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The kinetics of ferrite growth in Fe-C-Mn-Si using controlled decarburization experiments

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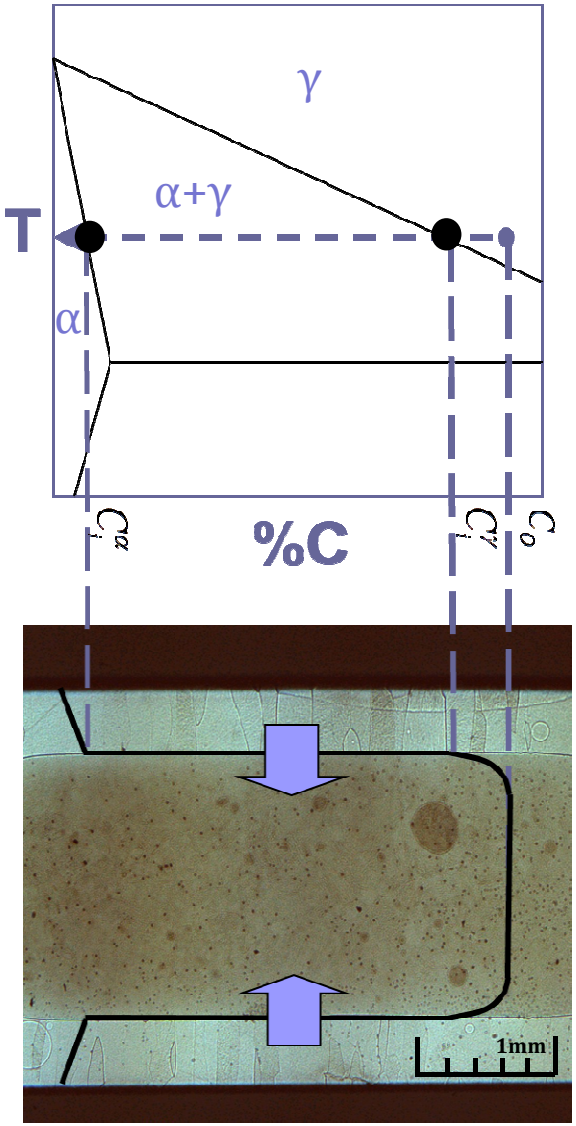
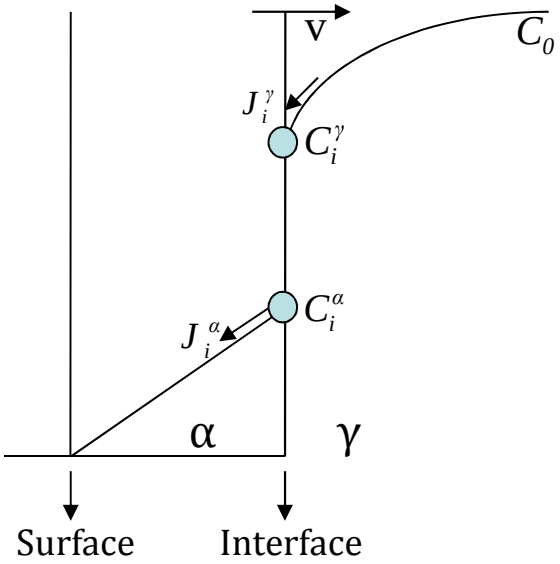
Monash Graduate Scholarship.

Outline

- Advantages and disadvantages of decarb experiments
- Objective – predicting ferrite growth in quaternary and higher order systems
- Alloy systems: Fe-C-Si, Fe-C-Mn & Fe-C-Si-Mn
- Experimental & modelling results
- Summary/Discussion points

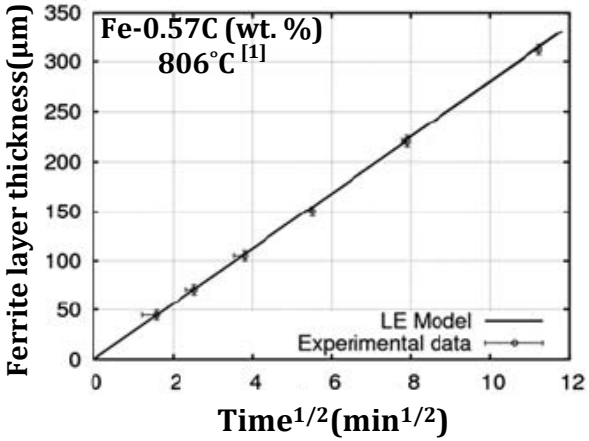
Background: Decarburization technique





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

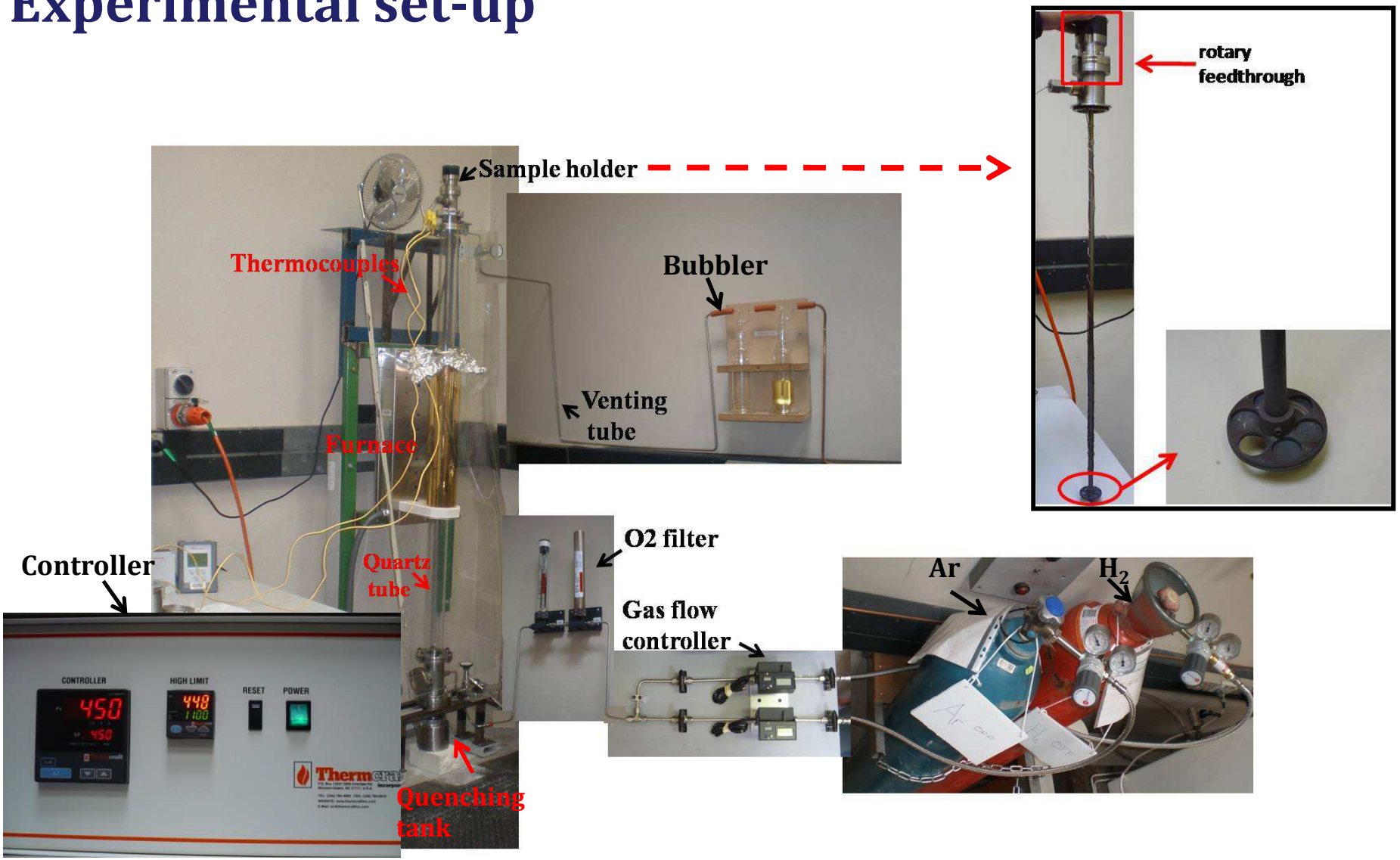
Local equilibrium assumption



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

[1] Béché A, Zurob HS, Hutchinson CR. Metall Trans A 2007;38A:2950-55

Experimental set-up



Objective of the study

Ferrite growth in Fe-C-X steels is usually used to test models of growth (e.g. those including solute drag).

Solute drag models contain parameters such as the binding energy and the trans-interface diffusivity that are currently difficult to predict. They can be 'tuned' using Fe-C-X kinetic experiments.

The objective of this study is to test how well we can predict the kinetics of growth in higher order systems (Fe-C-X-Y) using parameters tuned from ternary systems

Selected Fe-C-X-Y literature

- Tanaka *et al.* (1995)[2]: LE and PE phase boundaries for quaternary systems (Mn+(Si,Ni,Co)) calculated using the Central Atoms method.

- Aaronson *et al.* (2004)[3]: *Coupled Solute Drag Effect* – enhanced accumulation at interfaces due to strong C-X(Y) and/or X-Y interactions leading to enhanced SD effects

- Guo *et al.* (2006, 2007): A C-SDE was used to rationalize the kinetics of ferrite growth, and the transitions to different stages of growth in Fe-C-Mn-Si alloys[4,5].

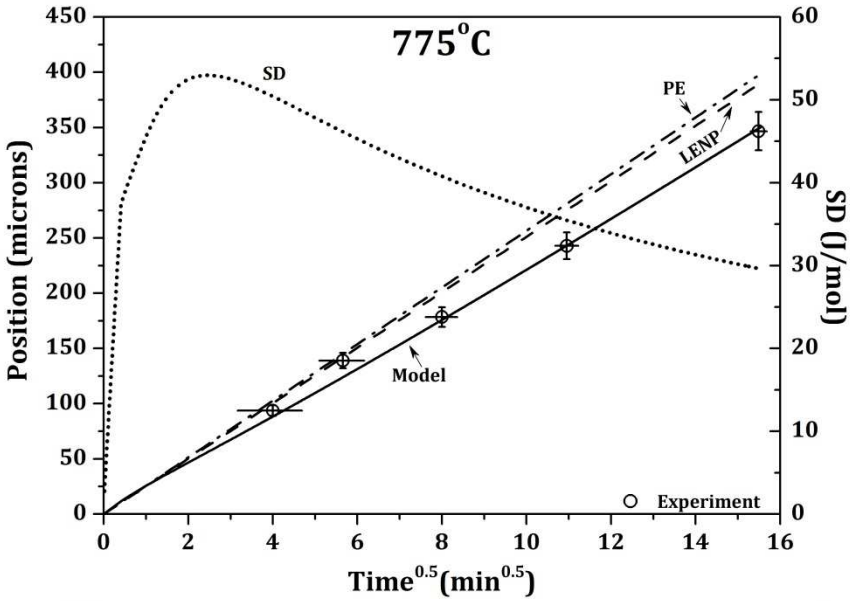
[2] Tanaka T, Aaronson HI, Enomoto M, MMTA 1995;26A:561-80
[3] Aaronson HI, Reynolds WT, Purdy GR,MMTA 2004;35A:1187-1210
[4] Guo H, Enomoto M. MMTA 2007;38A:1152-61
[5] Guo H, Purdy GR, Enomoto M, Aaronsom HI, MMTA, 2006;37A:1721-1729

