Recent models for the interface contact conditions for planar ferrite growth and some open questions

Cong Qiu and Christopher Hutchinson

Collaborators: Hatem Zurob, Goro Miyamoto and Tadashi Furuhara

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2. Three questions arising from discrepancies between model and experiment
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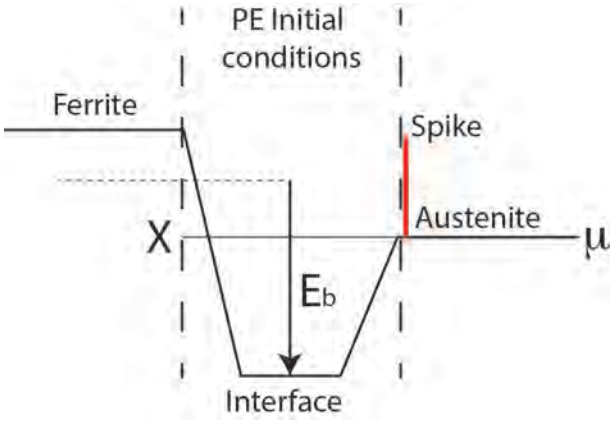
   b) Experimental observations of LENP kinetics
   c) Ferrite growth in Fe-C-Mn-Si and Fe-C-Mn-Mo

Recent interface models for planar γ/α contact conditions

Odqvist et al. (2002)



$\Delta G_{diss} = DF$

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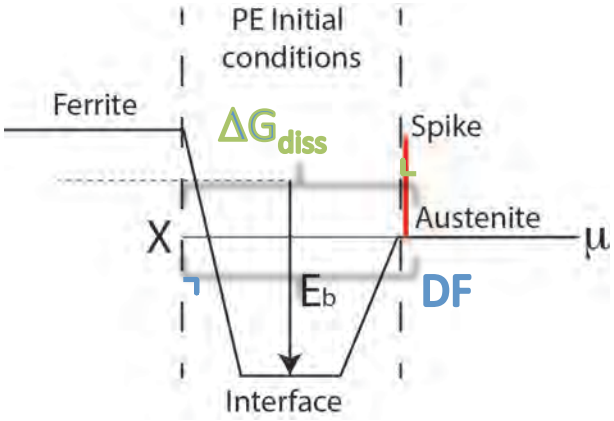

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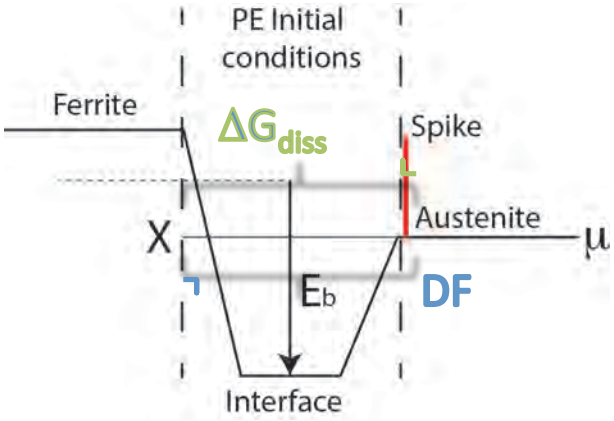

$$\Delta G_{diss} = DF$$

$$\mu_C^{\gamma/\alpha} = \mu_C^{\alpha/\gamma}$$

$$DF = U_{Fe}^{o}\left[\mu_{Fe}^{\gamma} - \mu_{Fe}^{\alpha}\right] + U_{X}^{o}\left[\mu_{X}^{\gamma} - \mu_{X}^{\alpha}\right]$$

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

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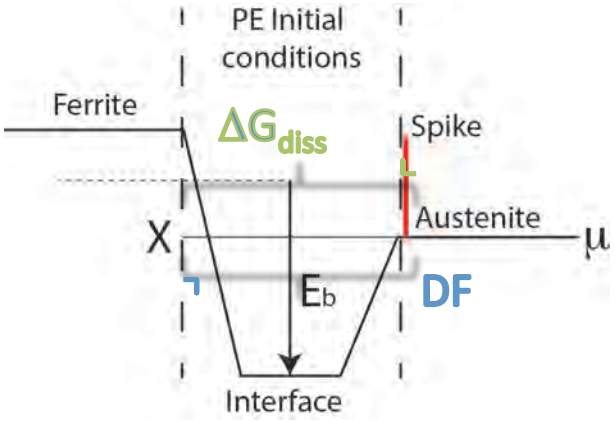

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$$D^t = D_{gb}$$

Applied to Fe-C-Ni precip data of Oi et al. (Acta, 1999)

Using a low tendency for Ni segregation, reasonable agreement with the parabolic rate constant at 700C can be obtained.
However, the limit for ferrite growth is closer to the PE boundary than the LENP boundary

Using a higher E_b did not solve the problem.

"It is evident that the present modeling must be modified radically in order to predict such conditions for their (Oi's alloy) alloy at 993K."

Recent interface models for planar γ/α contact conditions

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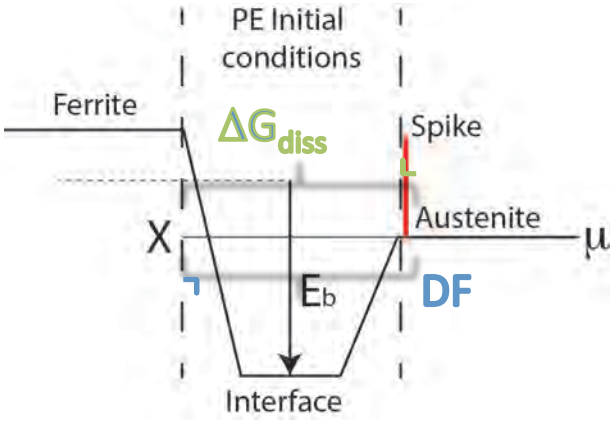

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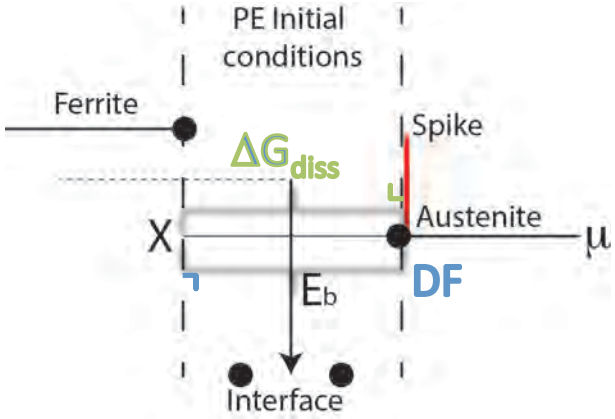
Zurob et al. (2013)



$$\Delta G_{diss} = DF$$

$$\mu_C^{\gamma/\alpha} = \mu_C^{\alpha/\gamma}$$

$$DF = \frac{U_{Fe}^{\gamma} + U_{Fe}^{\alpha}}{2}\left[\mu_{Fe}^{\gamma} - \mu_{Fe}^{\alpha}\right] + \frac{U_X^{\gamma} + U_X^{\alpha}}{2}\left[\mu_X^{\gamma} - \mu_X^{\alpha}\right]$$

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

$$D^t = \sqrt{D_\gamma^2 + D_\alpha^2}$$

Zurob et al. applied to Fe-C-Mn, Fe-C-Mo, Fe-C-Si, Fe-C-Co, precipitation, decarburization and kinetic transitions

Agreement was reasonable using single sets of E_b and D^t

Recent interface models for planar γ/α contact conditions

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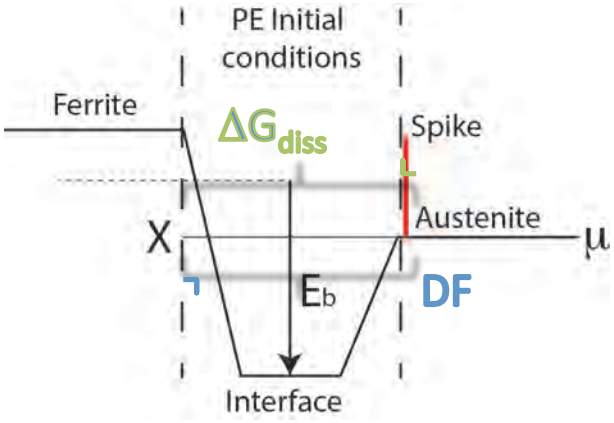

