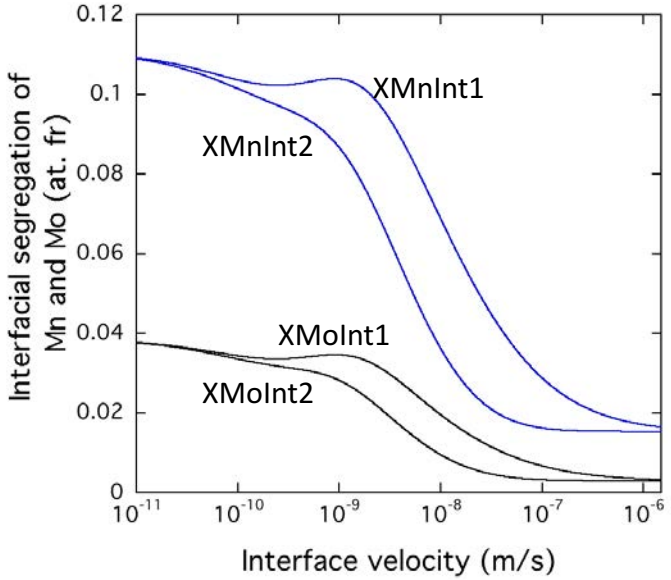
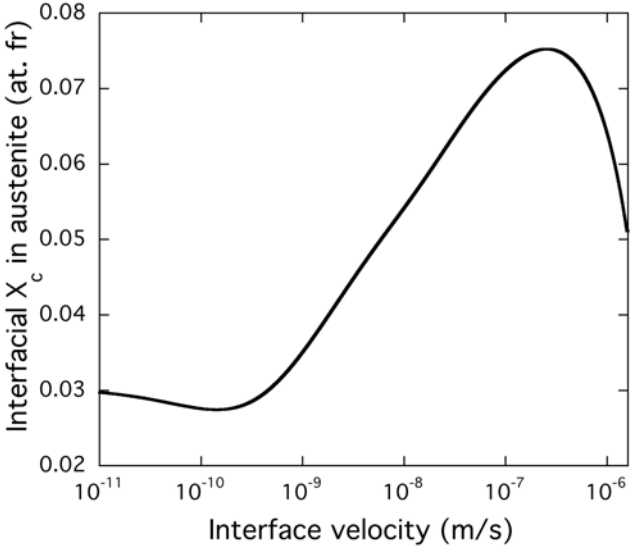