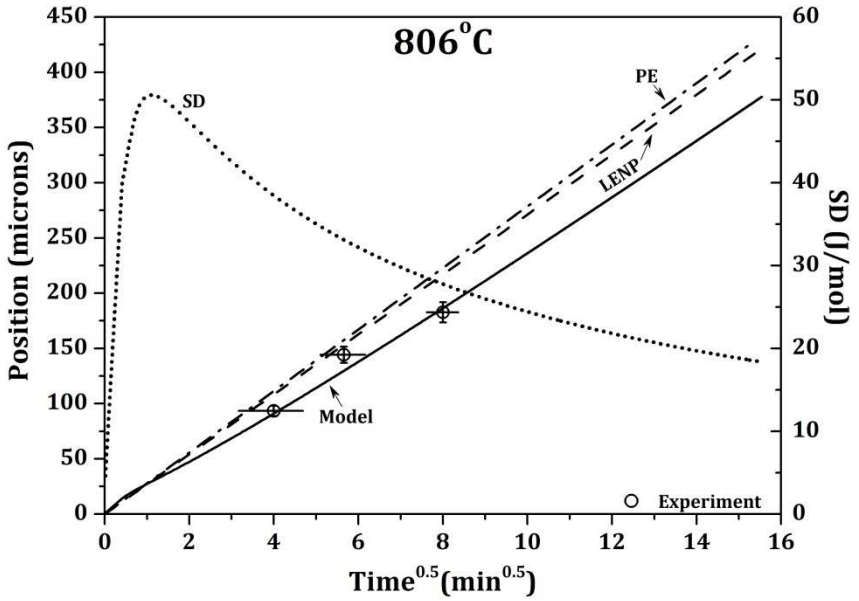
Alloy compositions

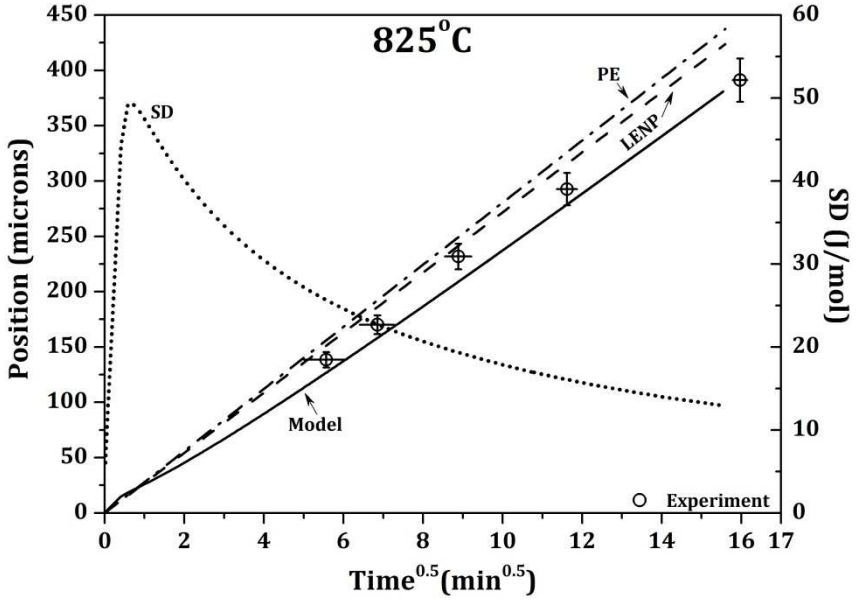
Alloy Composition (wt.%)	Decarburization temperatures (˚C)
Fe-0.74C-0.45Si	775, 806, 825, 850
Fe-0.76C-0.84Si	
Fe-0.75C-1.46Si	825, 850
Fe-0.53C-0.47Mn	765
Fe-0.50C-0.53Mn	830
Fe-0.57C-0.94Mn	755, 775, 806, 825
Fe-0.64C-0.56Mn-0.37Si	755, 775, 806, 825
Fe-0.66C-1.06Mn-0.92Si	
Fe-0.68C-1.58Mn-1.33Si	

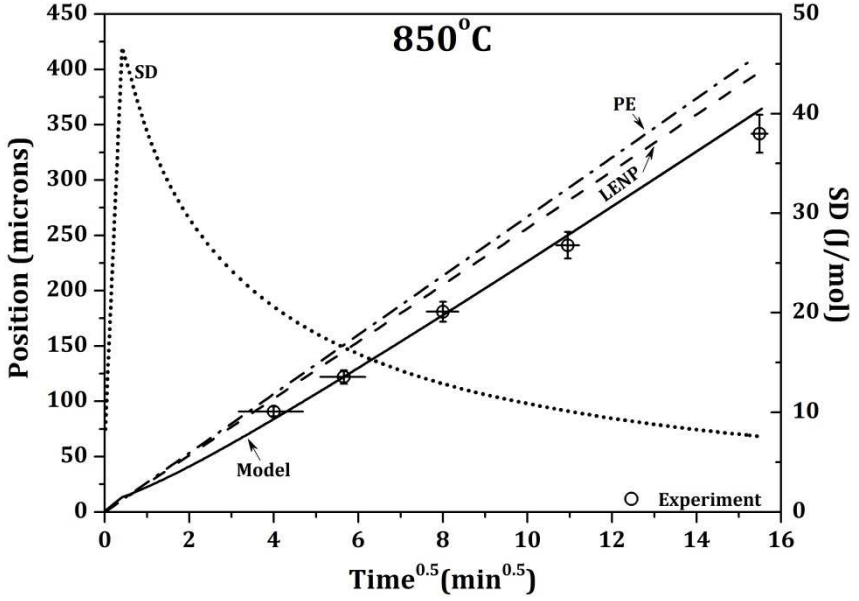
Each sample is electroplated with pure Fe (5-10μm) to minimize the effects of solute oxide on carbon removal.

Experimental results: Fe-0.74C-0.45Si (wt. %)

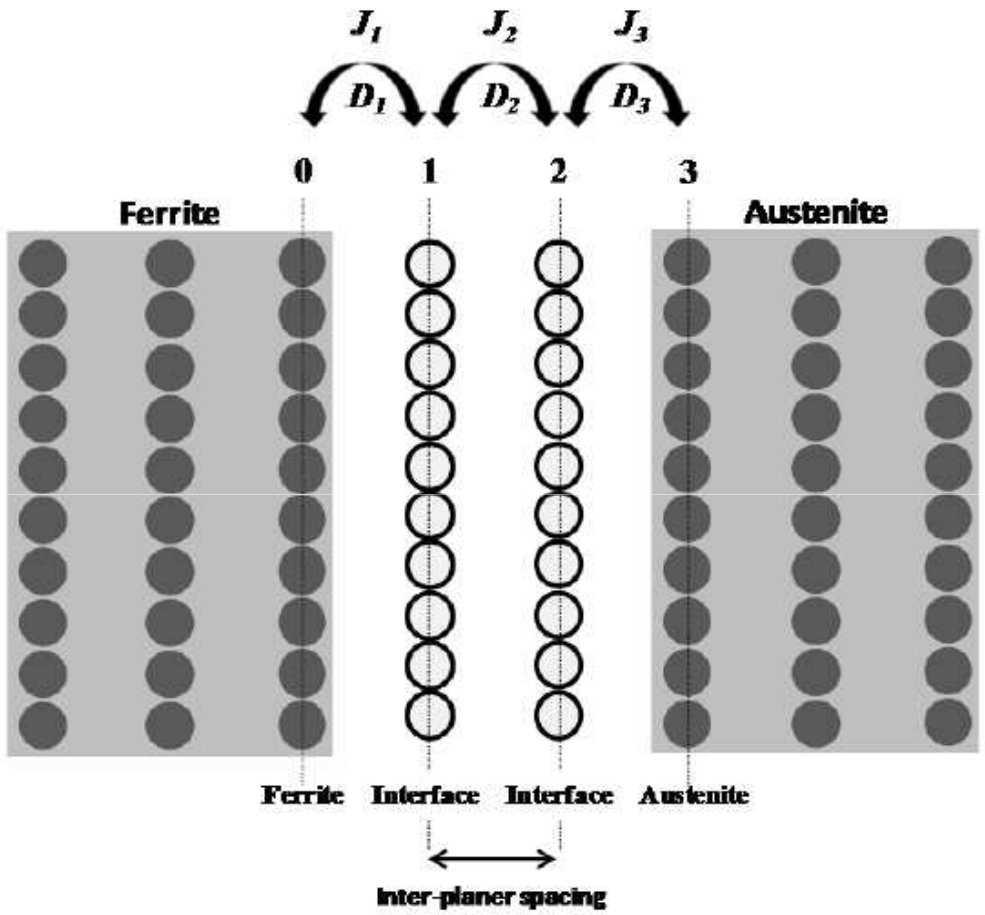








Interface model including 'solute-drag' [6]



$$J_X^1 = -\frac{D_X^1}{RT} x_{Fe}^0 x_X^0 \frac{(\mu_X^1 - \mu_X^0) - (\mu_{Fe}^1 - \mu_{Fe}^0)}{\delta}$$

$$J_X^2 = -\frac{D_X^2}{RT} x_{Fe}^1 x_X^1 \frac{(\mu_X^2 - \mu_X^1) - (\mu_{Fe}^2 - \mu_{Fe}^1)}{\delta}$$

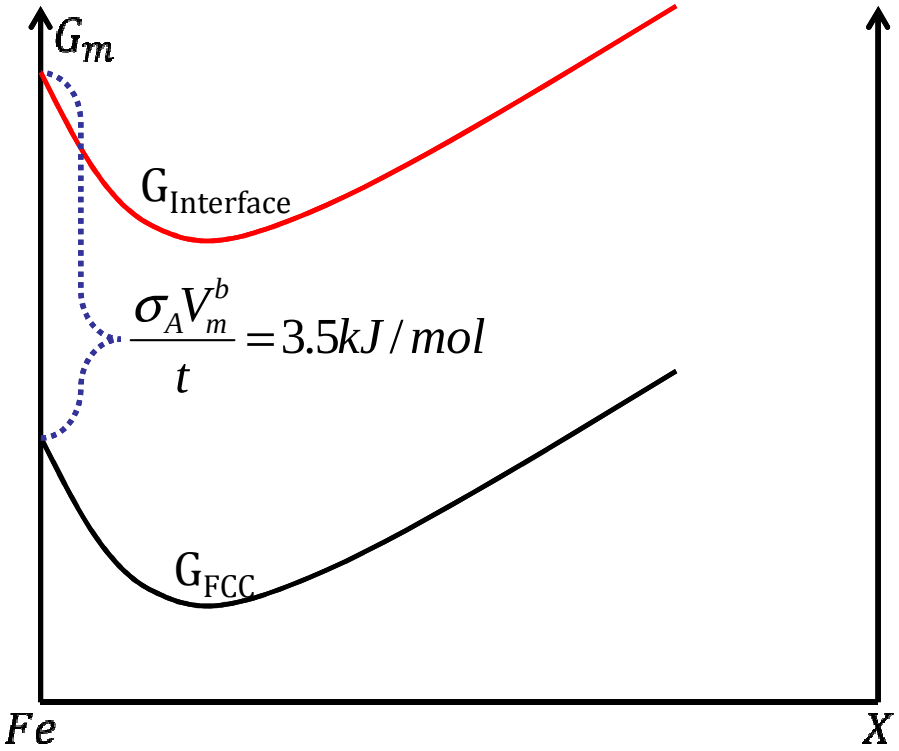
$$J_X^3 = -\frac{D_X^3}{RT} x_{Fe}^2 x_X^2 \frac{(\mu_X^3 - \mu_X^2) - (\mu_{Fe}^3 - \mu_{Fe}^2)}{\delta}$$

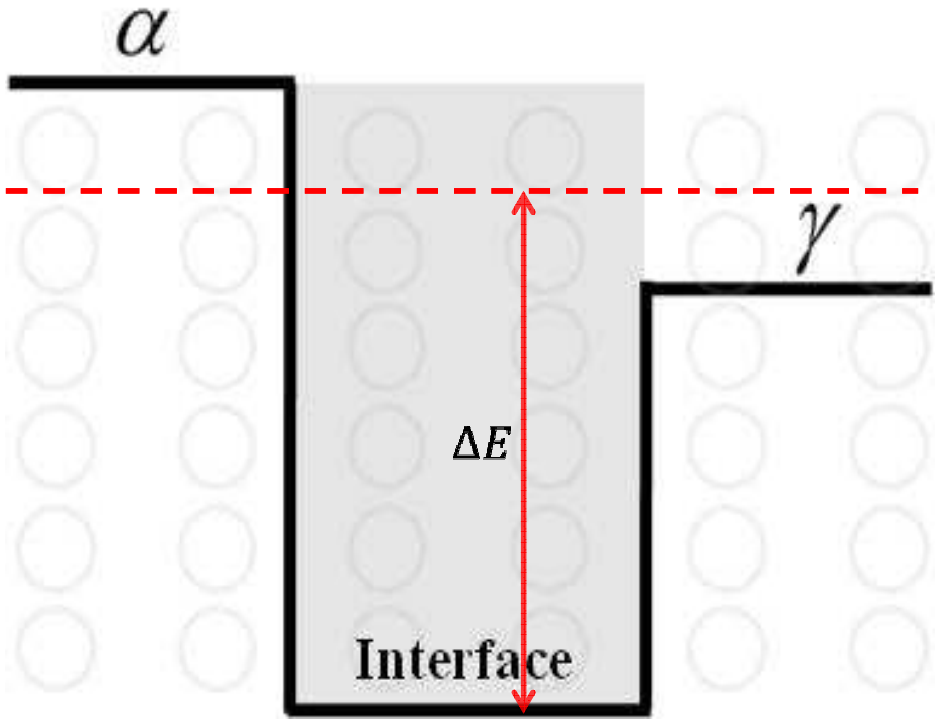
Hillert's expression for diffusional dissipation

$$\Delta G^{dissipated} = \sum_{i=1}^{i=3} -\frac{V_m}{v} \bullet J_X^i \bullet \left[(\mu_X^i - \mu_X^{i-1}) - (\mu_{Fe}^i - \mu_{Fe}^{i-1})\right]$$

[6] Zurob HS, Panahi D, Hutchinson CR, Brechet Y, Purdy GR, MMTA 2013;44:3456-71

Thermodynamic description of the interface [6]





The reference state for the free energy was shifted by 3.5kJ/mol to capture an interfacial energy of the order of 0.5 J/m².

The Fe-X interaction term is modified to provide a binding energy for X to the interface.