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$$D^t = D_{gb}$$

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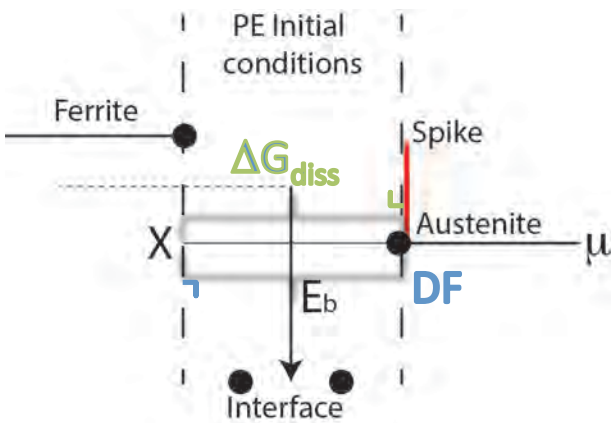

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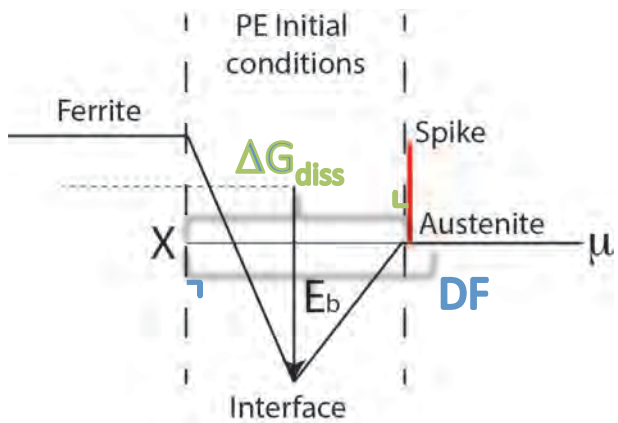
$$D^t = \sqrt{D_\gamma^2 + D_\alpha^2}$$

Chen & van der Zwagg (2014)



$$\Delta G_{diss} = DF$$

$$\mu_C^{\gamma/\alpha} \neq \mu_C^{\alpha/\gamma}$$

$$DF = U_{Fe}^{o}\left[\mu_{Fe}^{\gamma} - \mu_{Fe}^{\alpha}\right] + U_X^{o}\left[\mu_X^{\gamma} - \mu_X^{\alpha}\right] + U_C^{o}\left[\mu_C^{\gamma} - \mu_C^{\alpha}\right]$$

$$\Delta G_{diss} = -\int_{-\delta}^{+\delta} (U_X - U_X^{o}) \frac{dE}{dx} dx$$

$$D^t = \sqrt{D_\gamma^2 + D_\alpha^2 + D_{gb}^2}$$

Comparison of Odqvist et al. and Zurob et al. models

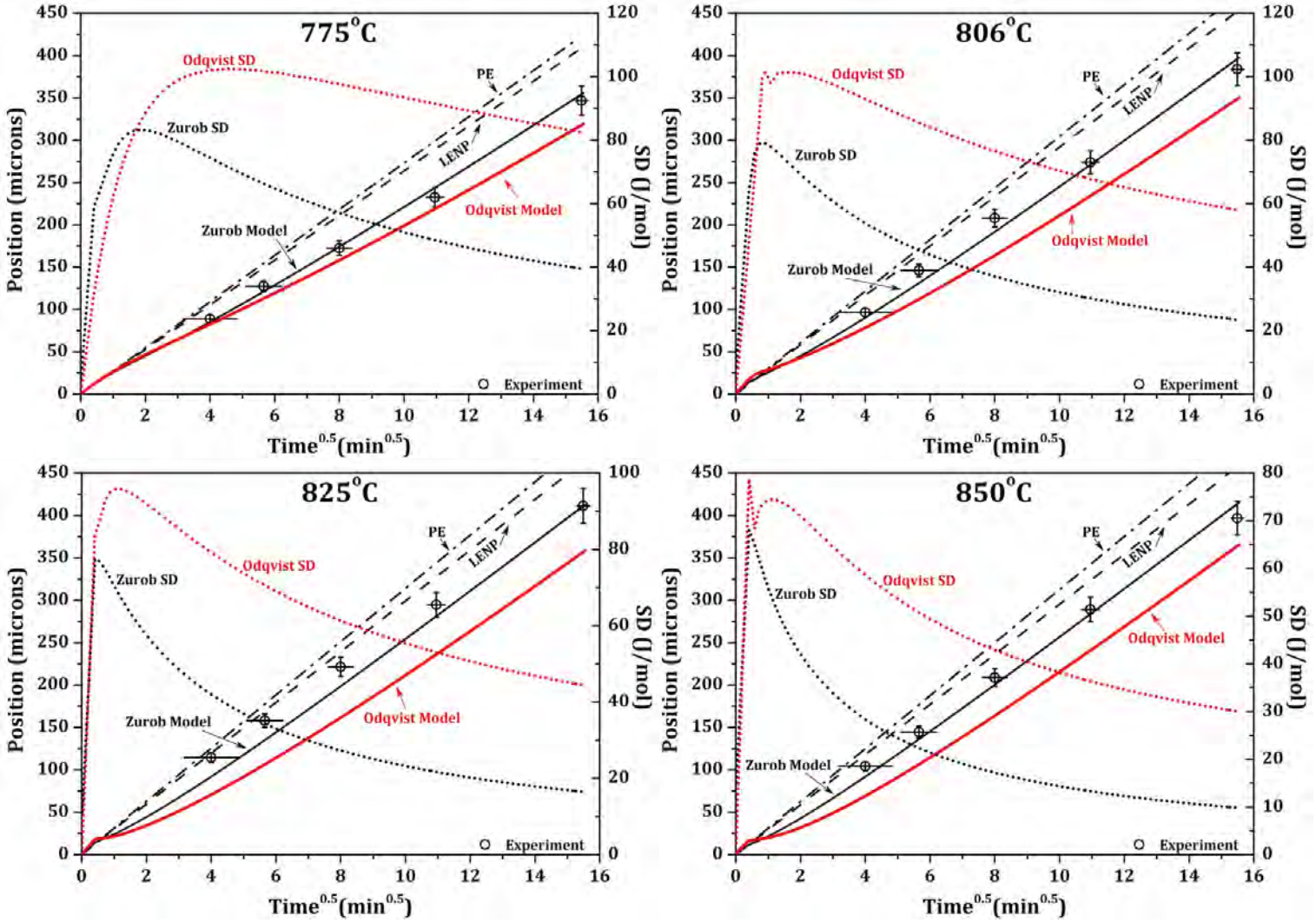
Decarburization

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

E_b (Zurob)=-9kJ/mol
D^t (Zurob)=D^γ

E_b (Odq)=-9kJ/mol
D^t (Odq)=D^γ (central zone)