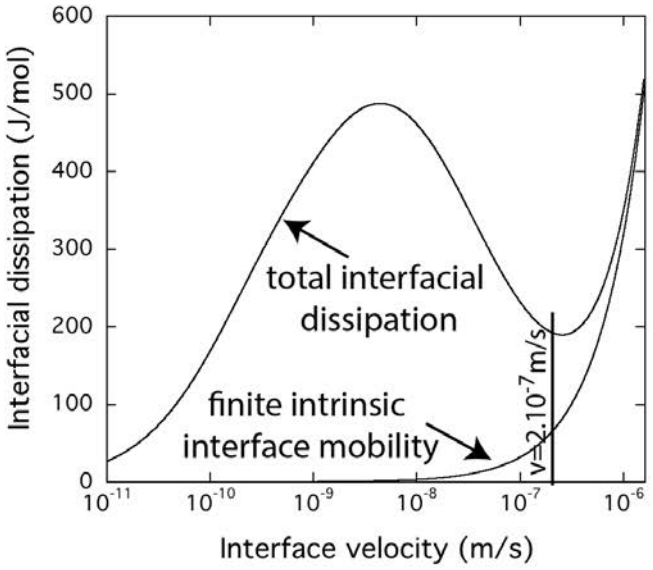


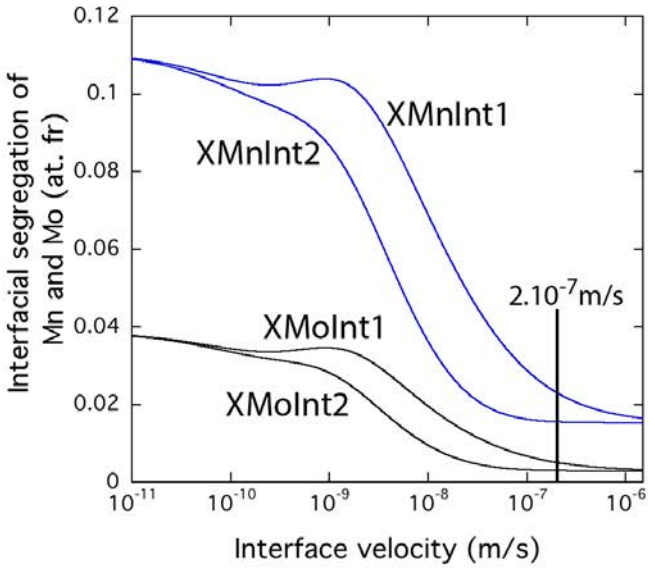


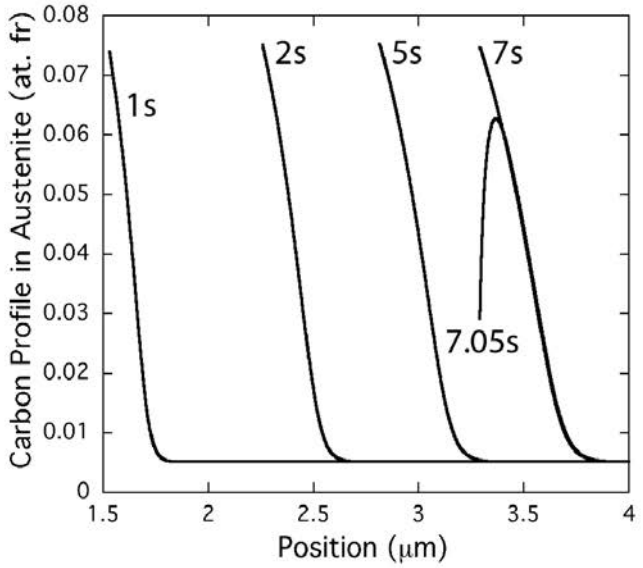
Ferrite formation in Fe-0.12C-1.5Mn-0.5Mo