[6] Zurob HS, Panahi D, Hutchinson CR, Brechet Y, Purdy GR, MMTA 2013;44:3456-71

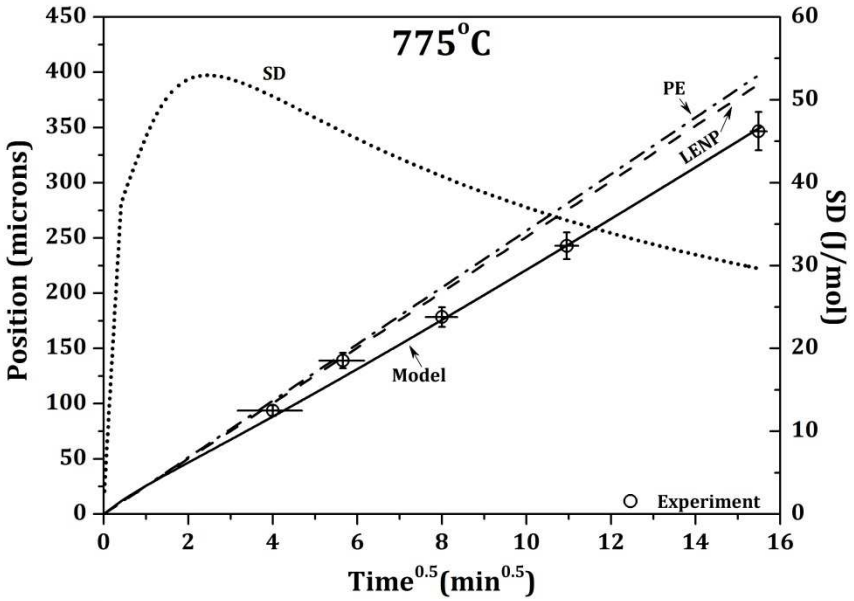
Interface parameters

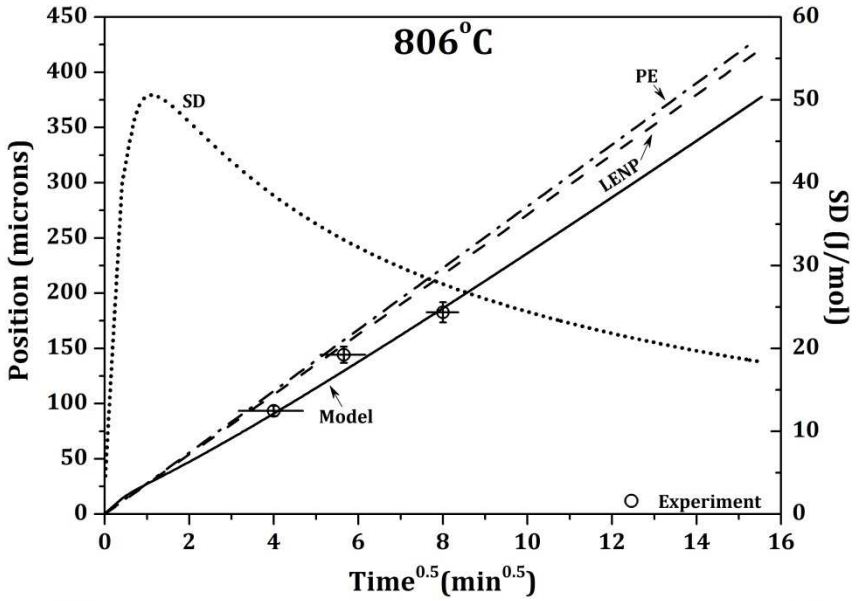
Alloy	Binding energy (with respect to mid-point of Mn or Si chemical potential in ferrite and austenite)
Fe-C-Si	-9.0kJ/mol
Fe-C-Mn	-2.5kJ/mol

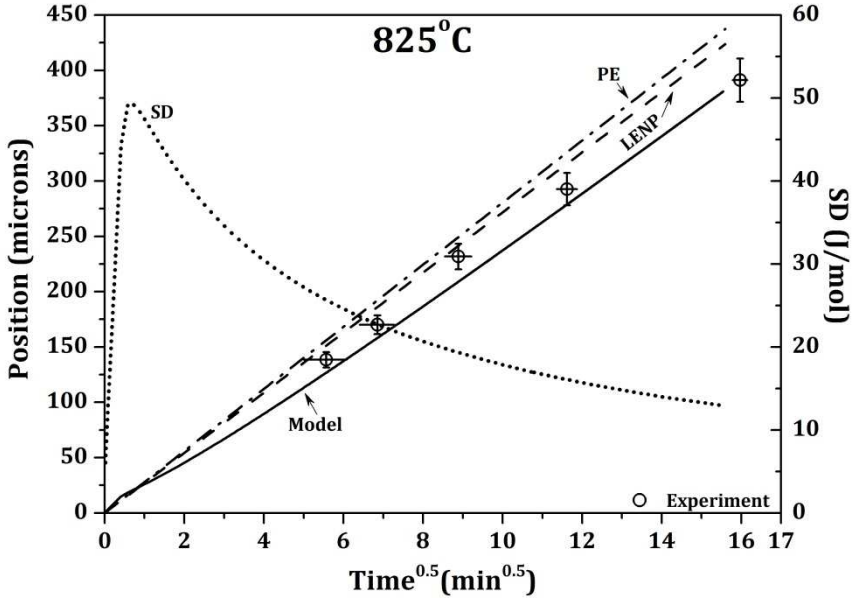
Alloy	D_1	D_2	D_3
Fe-C-Si	Si Diffusivity in Ferrite	Si Diffusivity in Austenite	Si Diffusivity in Austenite
Fe-C-Mn	Mn Diffusivity in Ferrite	$\sqrt{D_1 \bullet D_2}$	Mn Diffusivity in Austenite

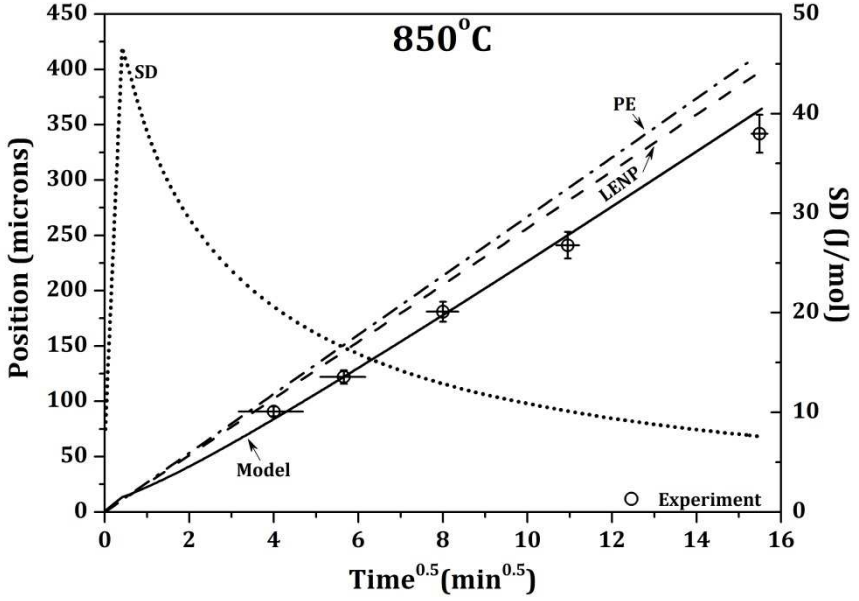
- Effect of solutes on carbon diffusivities in ferrite is also included (Dictra)

Ternary results: Fe-0.74C-0.45Si (wt. %)

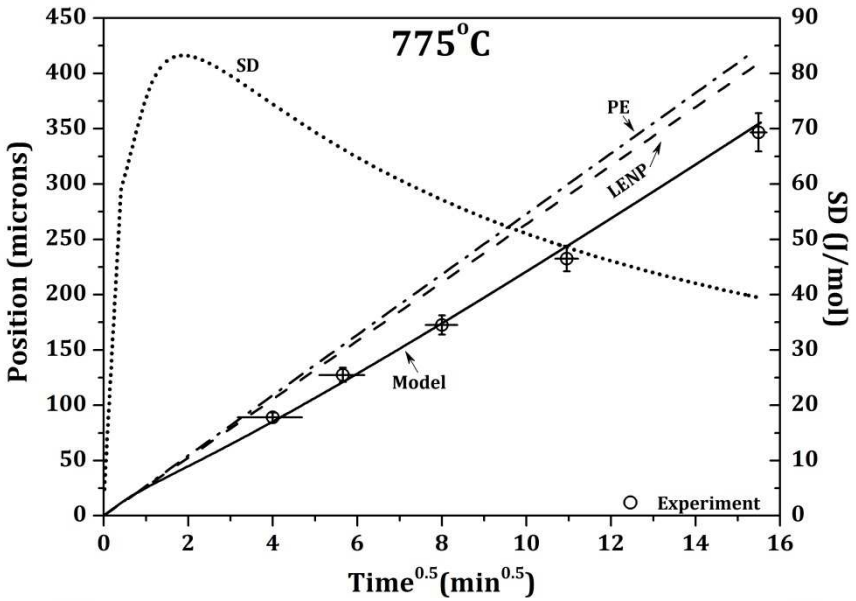


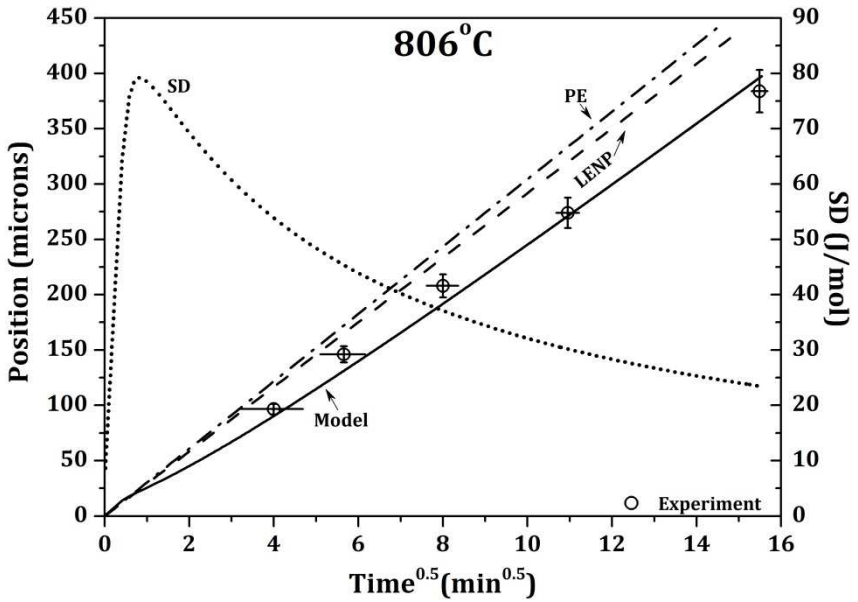


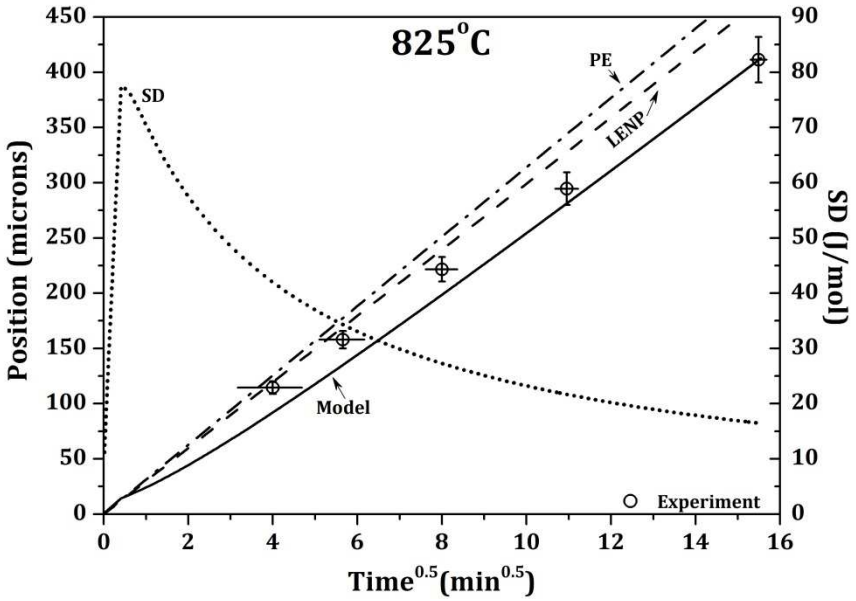


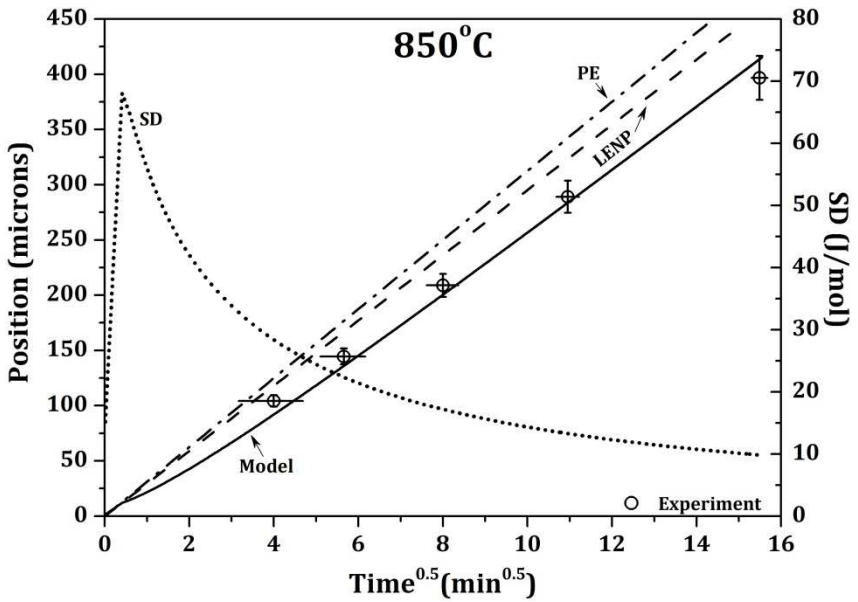


Ternary results: Fe-0.76C-0.84Si (wt. %)