Dissipation is slightly larger in Odqvist model



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E_b (Zurob)=-9kJ/mol
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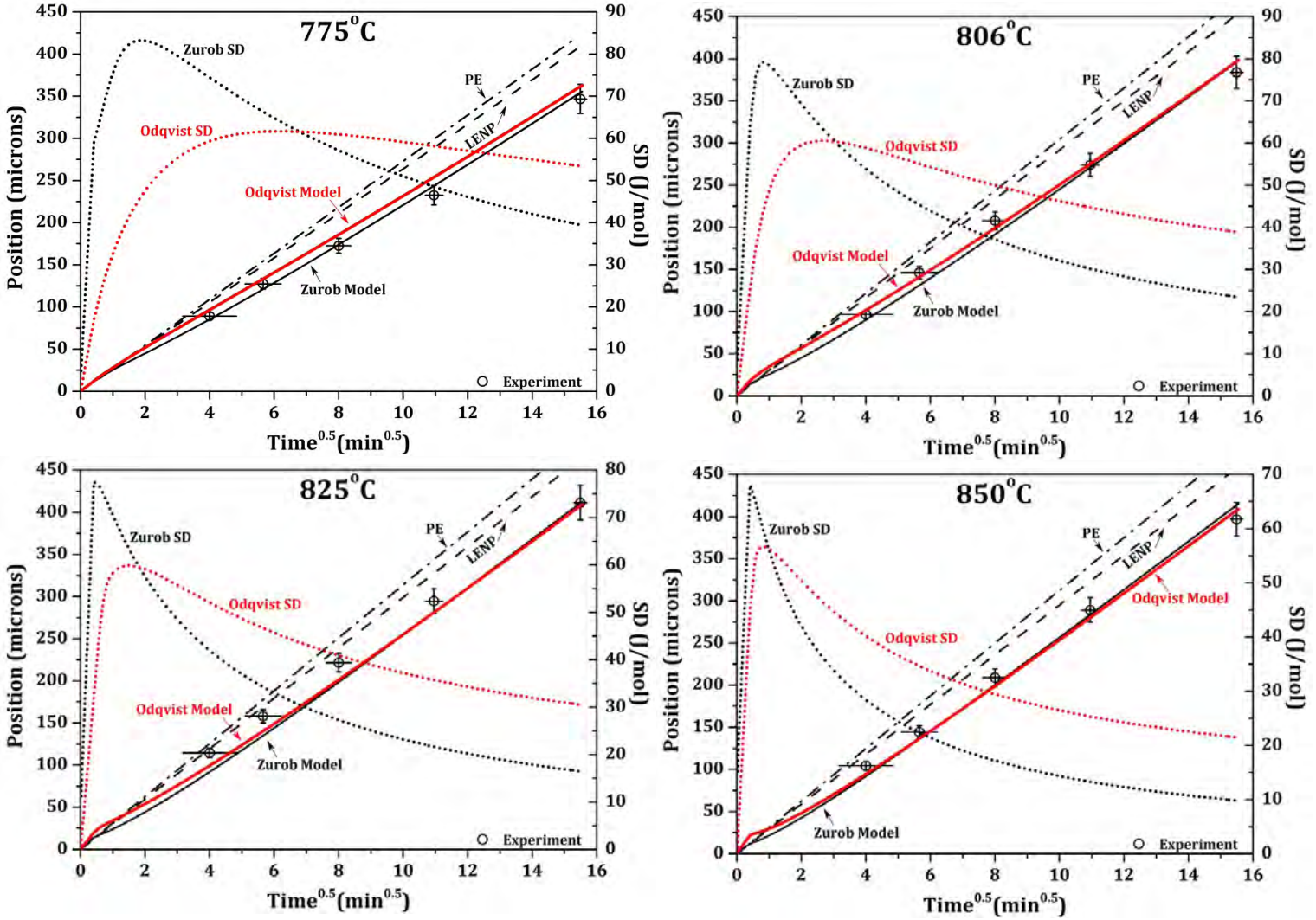
E_b (Odq)=**-7kJ/mol**
D^t (Odq)=D^γ (central zone)

Odqvist and Zurob work equally well



Comparison of Odqvist et al. and Zurob et al. models

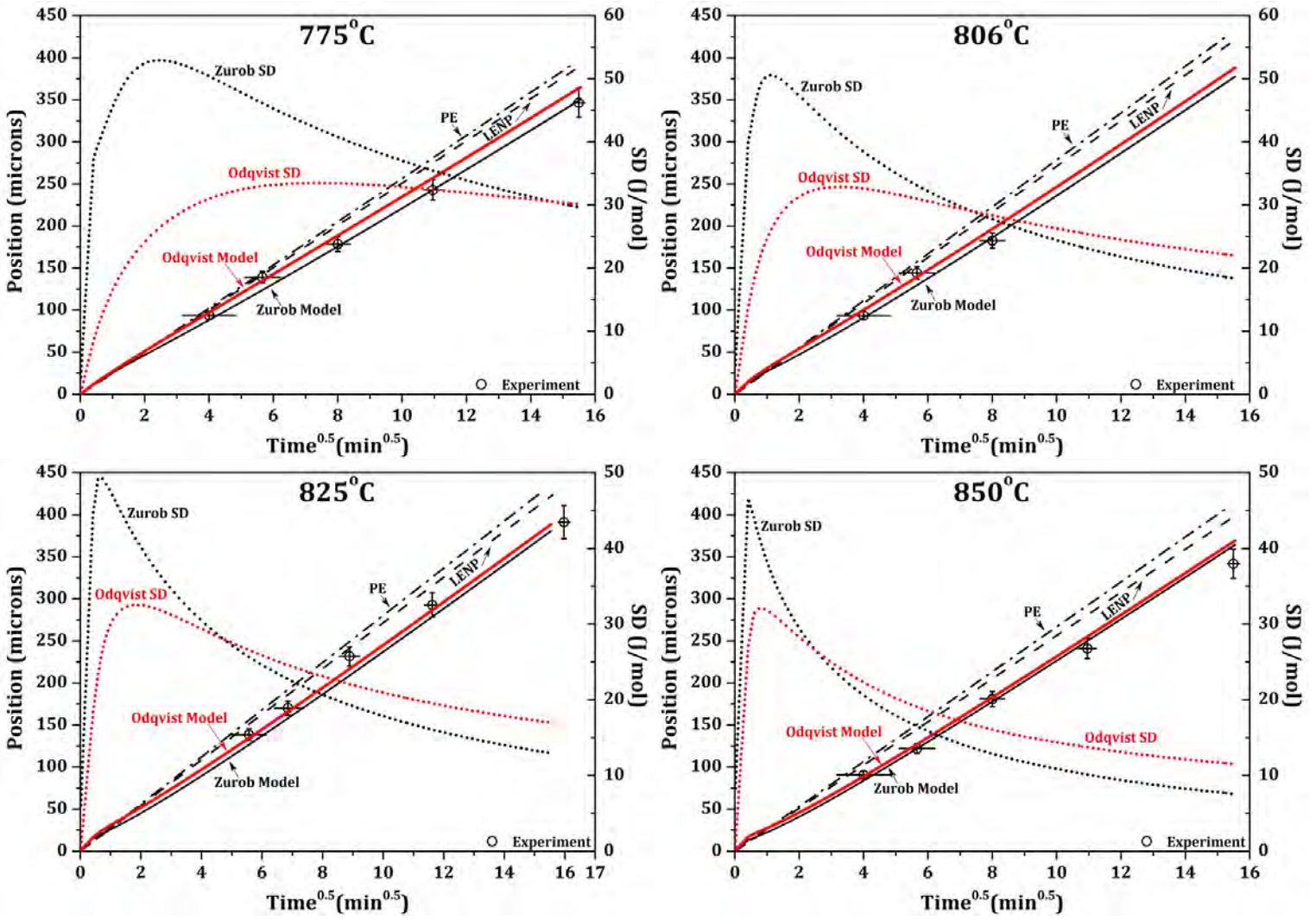
Decarburization

Fe-0.74C-0.45Si (wt. %)

E_b (Zurob)=-9kJ/mol
D^t (Zurob)=D^γ

E_b (Odq)=**-7kJ/mol**
D^t (Odq)=D^γ (central zone)