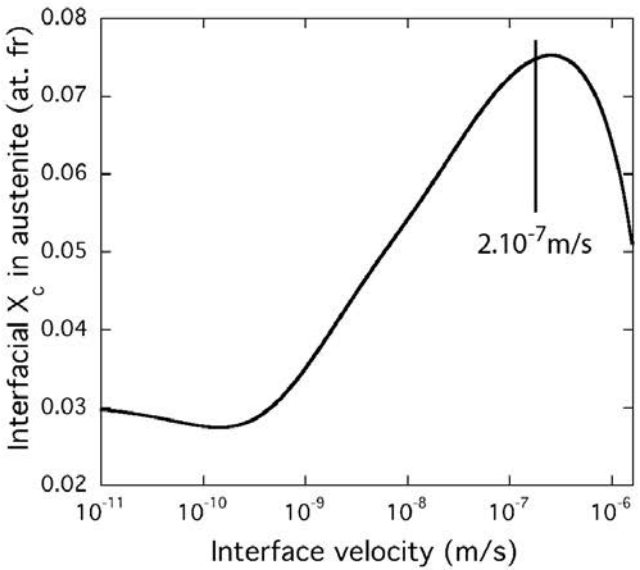
Fe-0.12C-1.5Mn-0.5Mo
@ 550C

Full kinetic calculation
Planar geometry,
10μm GS





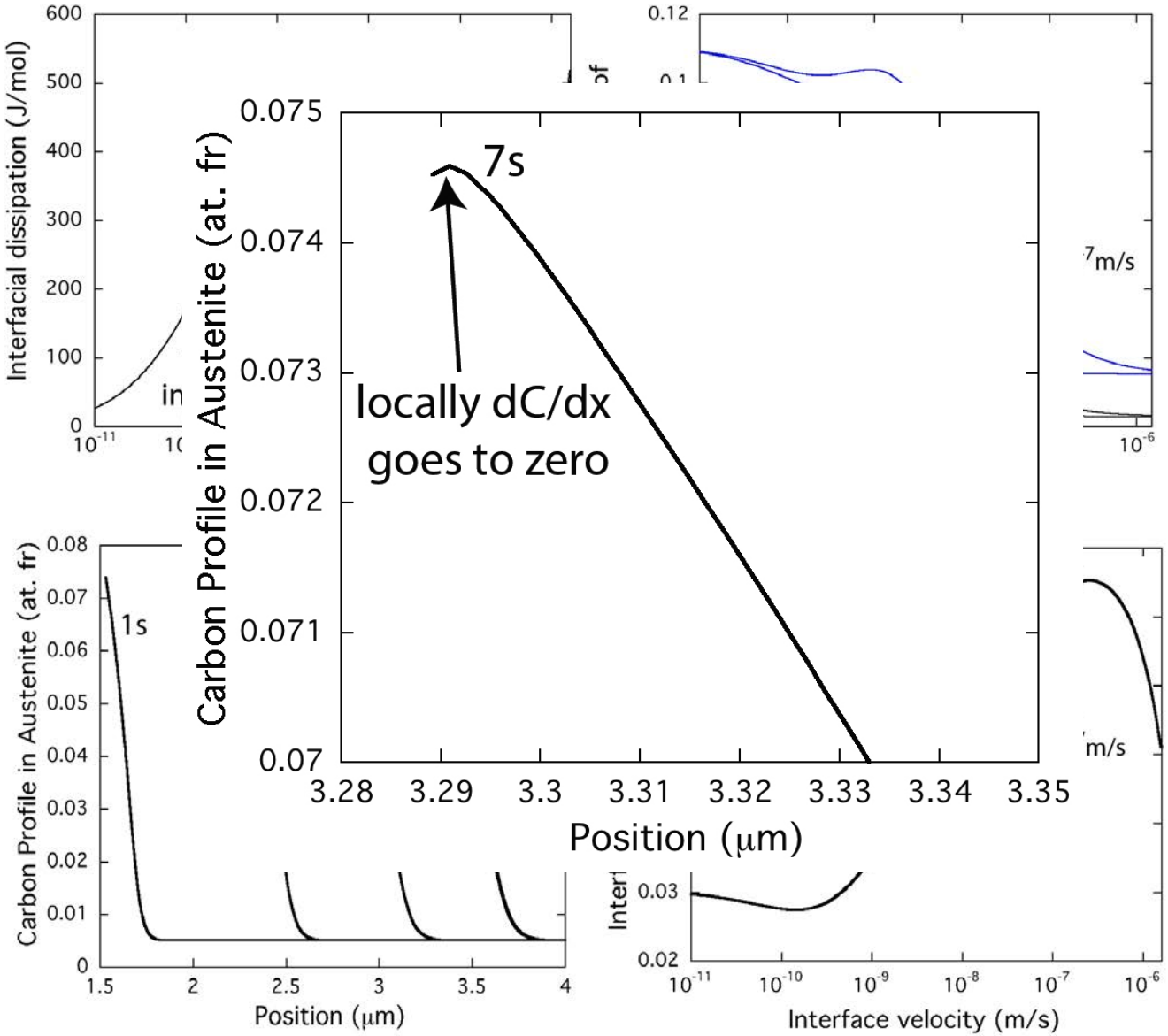




Ferrite formation in Fe-0.12C-1.5Mn-0.5Mo

Fe-0.12C-1.5Mn-0.5Mo
@ 550C

Full kinetic calculation
Planar geometry,
10μm GS

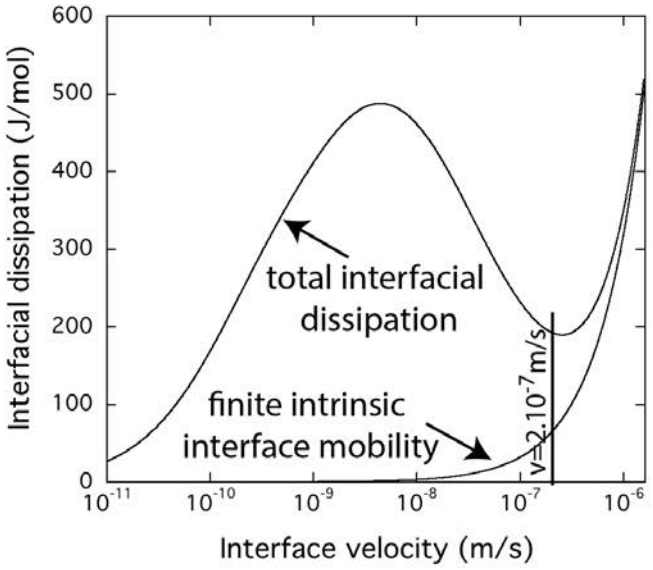


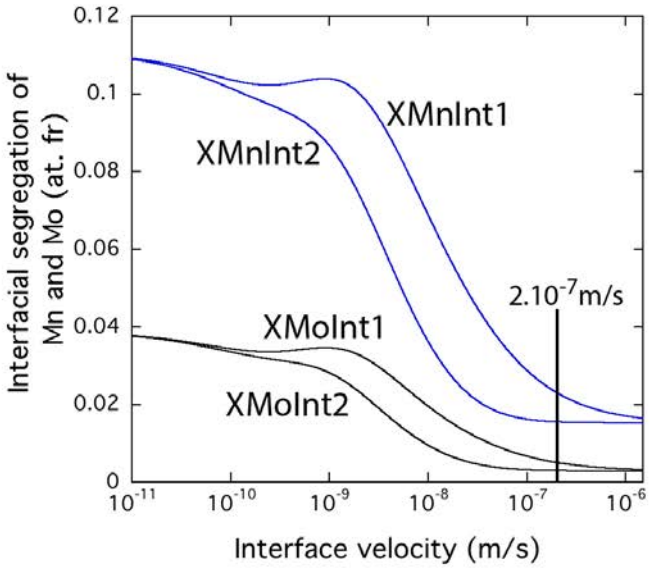
Ferrite formation in Fe-0.12C-1.5Mn-0.5Mo

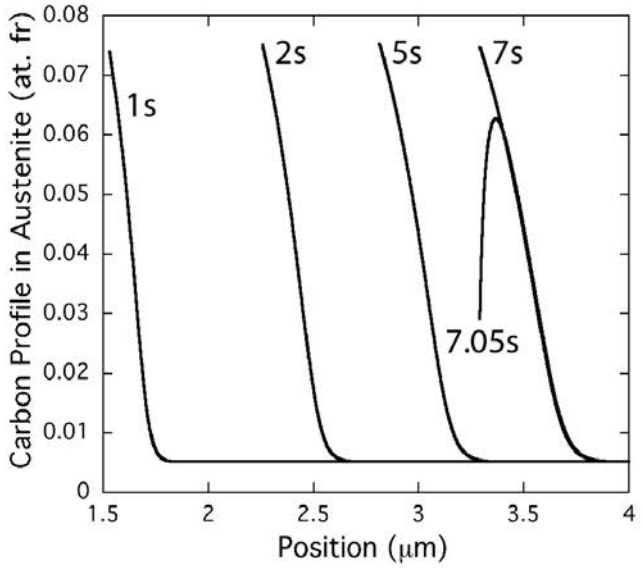
Fe-0.12C-1.5Mn-0.5Mo