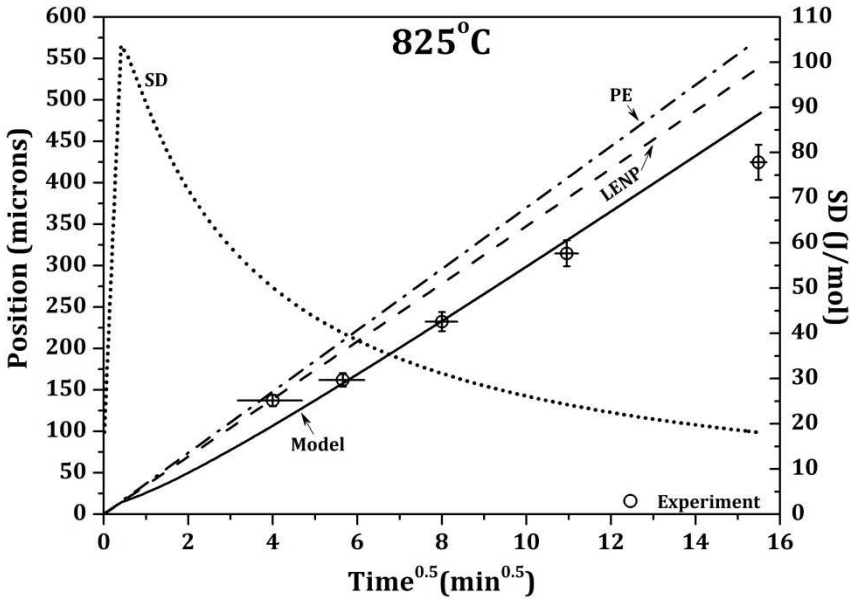


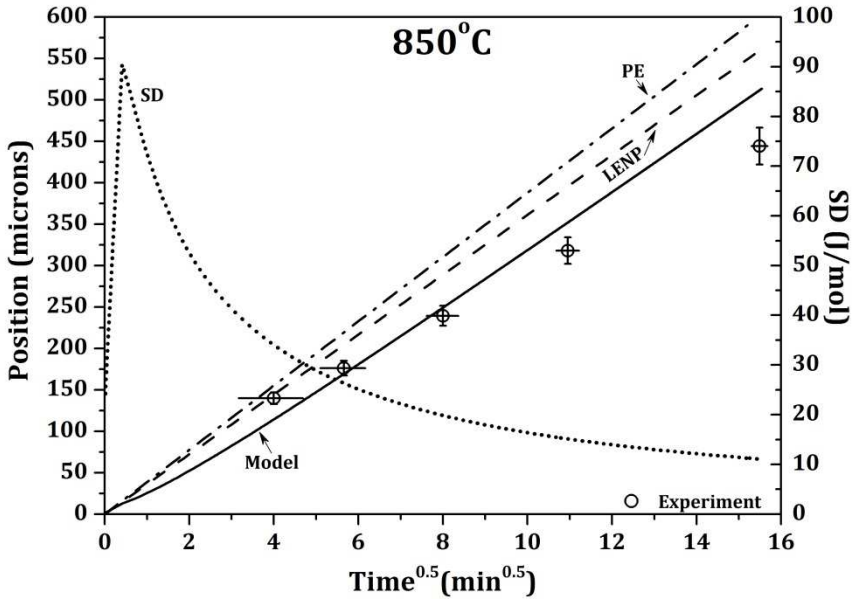






Ternary results: Fe-0.75C-1.46Si (wt. %)





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Fe-C-Mn	Mn Diffusivity in Ferrite	$\sqrt{D_1 \bullet D_2}$	Mn Diffusivity in Austenite

- Effect of solutes on carbon diffusivities in ferrite is also included (Dictra)

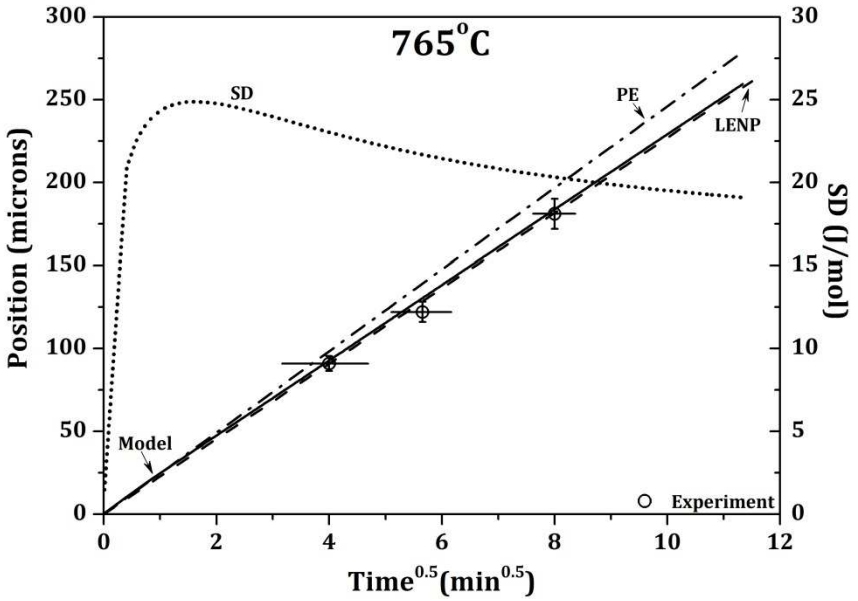
- The thermodynamic expressions for ferrite and austenite in Fe-C-Mn system are modified for more accurate thermodynamic description:

  $L(BCC,Fe,Mn:Va;0)=+20768.8-20.97*T$[2] $L(FCC,Fe,Mn:Va;0)=+11758-13.89*T$[6]

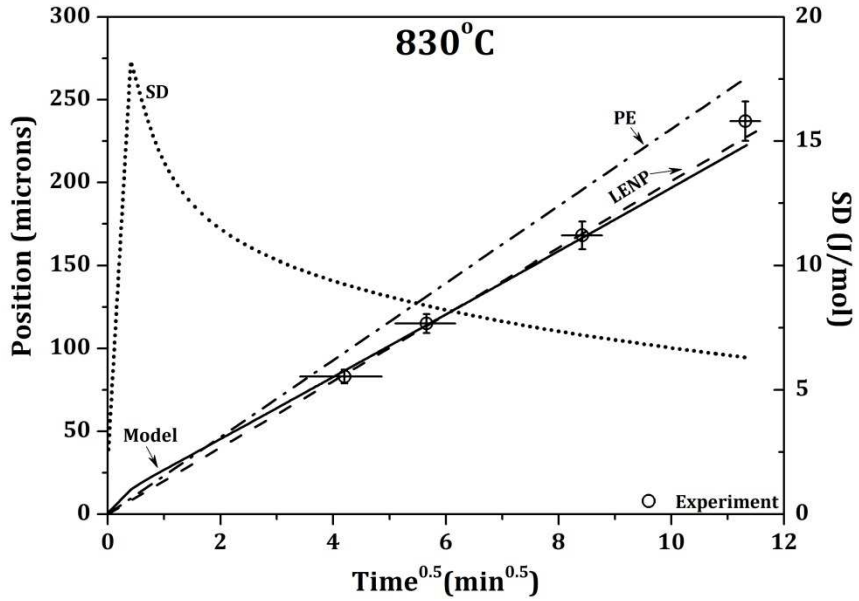
[6] Zurob HS, Panahi D, Hutchinson CR, Brechet Y, Purdy GR, MMTA 2013;44:3456-71

Ternary results: Fe-0. 5C-0.5Mn (wt. %)

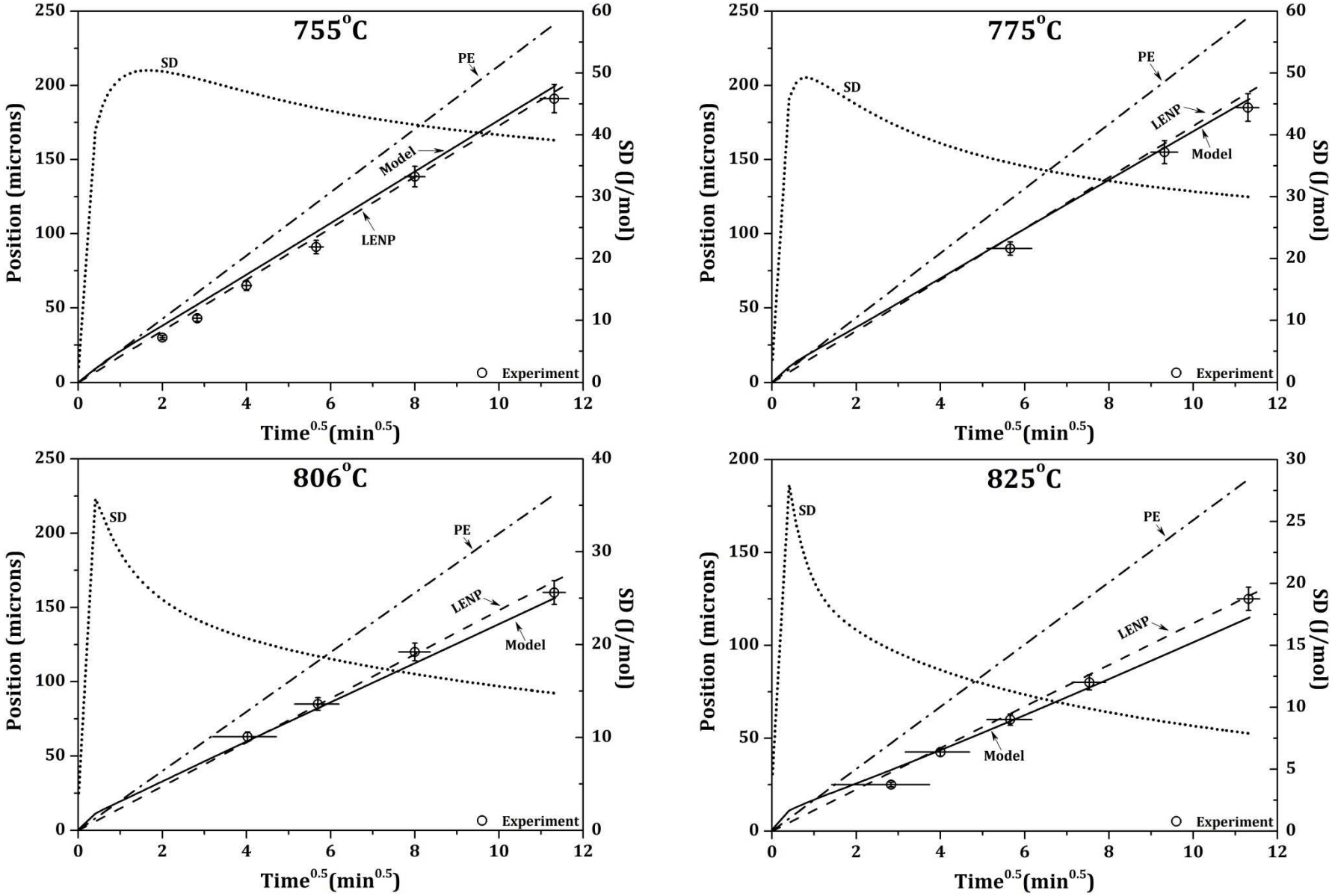
Fe-0.53C-0.47Mn



Fe-0.50C-0.53Mn



Ternary results: Fe-0. 57C-0.94Mn (wt. %)