Odqvist and Zurob work equally well



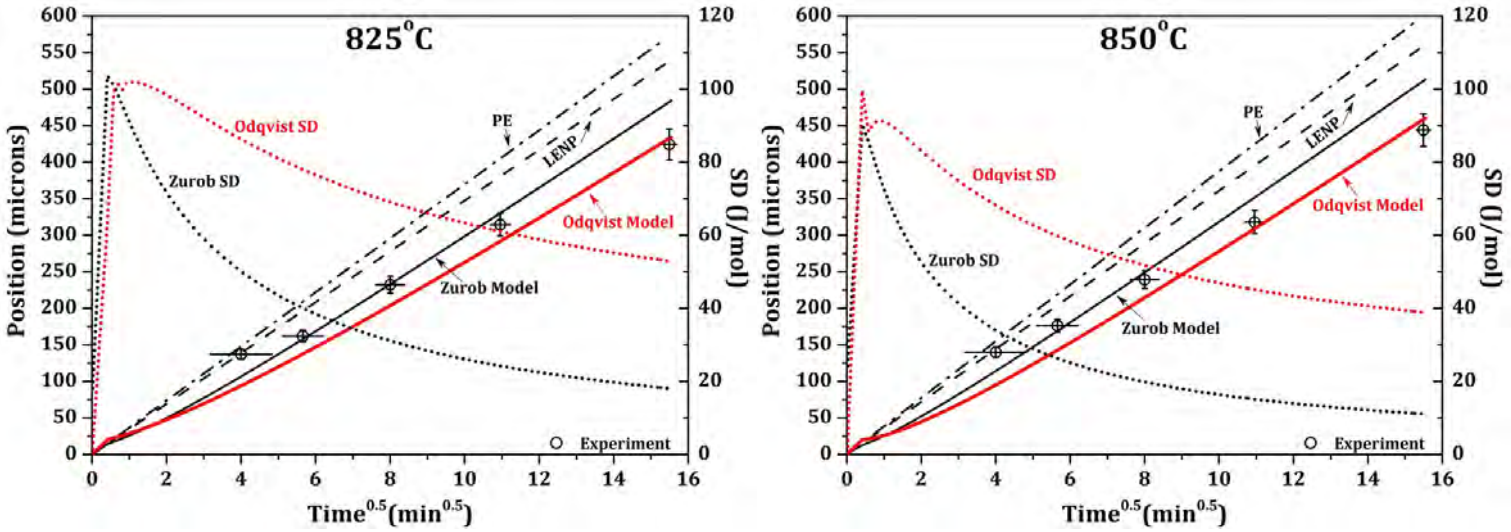
Comparison of Odqvist et al. and Zurob et al. models

Decarburization

Fe-0.75C-1.46Si (wt. %)

E_b (Zurob)=-9kJ/mol
D^t (Zurob)=D^γ

E_b (Odq)=**-7kJ/mol**
D^t (Odq)=D^γ (central zone)



The Odqvist and Zurob models give the same predictions, if the same kinetic parameters for the interface are used, with slightly different E_b

The discrete treatment of the interface (Zurob) has not changed significantly the results

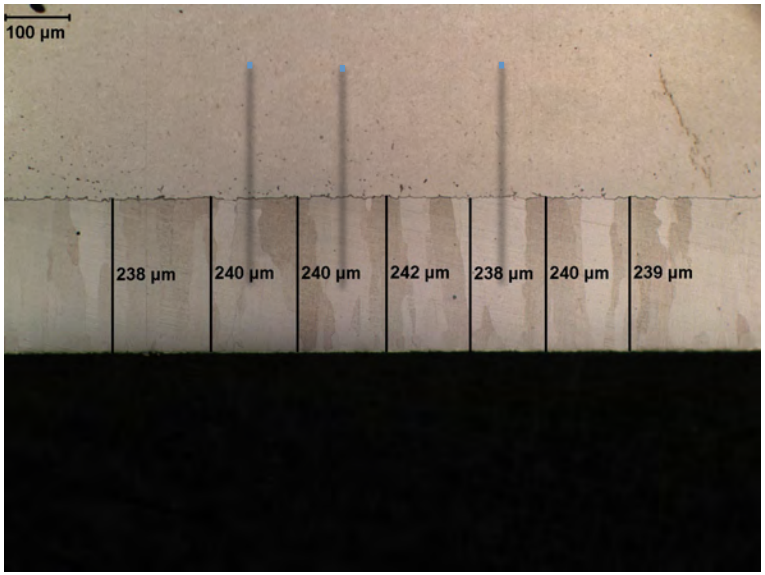
The lack of success of the Odqvist model (Acta 2003) compared with Zurob (MMTA 2013) was likely because of Odqvist's choice of a very large trans-interface diffusivity, D^{gb}

Can we probe more directly the contact conditions?

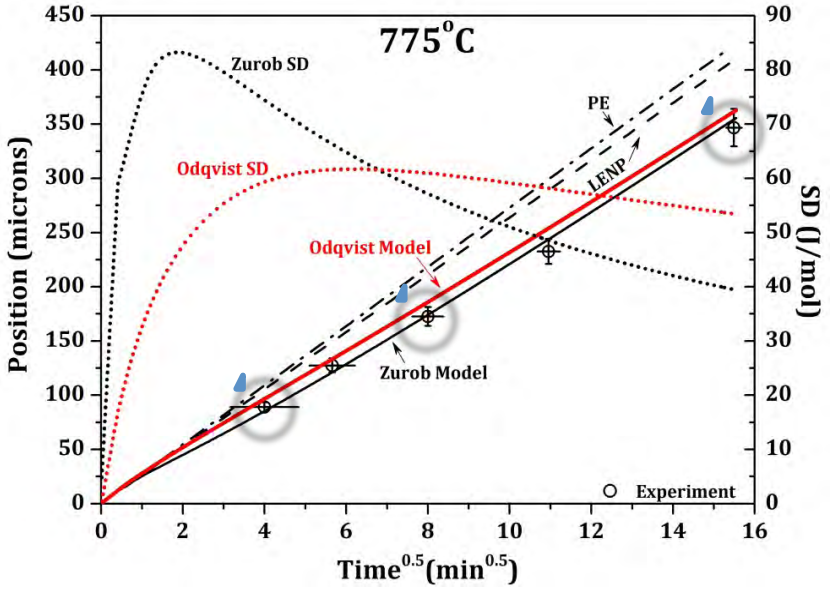
To complement the kinetics comparison we can also compare directly the carbon profiles