@ 550C

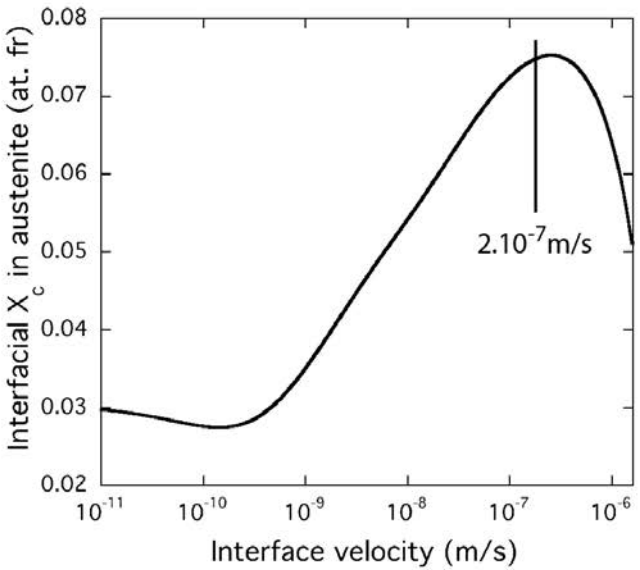
Full kinetic calculation
Planar geometry,
10μm GS

Negligible predicted segregation at the onset of stasis









Ferrite formation in Fe-0.12C-1.5Mn-0.5Mo

Fe-0.12C-1.5Mn-0.5Mo @ 550C

Full kinetic calculation
Planar geometry,
10μm GS

Negligible predicted segregation at the onset of stasis

We propose that stasis is caused by in the inversion of the carbon profile in austenite due to the time rate of change of the Carbon BC's.