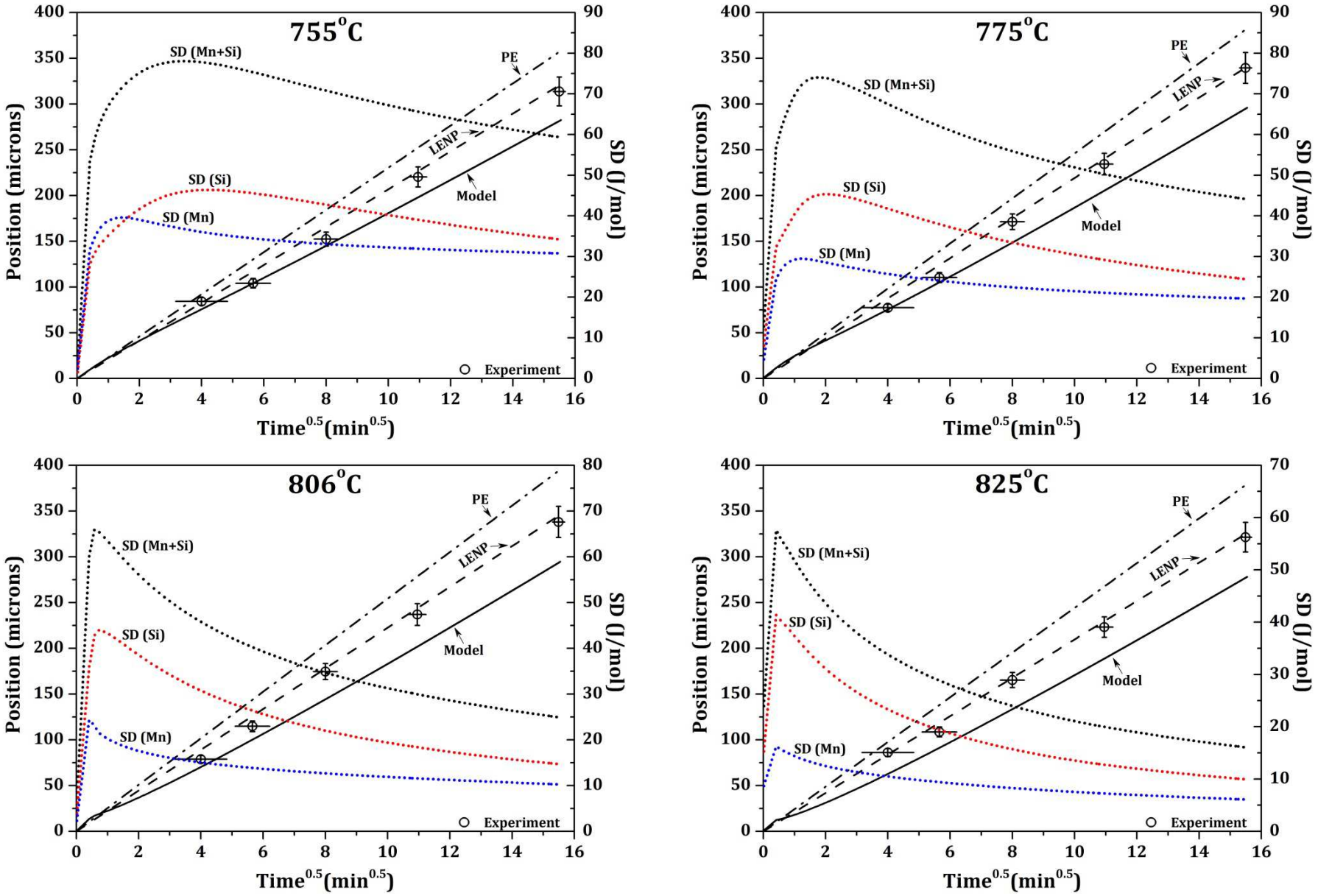


Extension to Fe-C-Mn-Si quaternary system

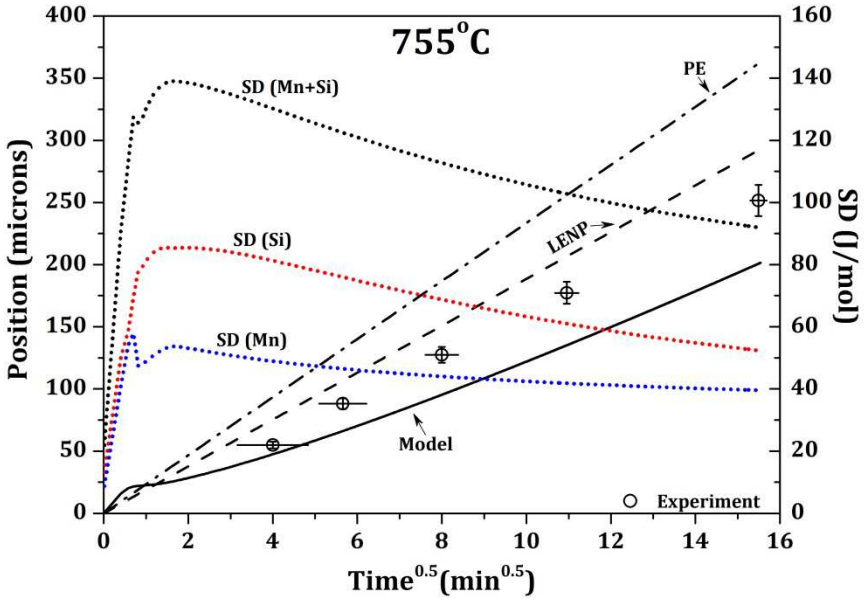
- Solute binding energies and trans-interface diffusivities calibrated from the ternary systems are used to test how well the kinetics in the quaternary systems are predicted.

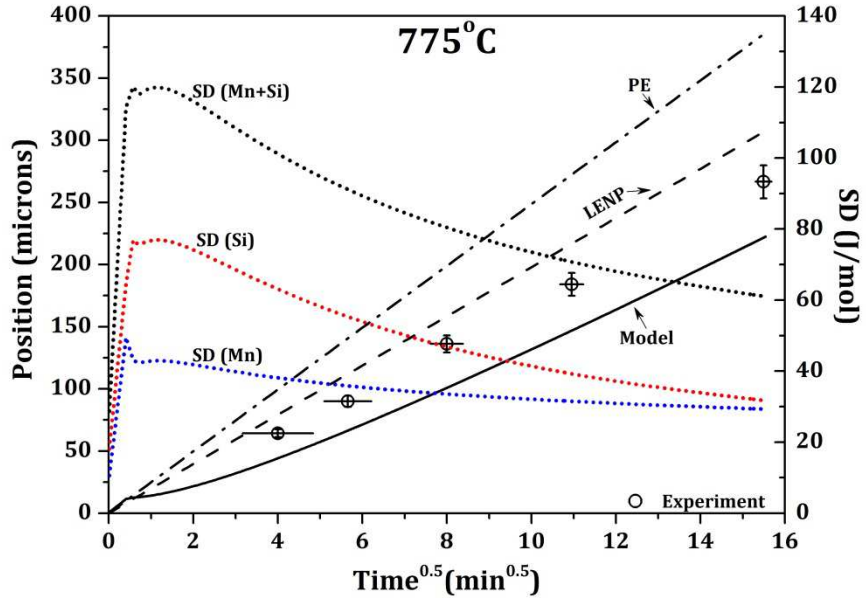
- Two conditions are examined:
  - The interaction between Mn & Si in the interface is the same as that in Austenite (ie. C-SDE exists)
  - No interaction between Mn & Si in the interface

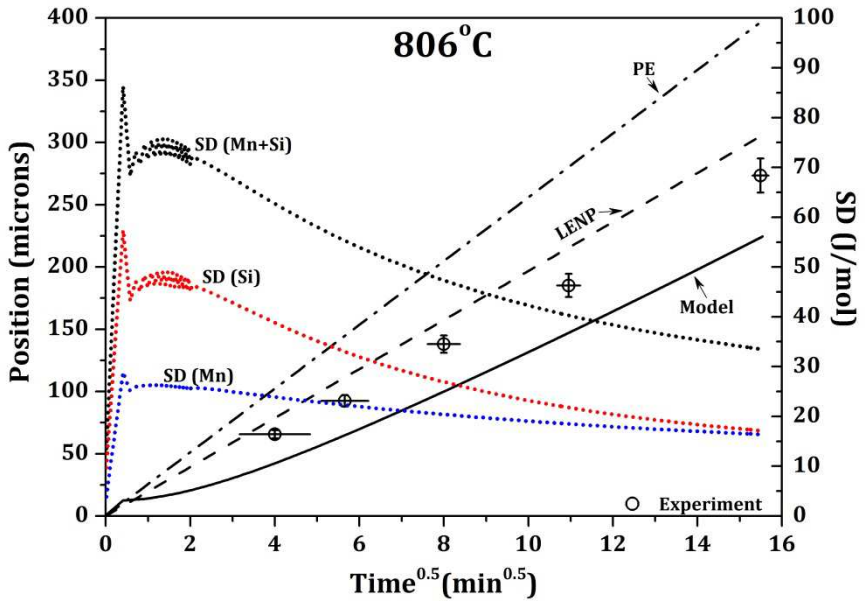
$(Mn:Si)^{I}=(Mn:Si)^{\gamma}$ for Fe-0.64C-0.56Mn-0.37Si (wt. %)

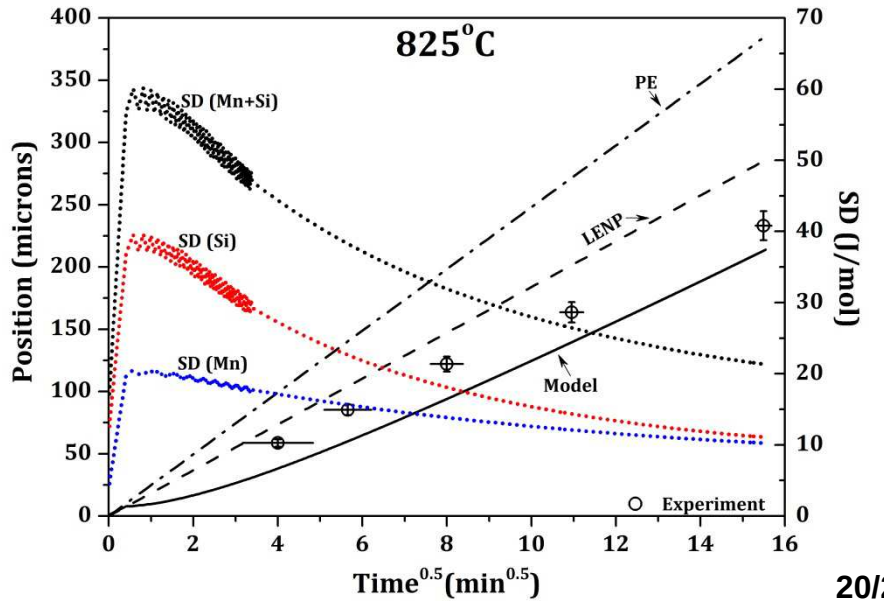


$(Mn:Si)^{I}=(Mn:Si)^{\gamma}$ for Fe-0.66C-1.06Mn-0.92Si (wt. %)