EPMA Measurements of Carbon profile
Goro Miyamoto & Tadashi Furuhara

Decarburization samples (planar interface)
0.84Si alloy – 775C: 16min, 64min, 4h

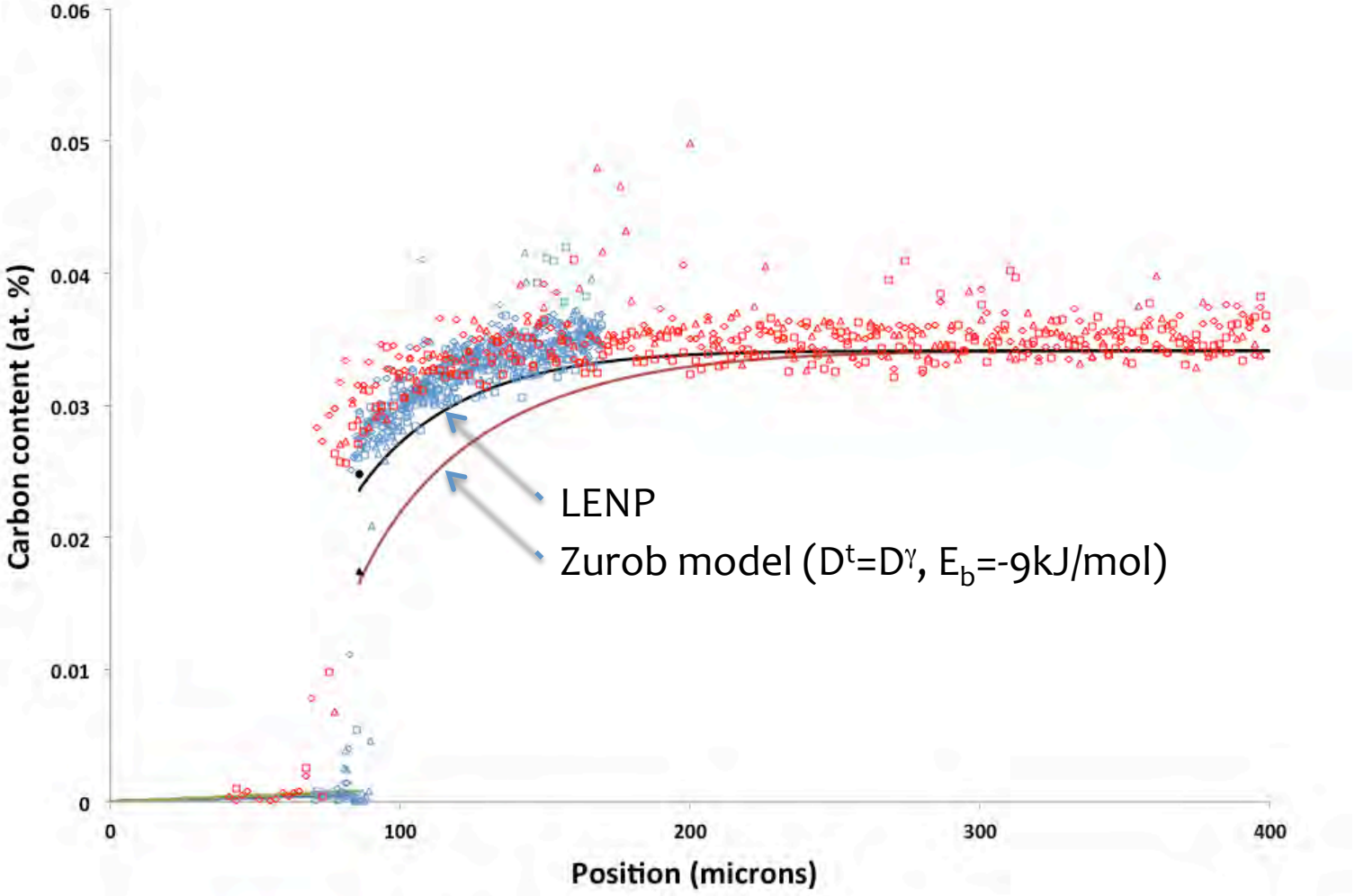


Fe-0.76C-0.84Si (wt. %)



EPMA measurements of Carbon profile

Miyamoto & Furuhara - Fe-0.76C-0.84Si (wt. %) Decarburized 775C 16min



EPMA measurements of Carbon profile

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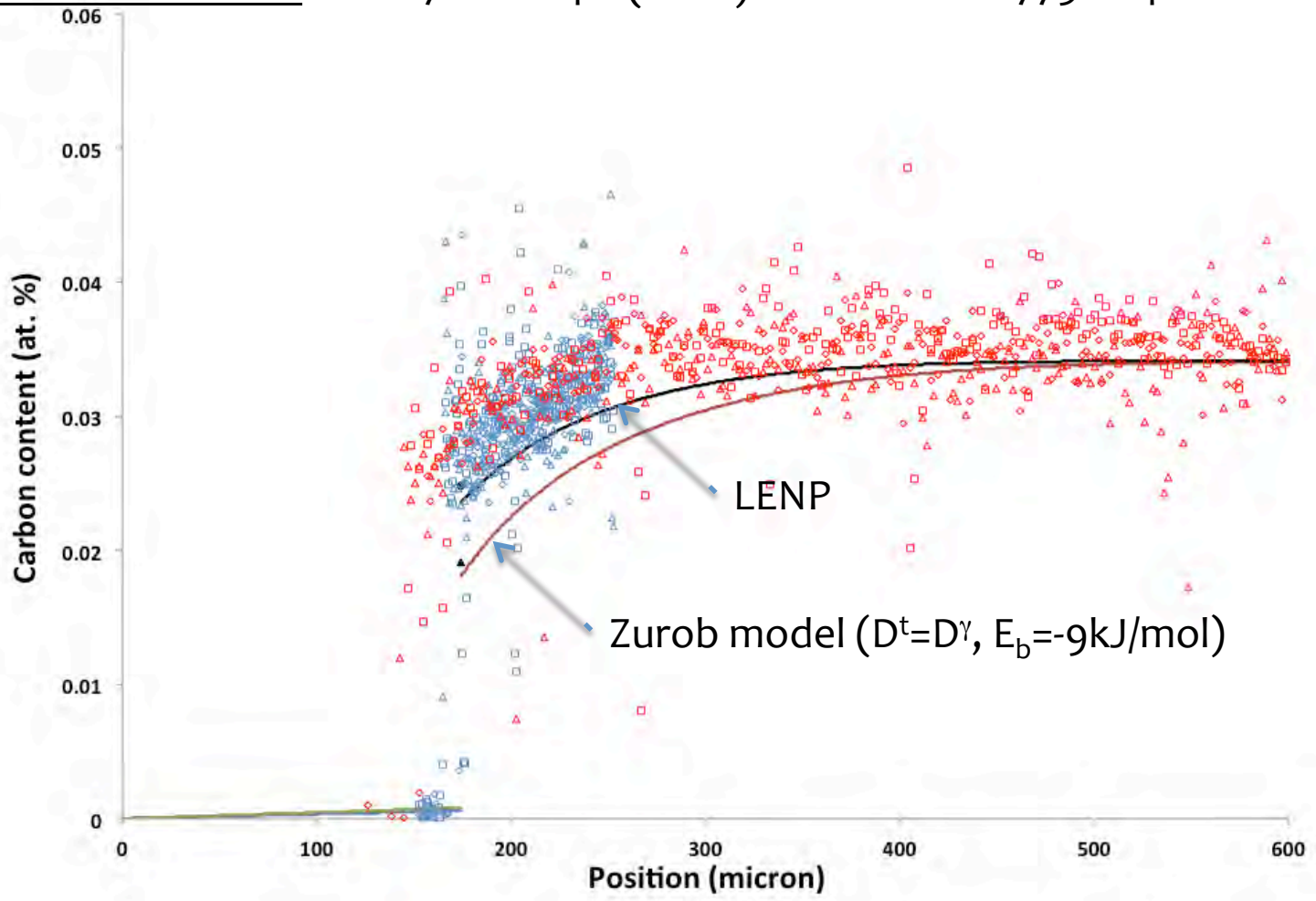