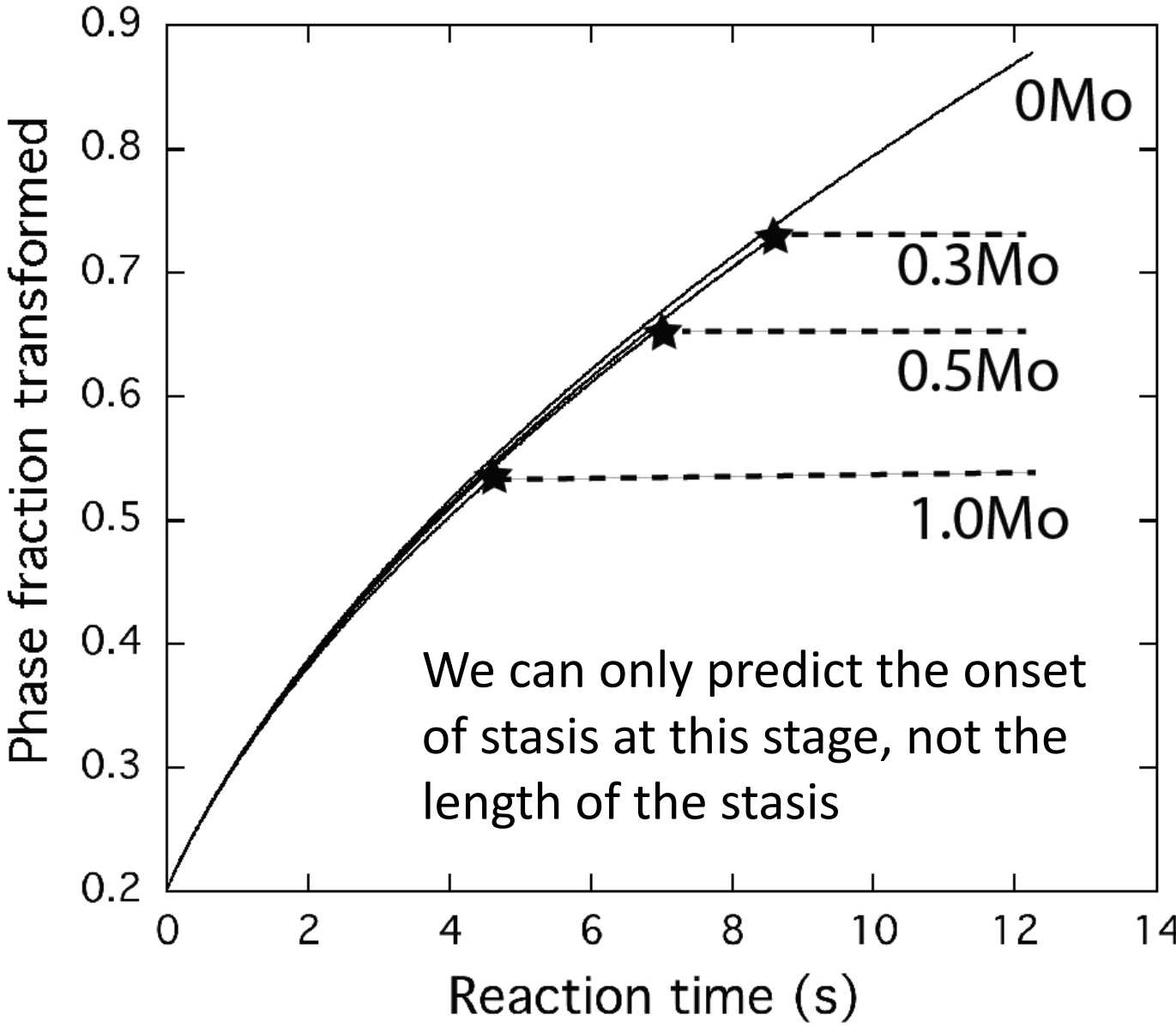
The BC's change because of SD, but it is not dSD that matters. It is the magnitude of dSD/dv compared with the flux of carbon away from the interface into the austenite that controls the inversion.