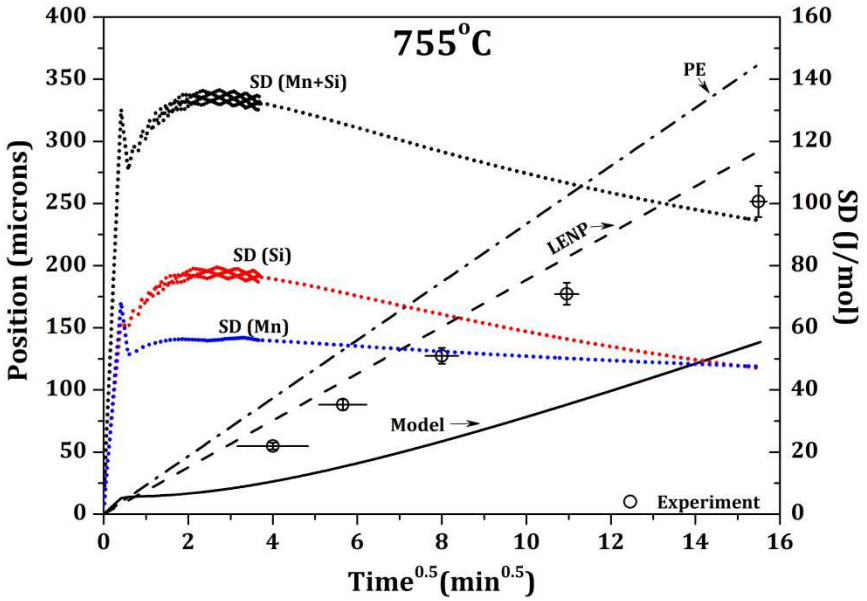


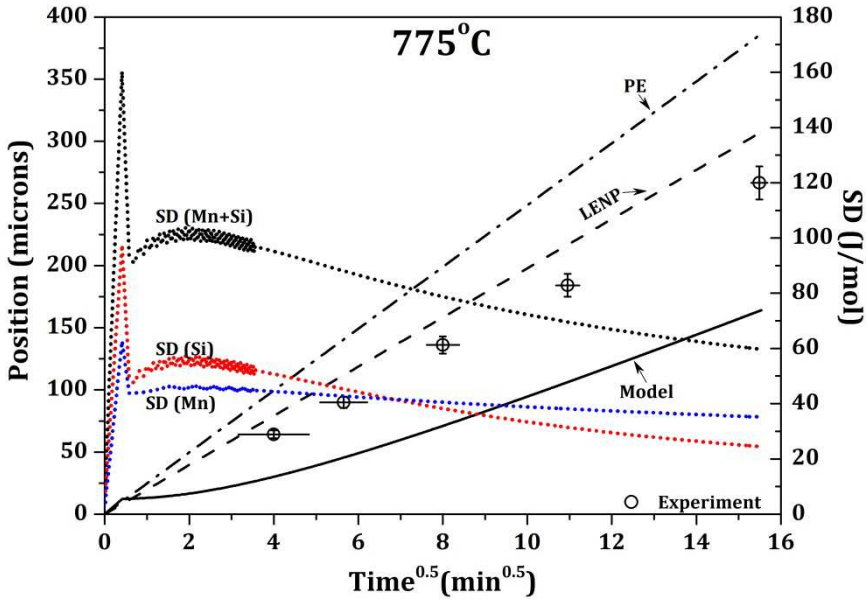


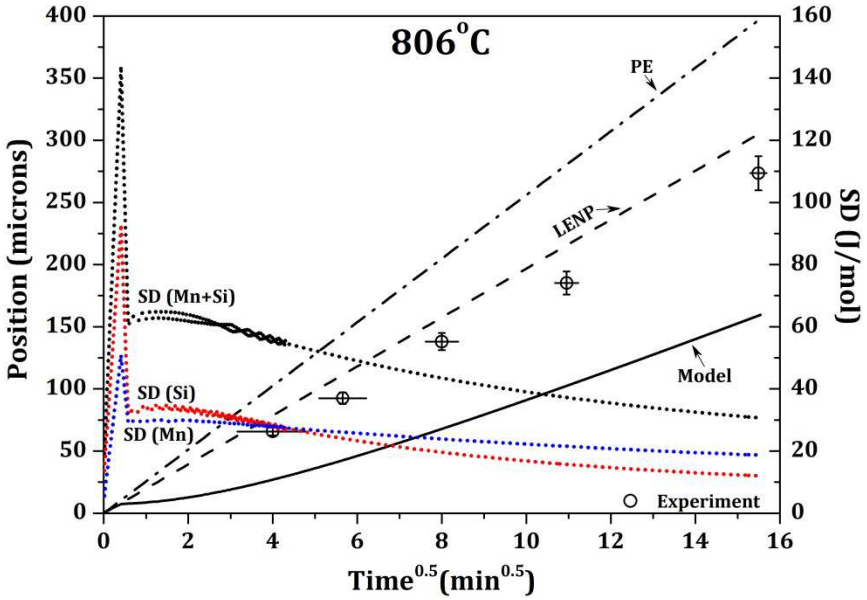


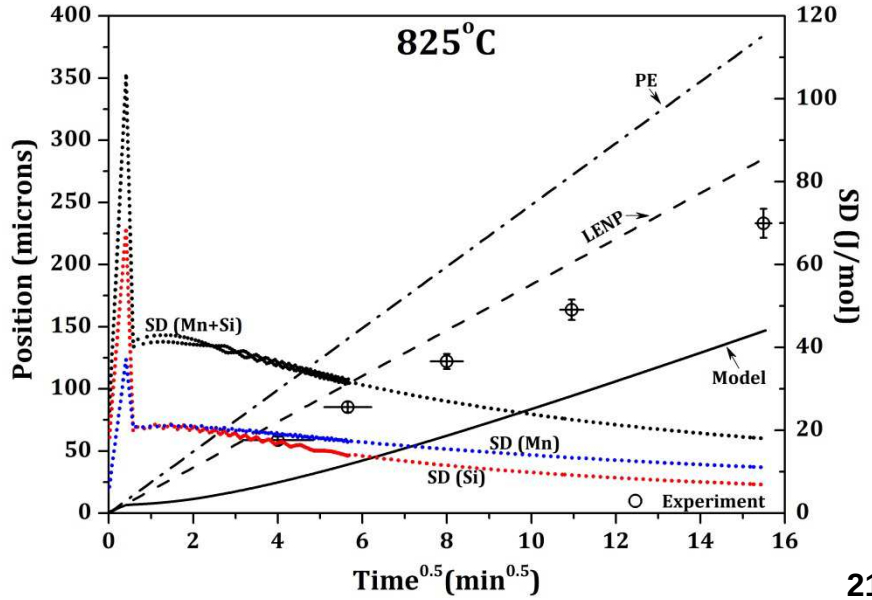


$(Mn:Si)^{I}=(Mn:Si)^{\gamma}$ for Fe-0.68C-1.58Mn-1.33Si (wt. %)

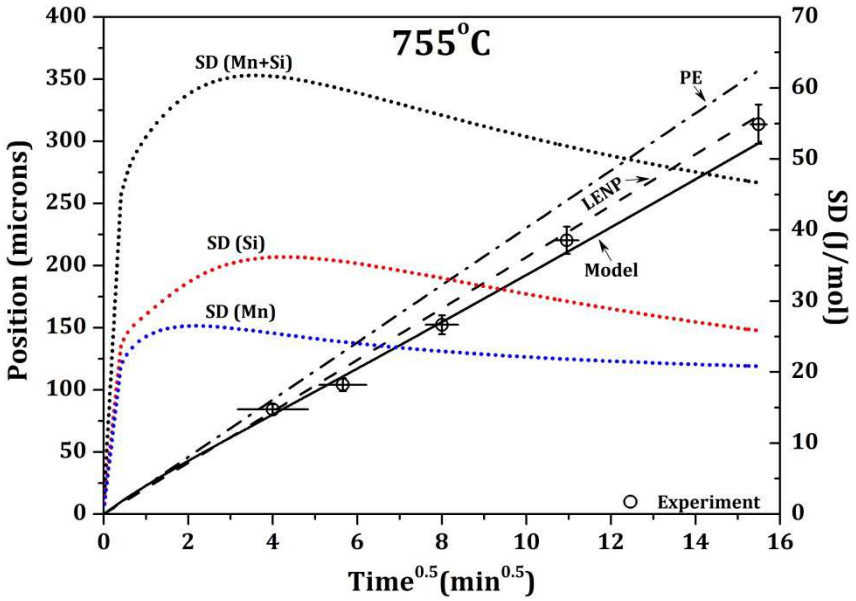


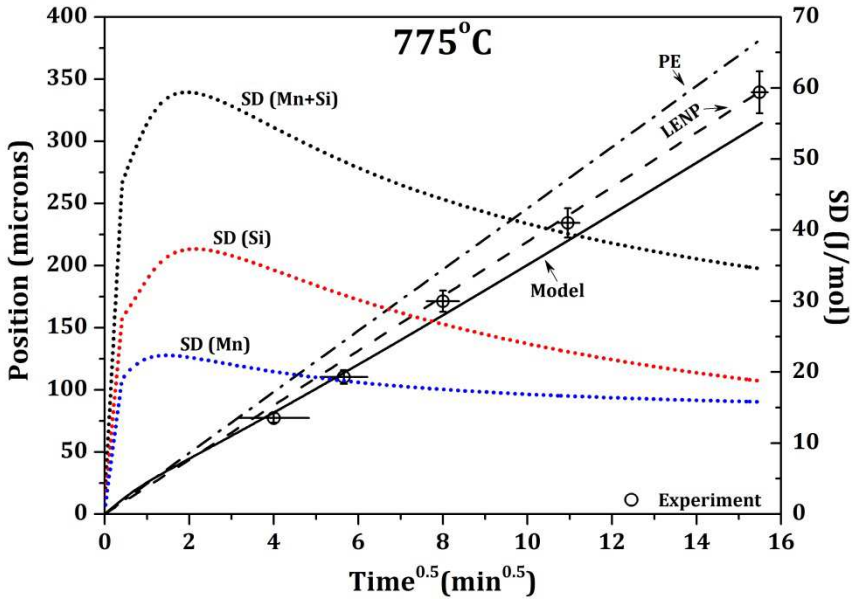


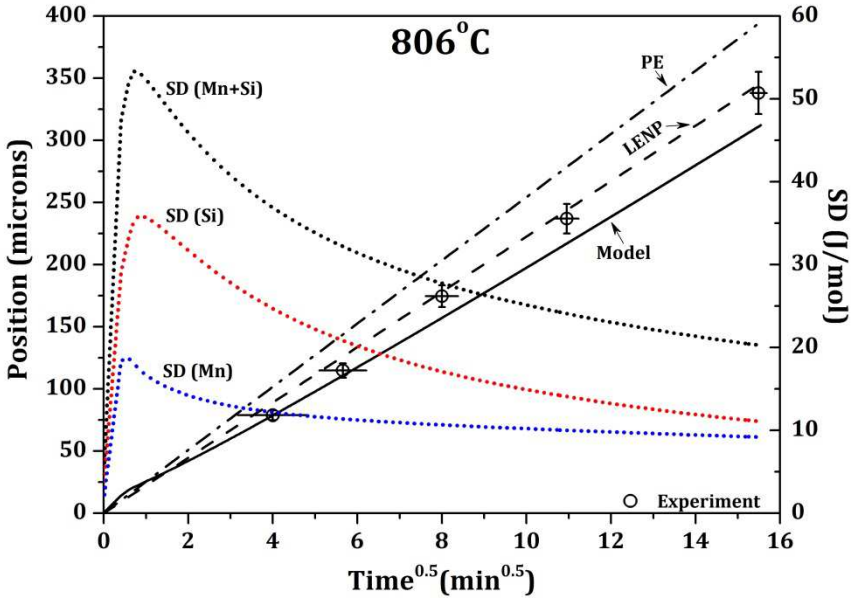


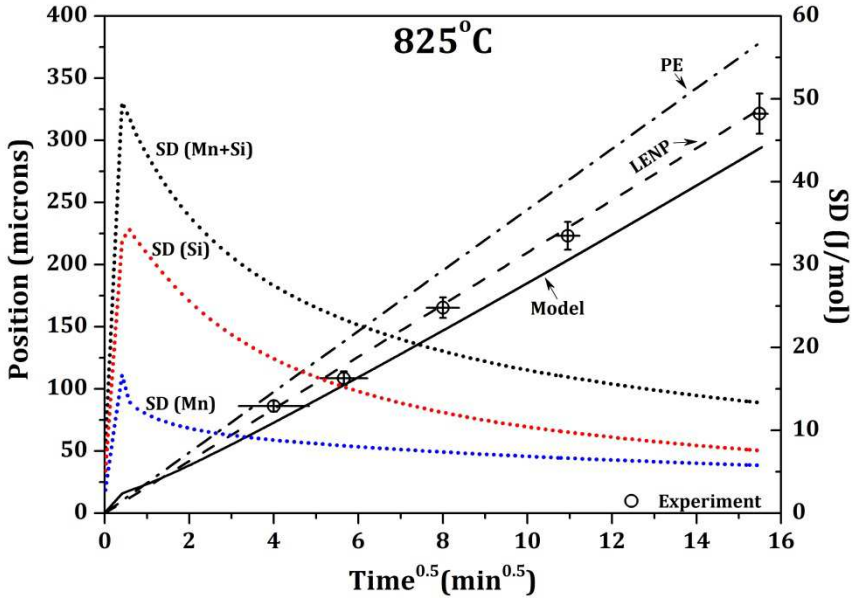


$(Mn:Si)^{I}$=0 for Fe-0.64C-0.56Mn-0.37Si (wt. %)









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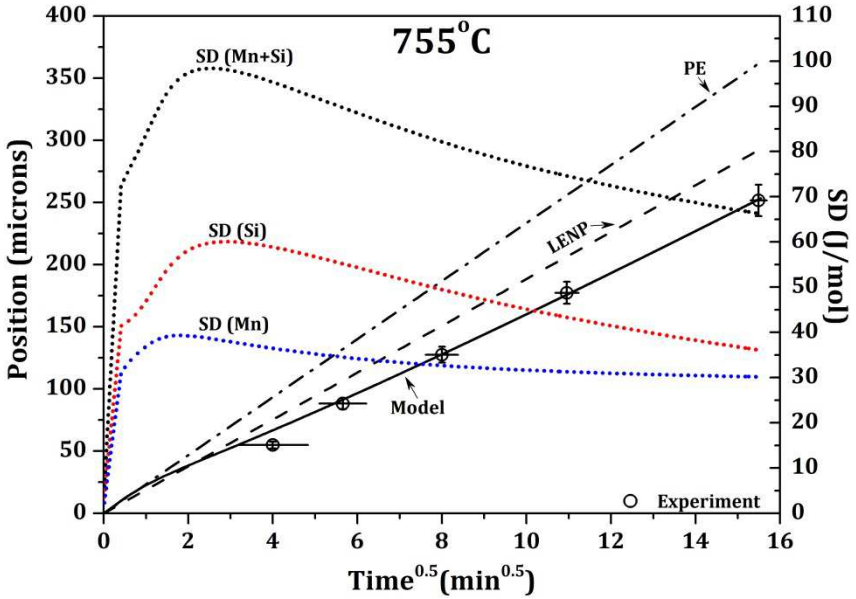