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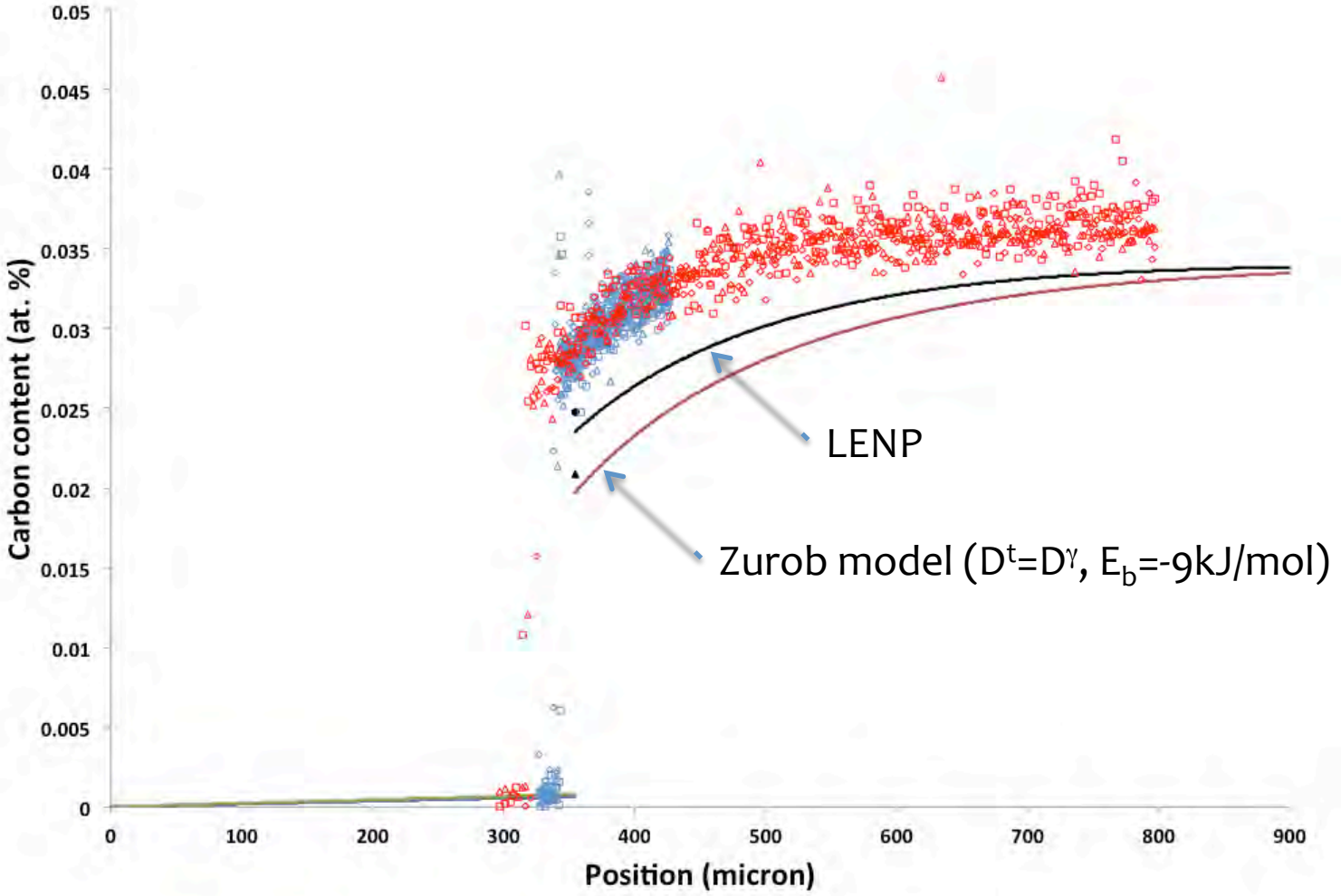
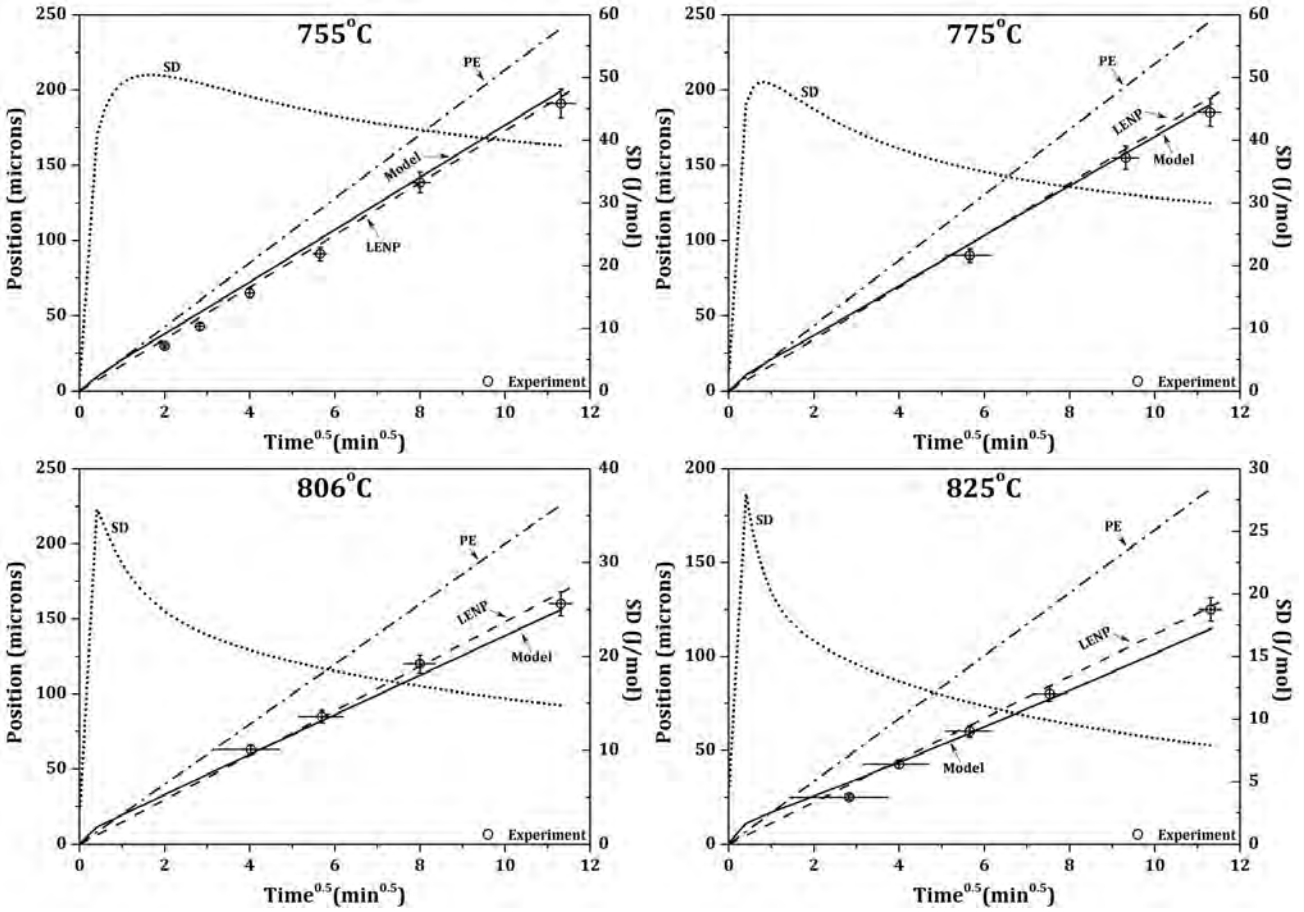


Observations of LENP during decarburization of Fe-C-X

LENP kinetics are frequently observed in Fe-C-Mn and Fe-C-Ni alloys

Current dissipation based models cannot exhibit true LENP behavior – it is a limit to be approached as *v* approaches zero

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



Observations of LENP during decarburization of Fe-C-X

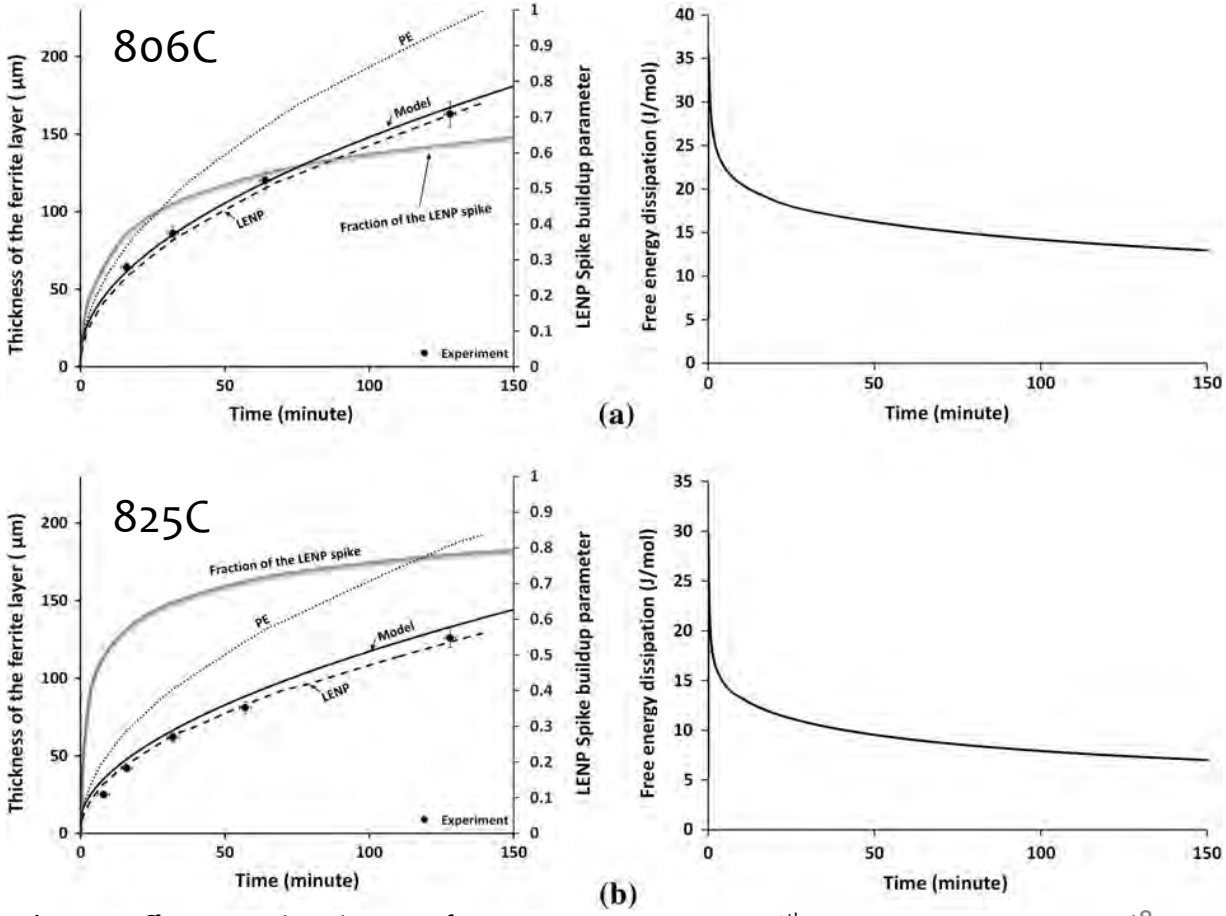
LENP kinetics are frequently observed in Fe-C-Mn and Fe-C-Ni alloys