Ferrite formation in Fe-0.12C-1.5Mn-0.5Mo

Fe-0.12C-1.5Mn-0.5Mo
@ 550C

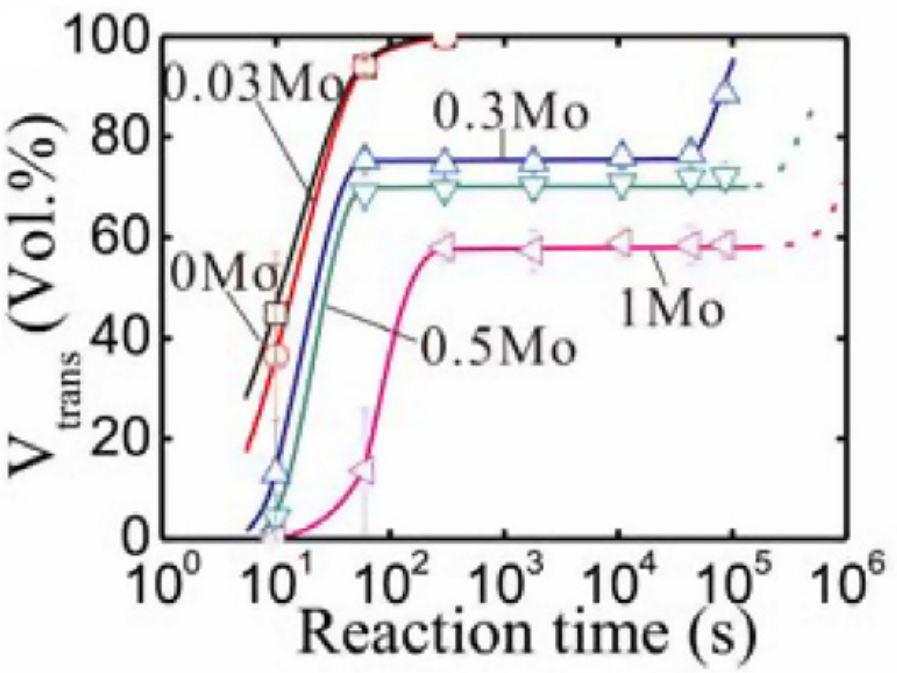
Full kinetic calculation
Planar geometry,
10μm GS

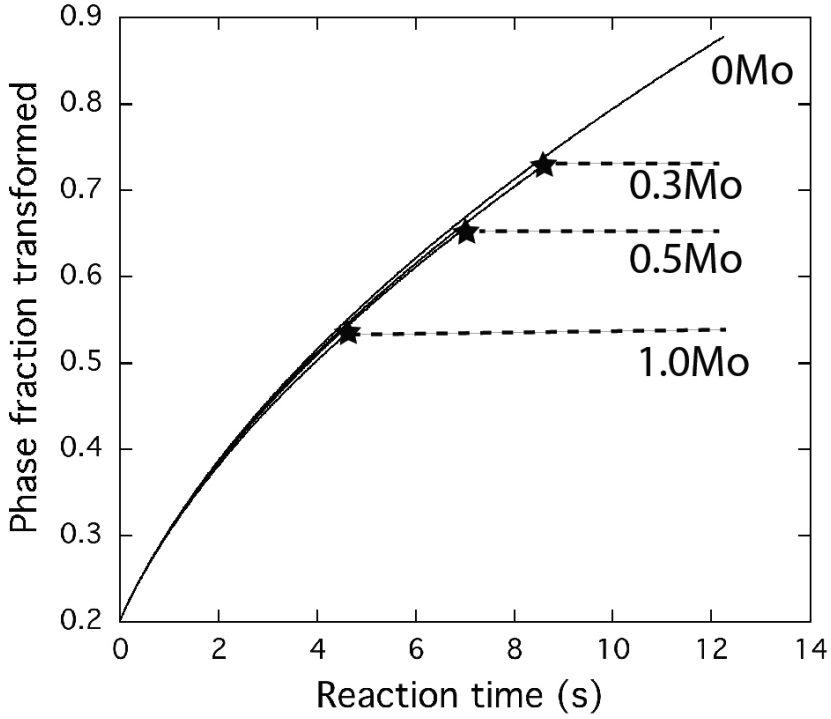
Negligible predicted segregation at the onset of stasis