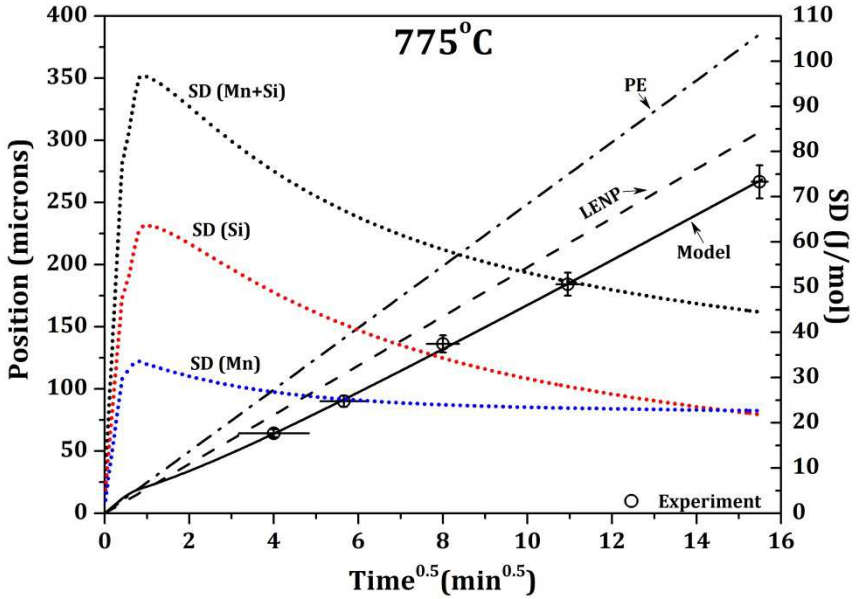

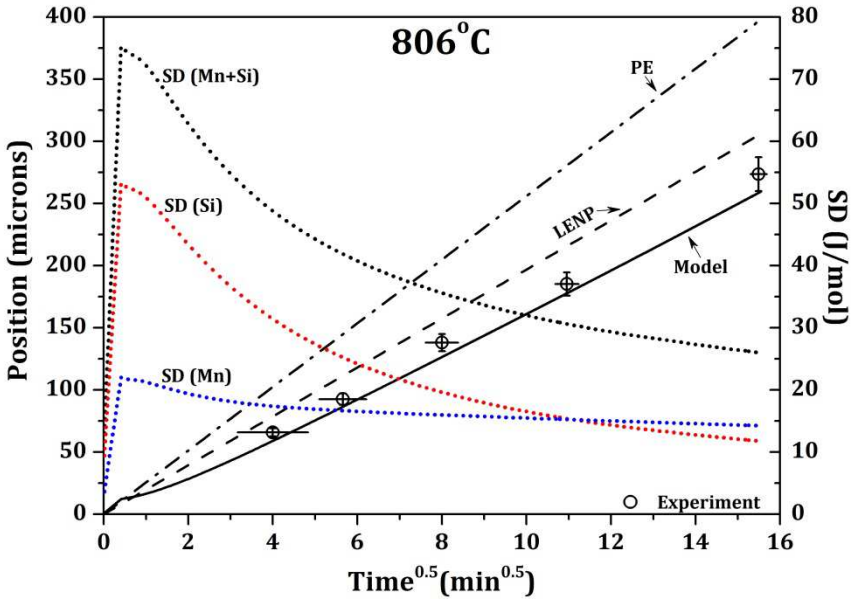

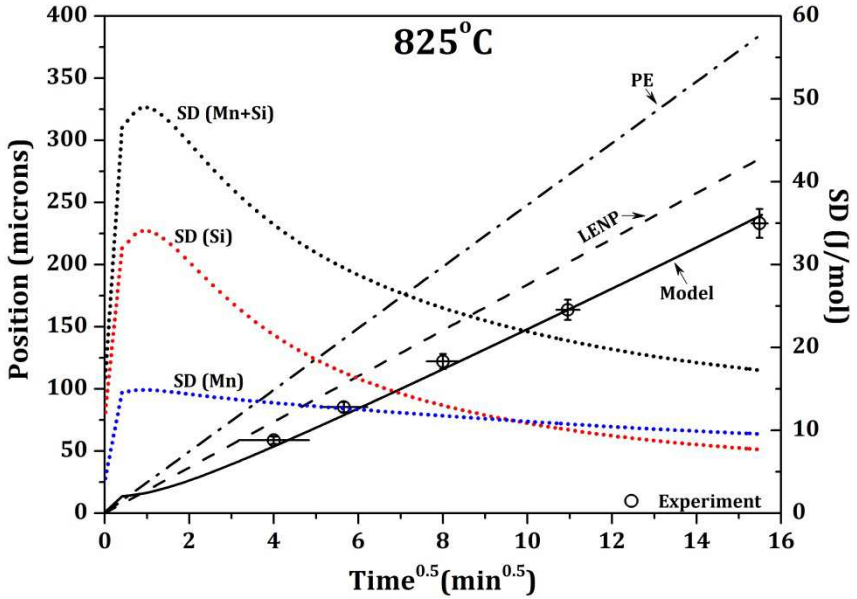

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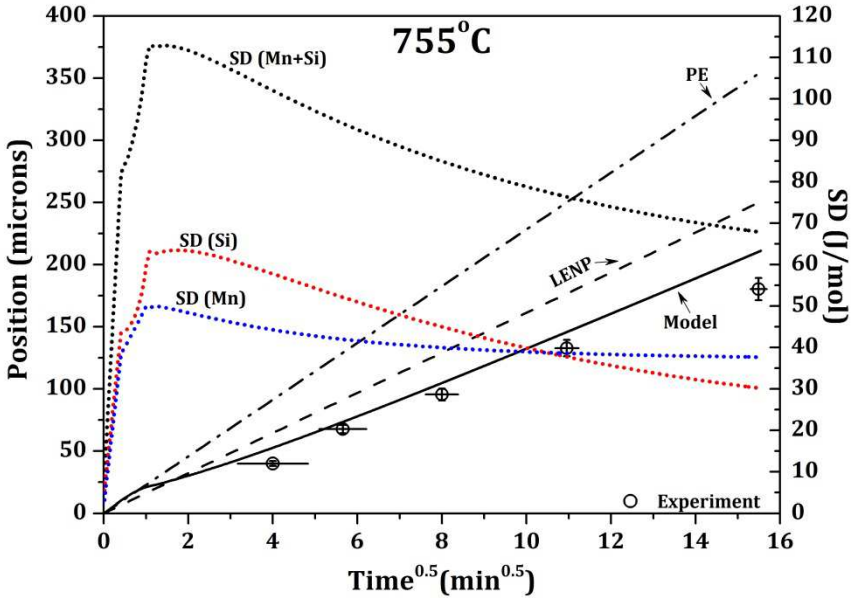
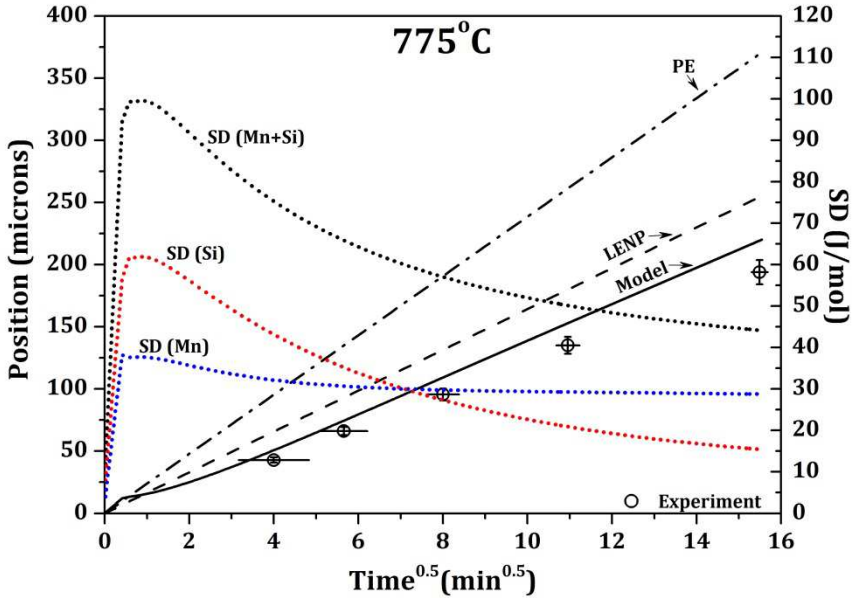
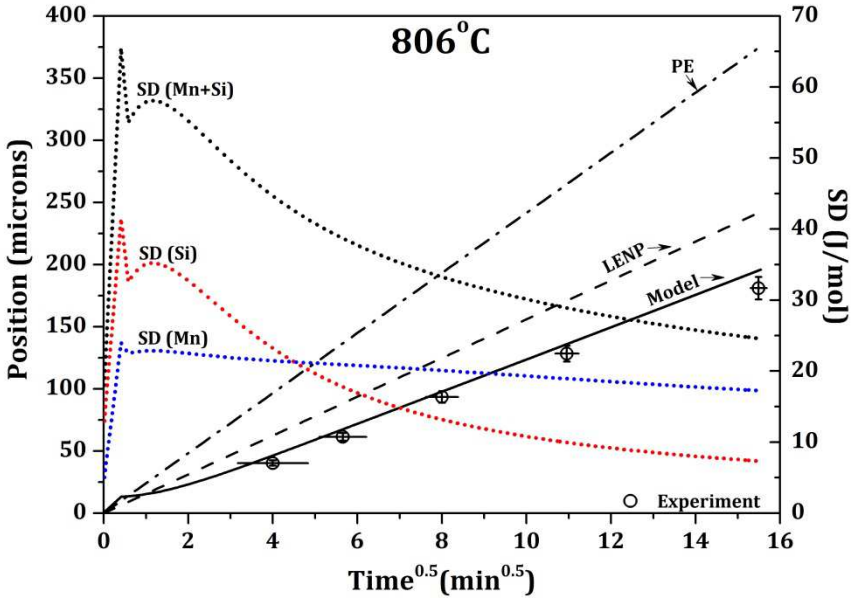
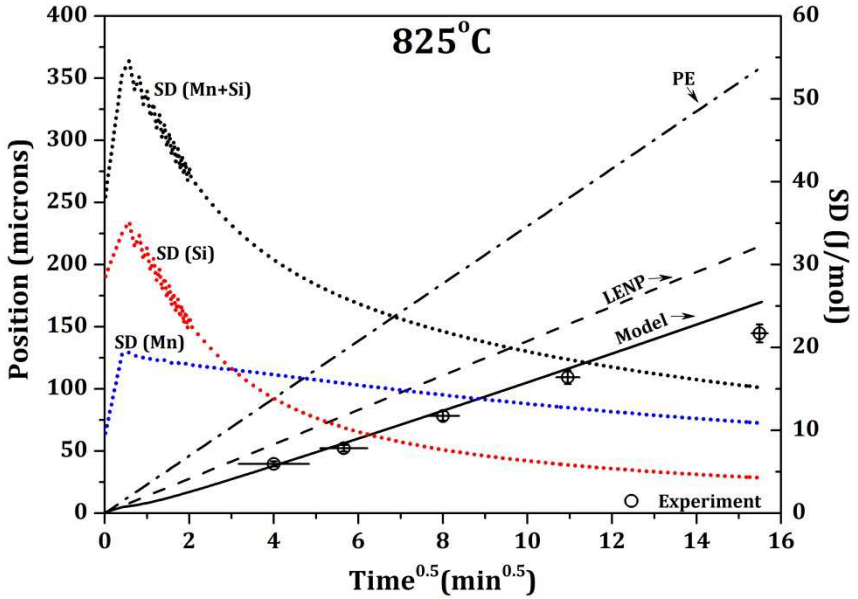








Summary

- Ferrite growth kinetics of Fe-C-Mn-Si alloys can be reasonably well described using parameters tuned from ternary systems

- For the velocities encountered in decarb experiments, the kinetics of ferrite growth in Fe-C-Mn-Si are well described using no interaction between Mn and Si in the interface.