The dissipation models can exhibit LENP kinetics by a choice of E_b and D^t that results in a partial spike combined with a dissipation that leads to kinetics that look like LENP

Question: what is the reason for E_b and D^t to have these particular values?

It is difficult to accept that it is a coincidence that the kinetics are the same as LENP

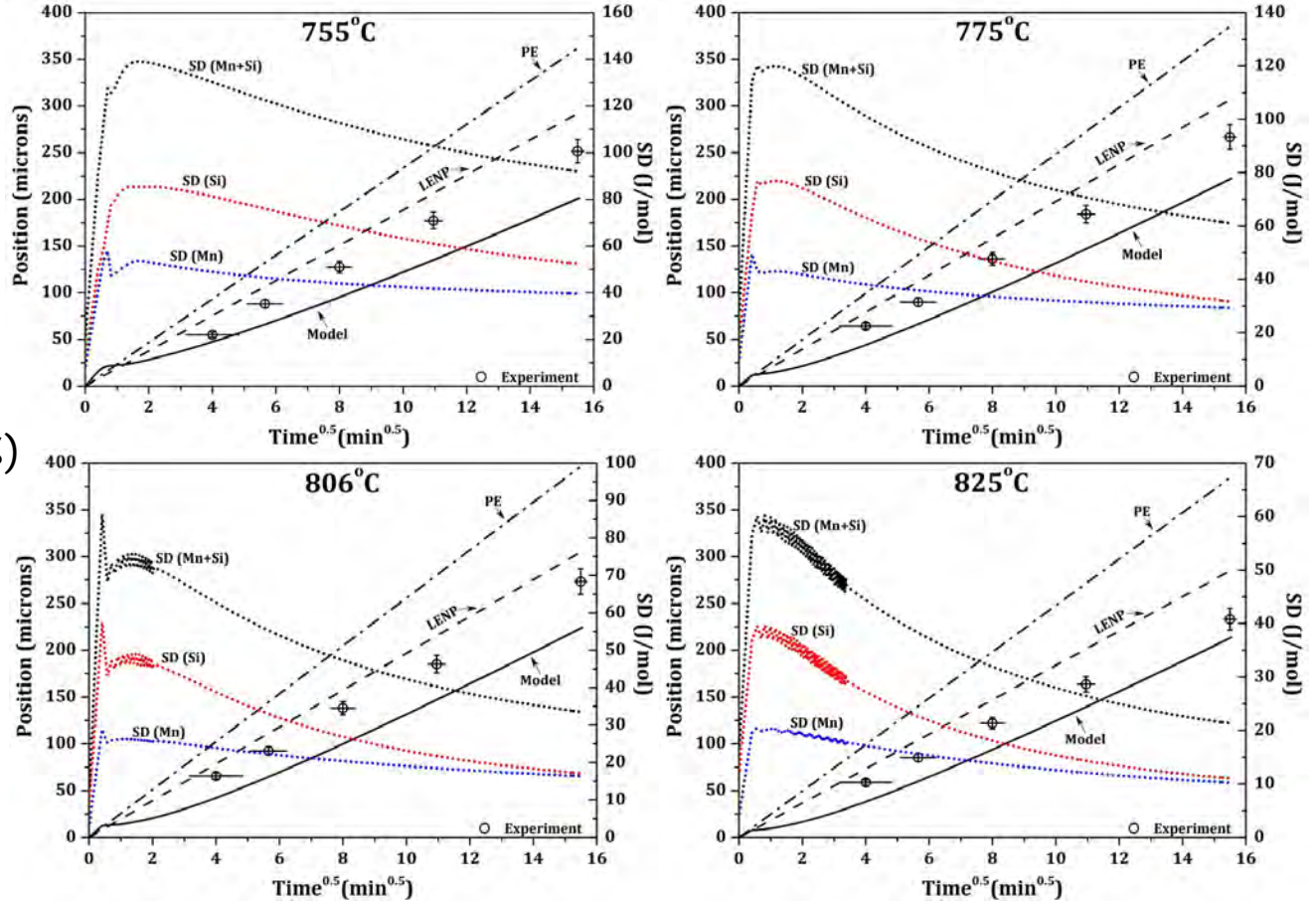
e.g. Zurob et al. model (MMTA 2013): Fe-0.57C-0.94Mn (wt. %)



Growth kinetics during decarburization of Fe-C-Mn-Si

ALEMI (Delft) – we illustrated the surprising observation that to describe the kinetics of ferrite growth in Fe-C-Mn-Si we must set the interaction between Mn and Si in the interface to zero! ie. anti-CSDE

$(Mn:Si)^{I}=(Mn:Si)^{\gamma}$ for Fe-0.66C-1.06Mn-0.92Si (wt. %)