Ferrite formation in Fe-0.12C-1.5Mn-0.5Mo

Xia, Acta 2015
Fe-0.12C-1.5Mn-(xMo) @ 550C





Conclusions

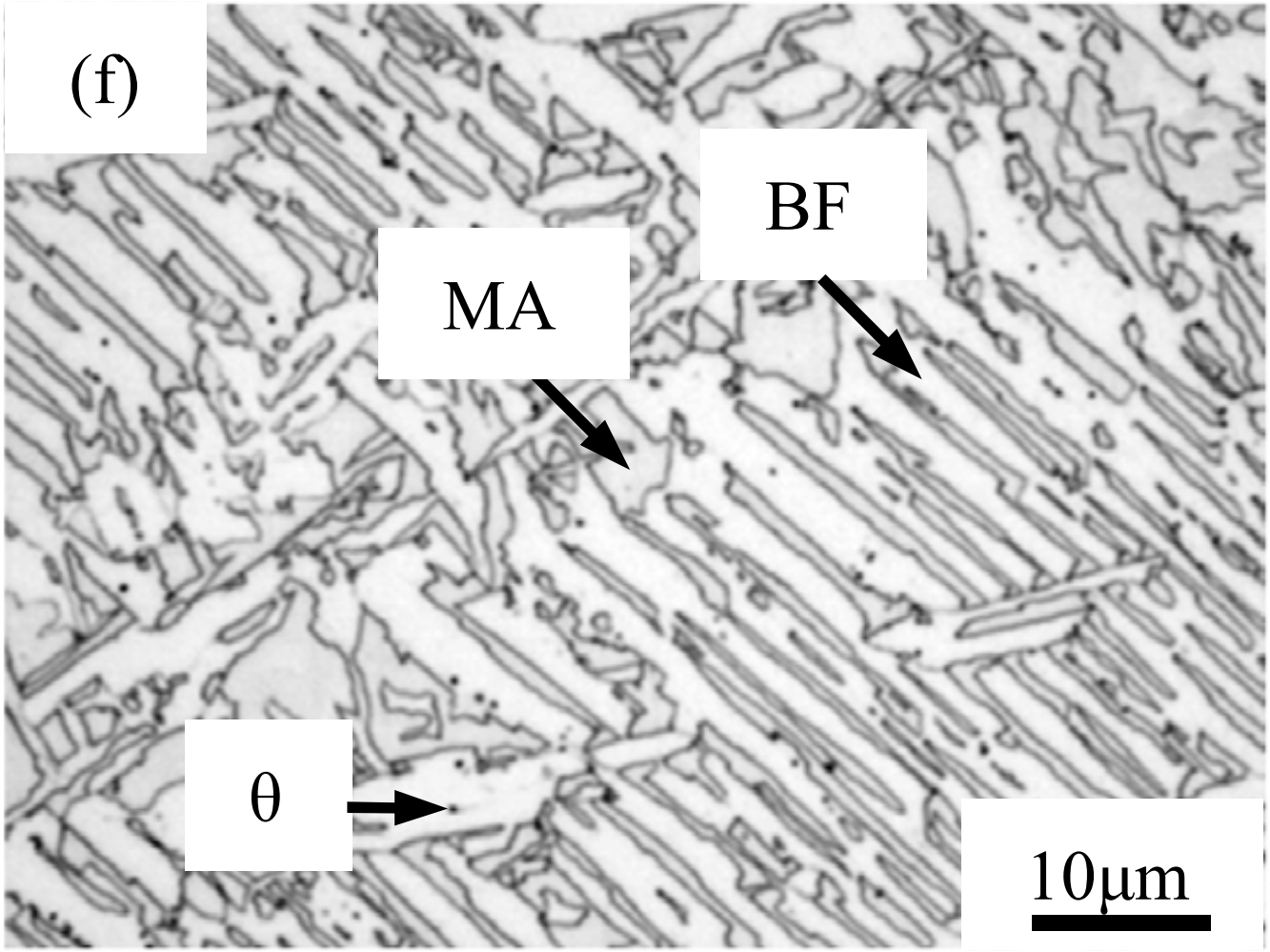
- We can be optimistic about predicting ferrite growth in higher order systems based on SD parameters tunes on ternaries.
- However, carbon cannot be neglected and it may affect the substitutional behavior at the interface in a non-negligible manner (Enomoto, 1999)
- Temp dependence of D^{trans} remains an issue and computational approaches to address this must be developed (e.g. Schuh)
- We propose a new explanation for transformation stasis associated with local inversion of the carbon profile in austenite. This results from the competition between the time rate of change of the carbon boundary conditions and the flux of carbon away from the interface.
- It is dSD/dv, not dSD that matters.