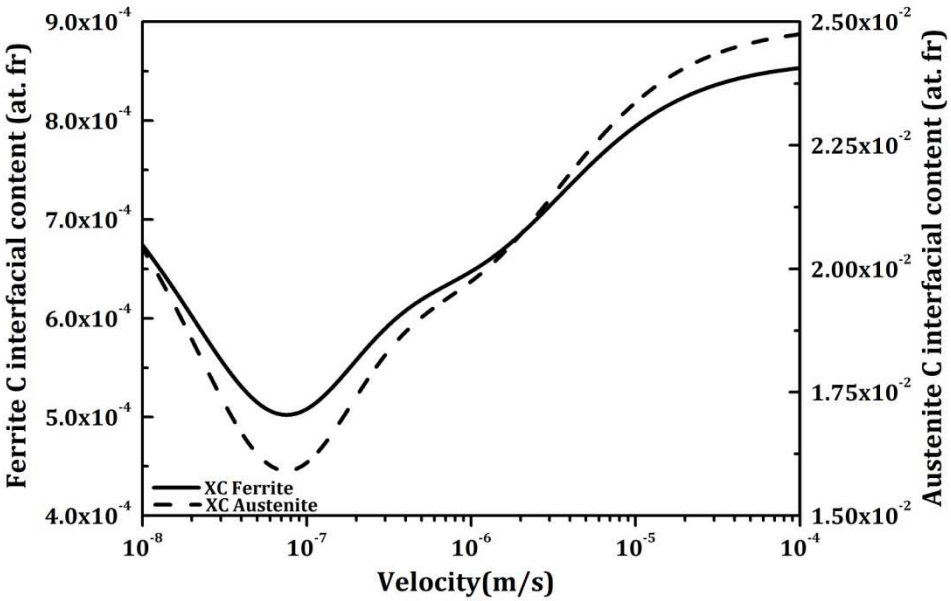
Discussion Points

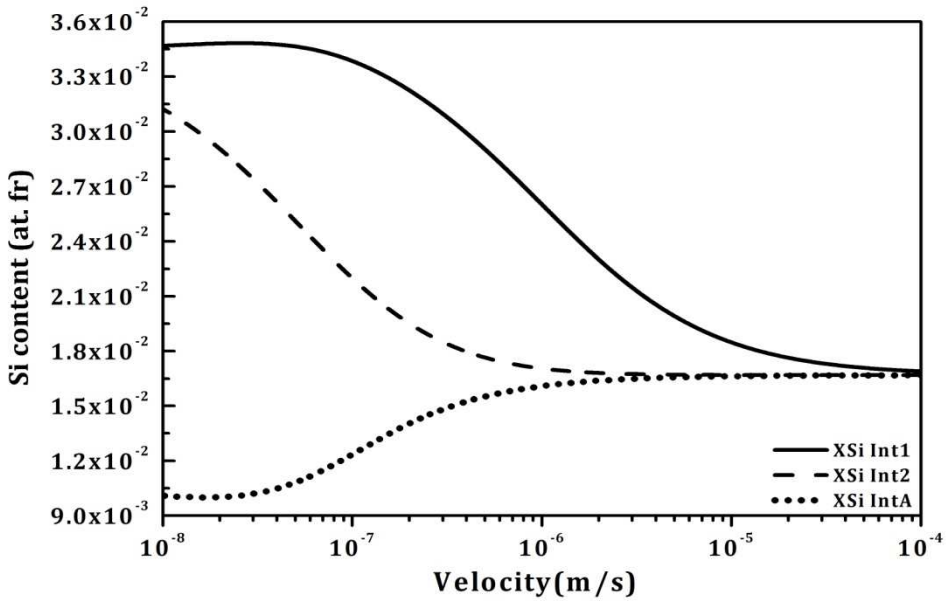
A suitable method to select the binding energy and cross-interface diffusivities (fga for Mn & faa for Si?) remains unresolved.

In Fe-C-Mn, the kinetics agree perfectly with LENP. It may seem too much of a coincidence for SD to be exactly the correct magnitude to give this overall effect.

The question of summing SD from different elements may require discussion (SD=SD(Mn)+SD(Si), SD=largest of SD(Mn) or SD(Si)?, etc.)

Interfacial Compositions: Fe-0.76C-0.84Si (wt. %) at 775°C





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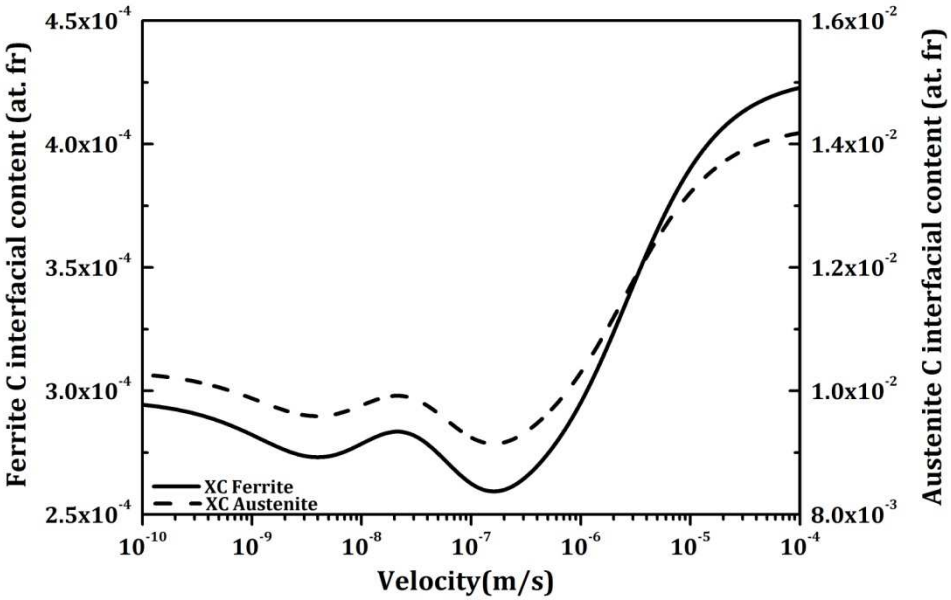
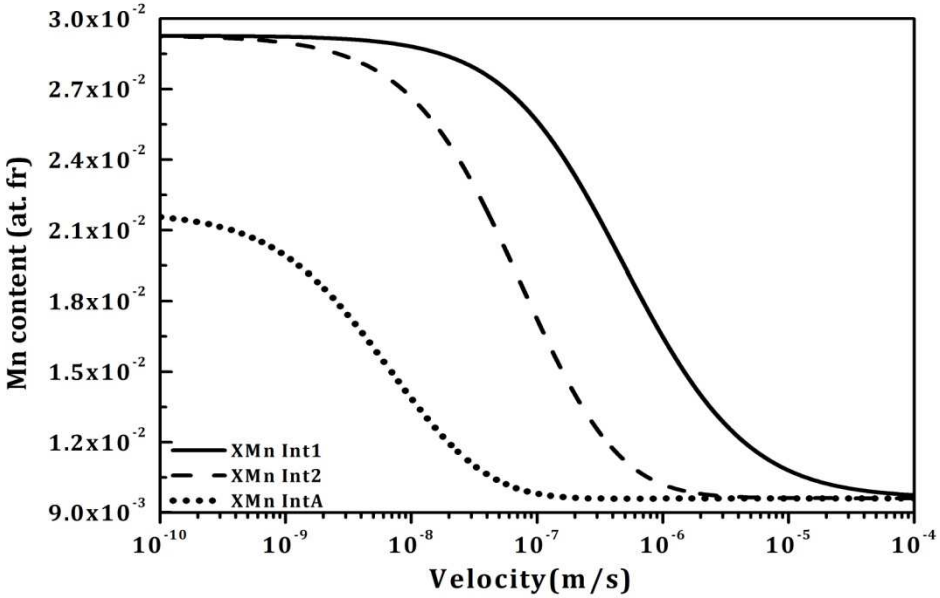
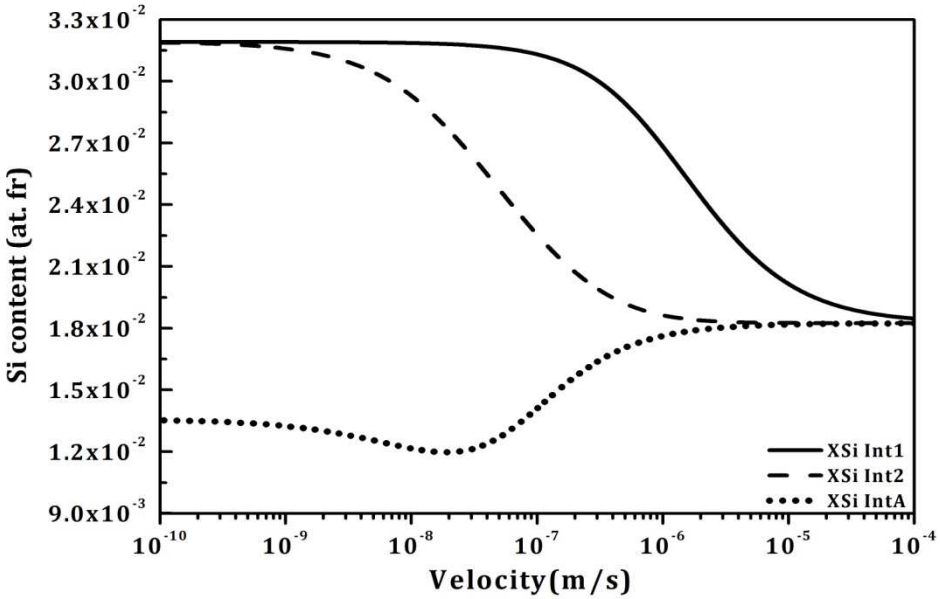
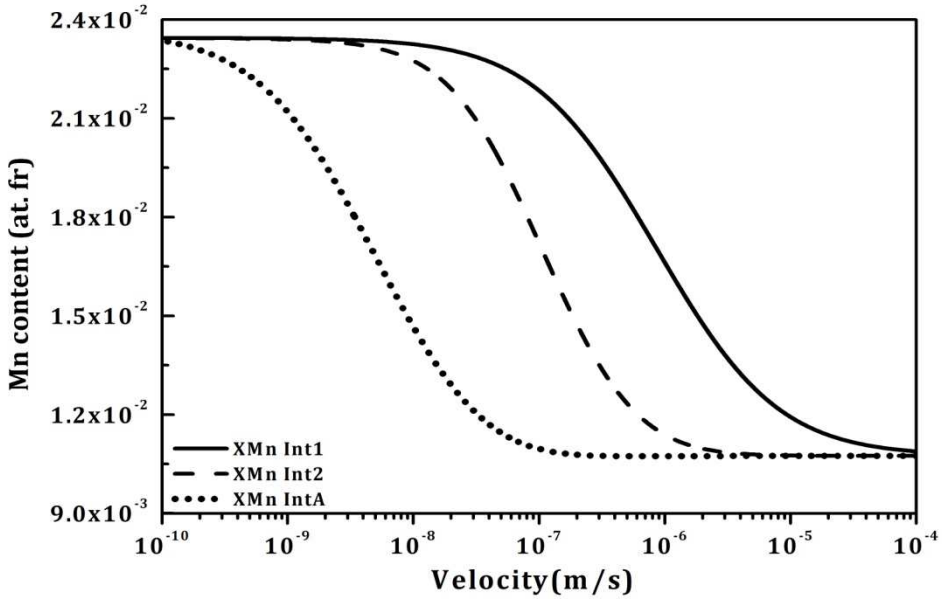
Interfacial Compositions: Fe-0. 57C-0.94Mn (wt. %) at 775°C

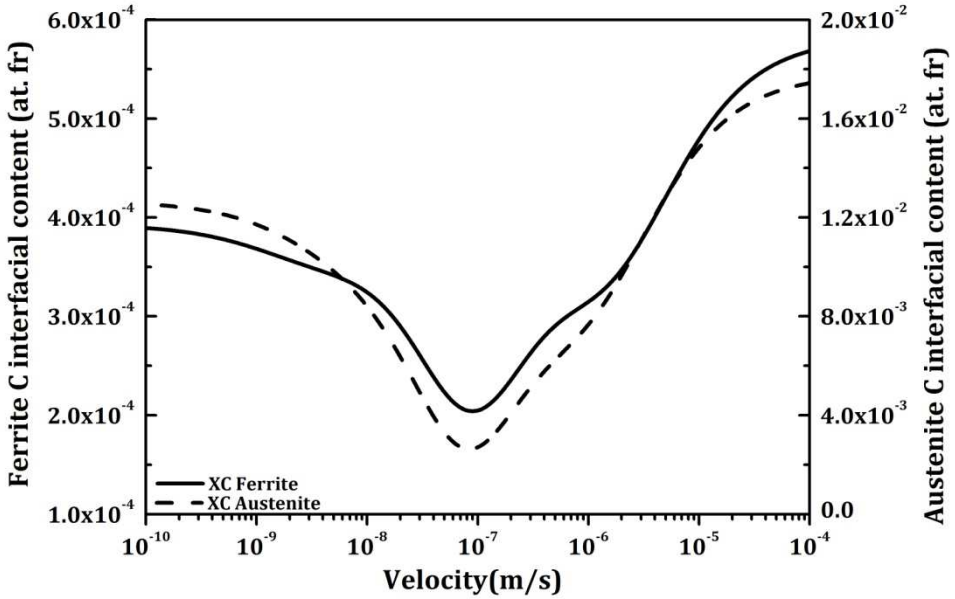




Interfacial Compositions for $(Mn:Si)^{I}=0$: Fe-0.66C-1.06Mn-0.92Si at 775°C







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