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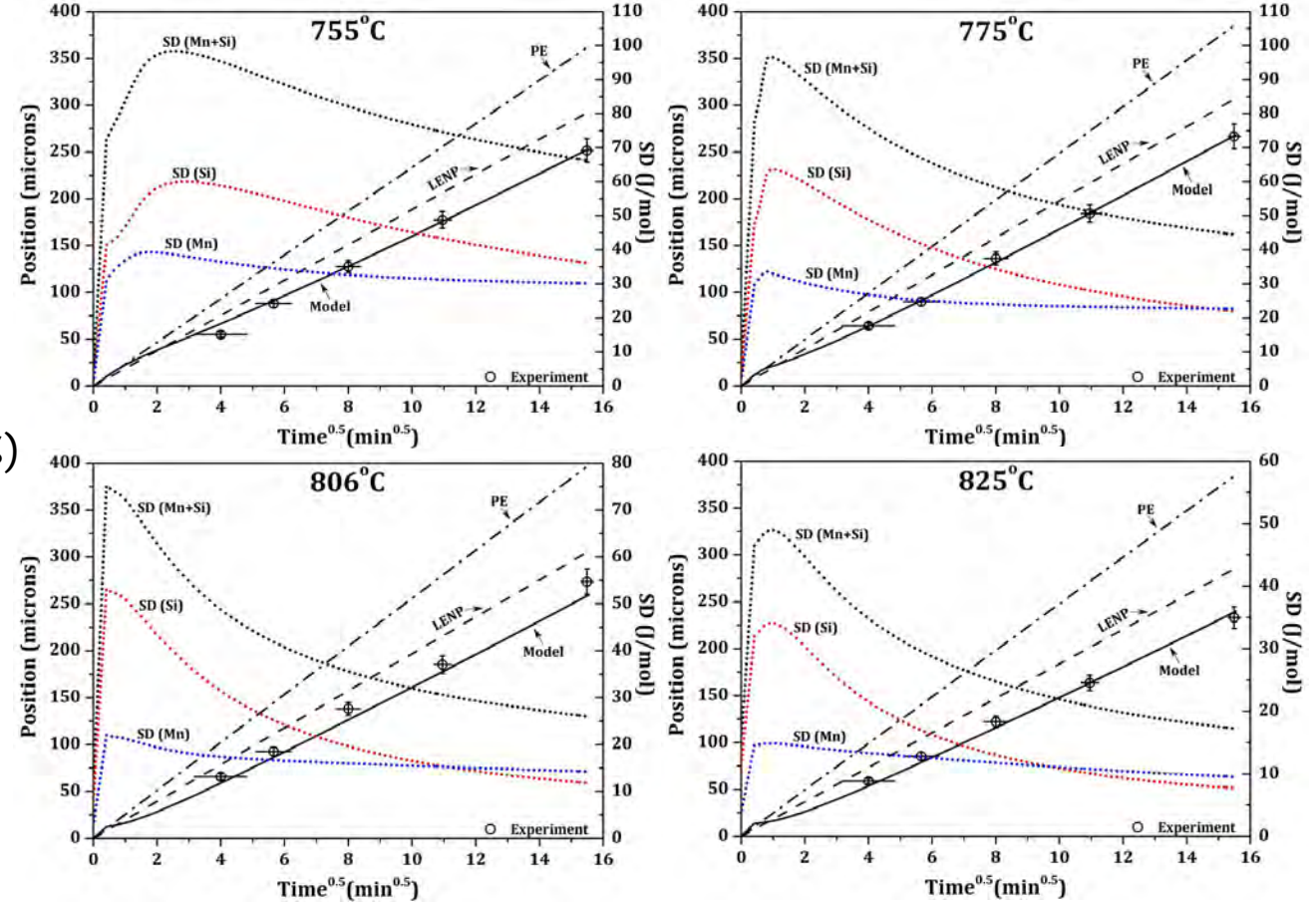
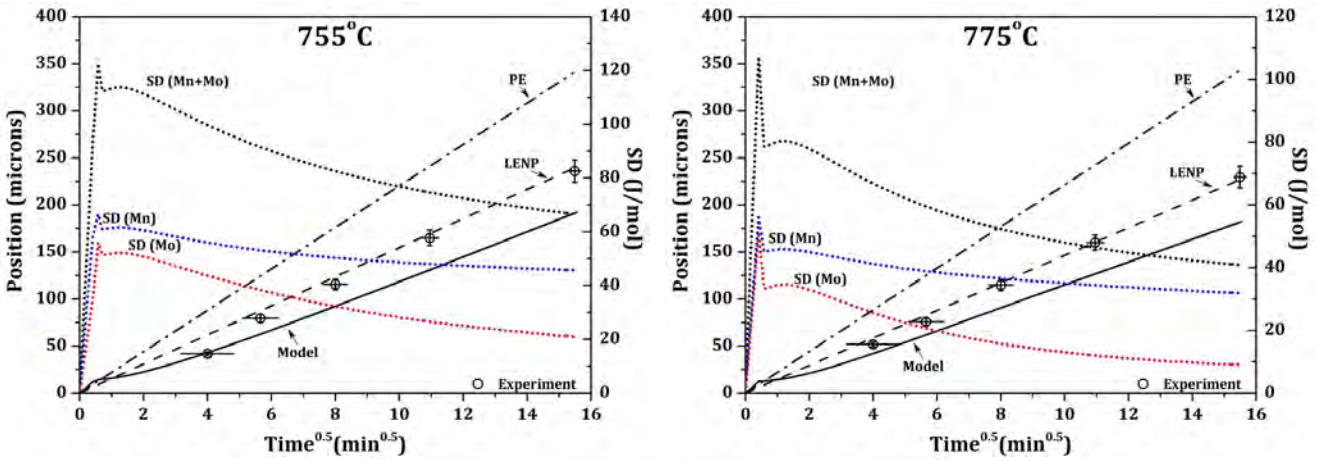
$(Mn:Si)^{I}=0$ for
Fe-0.66C-1.06Mn-0.92Si (wt. %)



Growth kinetics during decarburization of Fe-C-Mn-Mo

Miyamoto and Furuhara supplied an Fe-C-Mn-Mo quaternary alloy

$(Mn:Mo)^{I}=(Mn:Mo)^{\gamma}$ for Fe-0.48C-1.36Mn-0.42Mo (wt. %)

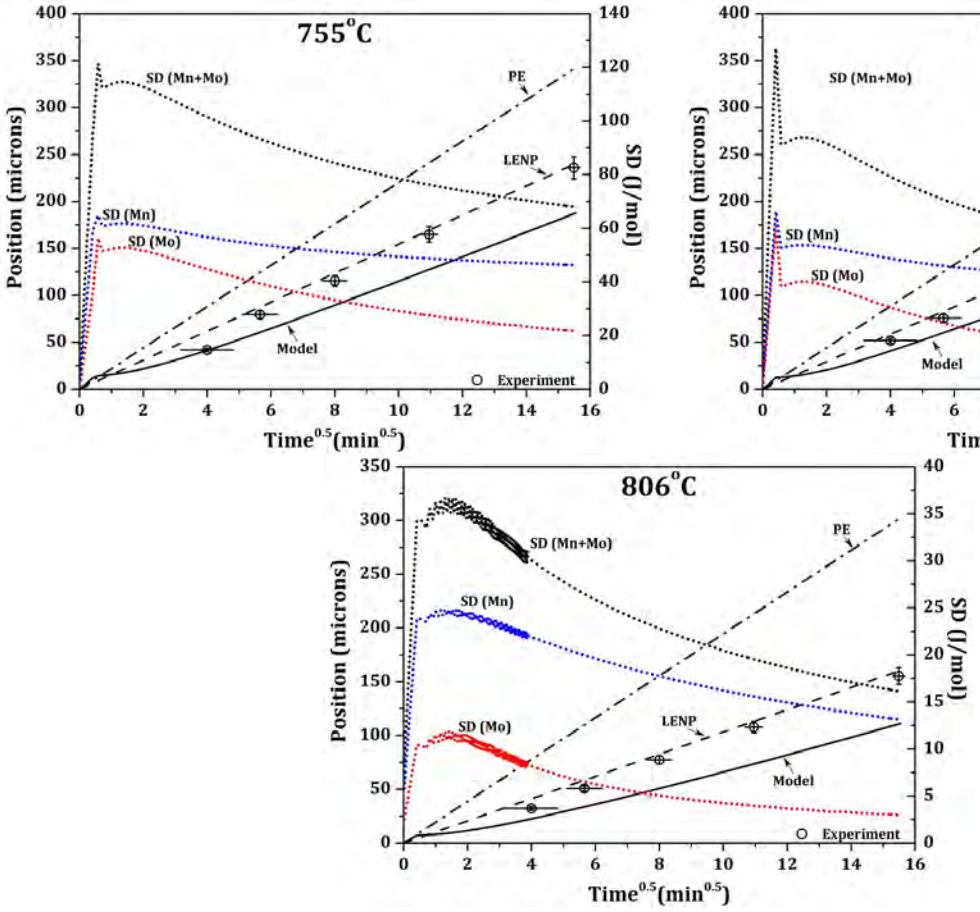


As was the case with Fe-C-Mn-Si, the dissipation is overestimated significantly if a Mn-Mo interaction similar to that in the austenite is assumed inside the interface

Growth kinetics during decarburization of Fe-C-Mn-Mo

Miyamoto and Furuhara supplied an Fe-C-Mn-Mo quaternary alloy

$(Mn:Mo)^{I}$=0 for Fe-0.48C-1.36Mn-0.42Mo (wt. %)



Things are no better if the Mn-Mo interaction in the interface is set to zero.

Perspectives

- Odqvist et al. and Zurob et al. models for the interface contact conditions are essentially the same. Odqvist's comparative lack of success is likely because the D^t chosen was much too high

- Chen and van der Zwagg model belongs to the same family. The major difference is there exists a C chemical potential difference across the interface. It is an interesting discussion point for our community

- EPMA measurements of C profiles may provide new and extremely useful data. Preliminary measurements do not agree well with dissipation based models

- The family of dissipation models discussed cannot give true LENP kinetics – however, appropriate choices of E_b and D^t can give kinetics that look like LENP. Is this reasonable? Occam's razor!

- Using SD interface parameters 'tuned' on ternary Fe-C-Mn and Fe-C-Mo systems (as functions of T and X), the dissipation in Fe-C-Mn-Mo is significantly over-estimated.