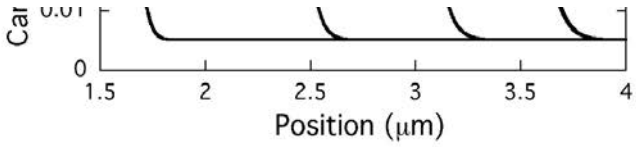
Ferrite formation in Fe-0.12C-1.5Mn-0.5Mo

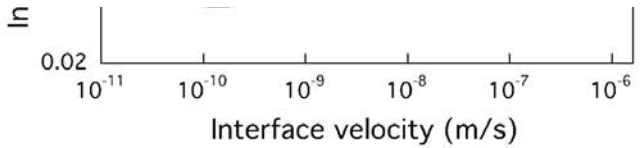
MONASH University

Fe-0.12C-1.5Mn-0.5Mo
@ 550C

Full kinetic calculation
Planar geometry,
10μm GS





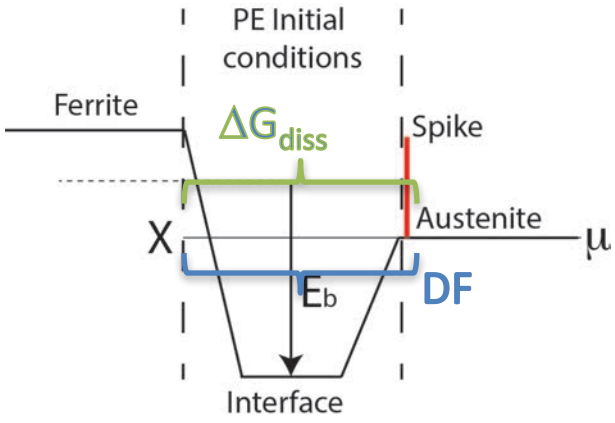


McMaster University

Solute Drag and Coupled Solute Drag

Application to ferrite formation from austenite in Fe-C-X – Odqvist-Zurob model

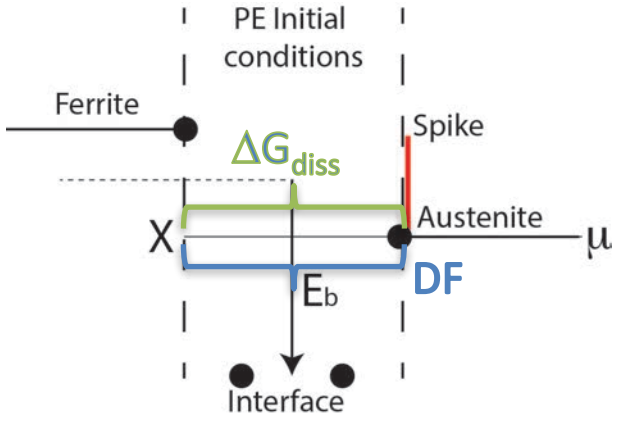
Odqvist et al. (2002)



$$\Delta G_{diss} = -\int_{-\infty}^{+\infty} (U_X - U_X^o)\frac{d(\mu_X - \mu_{Fe})}{dx}dx$$

$$D^t = D_{gb}$$

Zurob et al. (2013)



$$\Delta G_{diss} = \sum_{i=1}^{3} -\frac{V_m}{v} J_X^i \begin{bmatrix} (\mu_X^i - \mu_X^{i-1}) \\ -(\mu_{Fe}^i - \mu_{Fe}^{i-1}) \end{bmatrix}$$

$$D^t = \sqrt{D_\gamma\, D_\alpha}$$

Key issue – choices of E_b and Dt (and temp dependencies)

CSD – enhanced SD effect from solute-solute interactions in the interface