June 7, 2011

Alloying element partition and growth kinetics of proeutectoid ferrite in hot-deformed Fe-C-Mn-Si quaternary austenite

R. Wei, K.Kanno and M. Enomoto

Department of Materials Science and Engineering
Ibaraki University

Background

- A large amount of data is available on the hardenability of low alloy steel.

- The effects of alloying elements on proeutectoid ferrite transformation in Fe-C-X ternary alloys have been studied extensively.

- The transformation behavior in Fe-C-X_1-X_2 quaternary alloys may not be just the average of the ternary alloys because alloying elements have an interaction with each other. These are tentatively called the synergistic effects.

Synergistic effects

Synergistic effects can arise from,

a) Diffusional interaction between alloying elements

b) Co-segregation at phase boundaries

c) Differences in partitioning behavior

a) Diffusional interaction between alloying elements

- Cross diffusion coefficient

$$J_i = -D_{ii}\frac{\partial c_i}{\partial x} - D_{ij}\frac{\partial c_i}{\partial x}$$

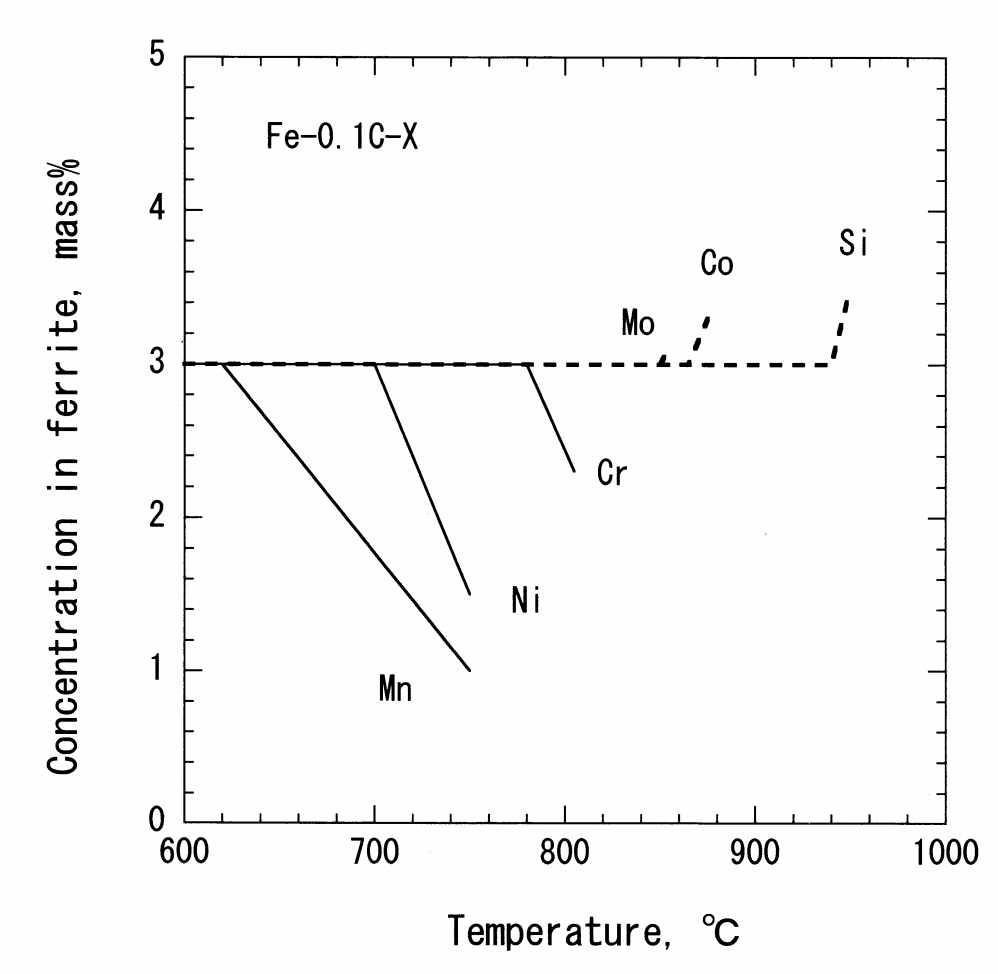
$$\frac{D_{ij}}{D_{ii}} = \varepsilon_{ij} x_i$$

directly related to thermodynamic effect

c) Co-segregation at interphase boundaries

- Segregation data, available for Mo and Mn, may be due to co-segregation with carbon.
- Co-segregation between substitutional elements at phase boundaries are very scarce.

3) Experimentally observed partitioning of alloying elements in Fe-0.1C-X alloys (schematic)



Experiment, results and discussion

- STEM-EDX analysis of the composition of ferrite formed from deformed Fe-0.1C-3Mn-1.5Si austenite
- Measurement of growth rate of ferrite

- Calculation of local equilibrium interfacial tie-line composition and growth rate of ferrite in quaternary alloys

  Coates equation

  TCC/ carbon-component ray

  DICTRA

Alloy specimen and heat treatment

Fe-0.1C-3Mn-1.5Si wt pct.

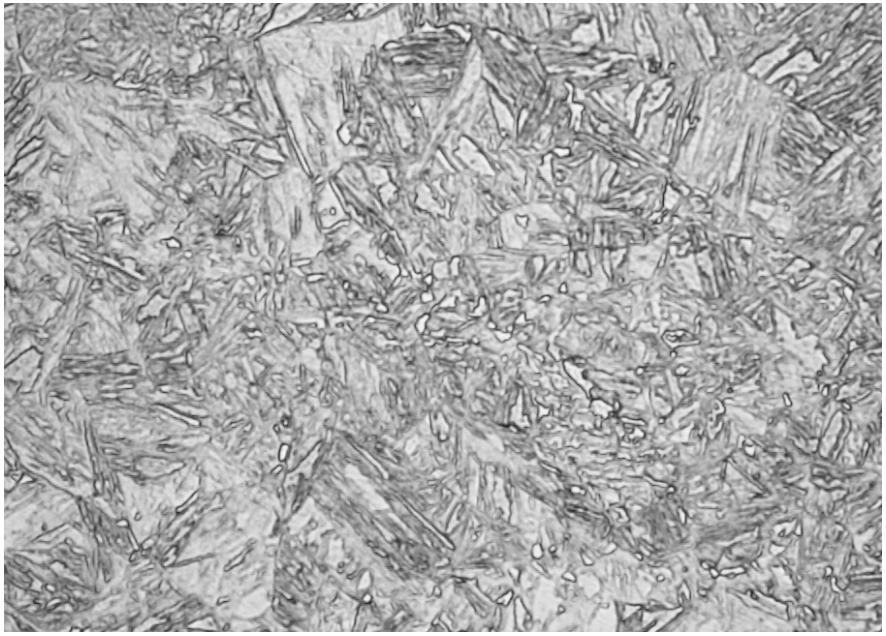
C	Mn	Si	P	Al	S	N(ppm)	O(ppm)
0.099	3.00	1.51	0.002	0.003	0.001	9	10

Heat treatment

Austenitized at 1200°C for 5 min, rapidly cooled to the reaction temperature, deformed 25 or 50% at a strain rate $1s^{-1}$, isothermally held for 60~1800s and quenched. The deformation was conducted by hot-deformation simulator (THERMEC-MASTER).

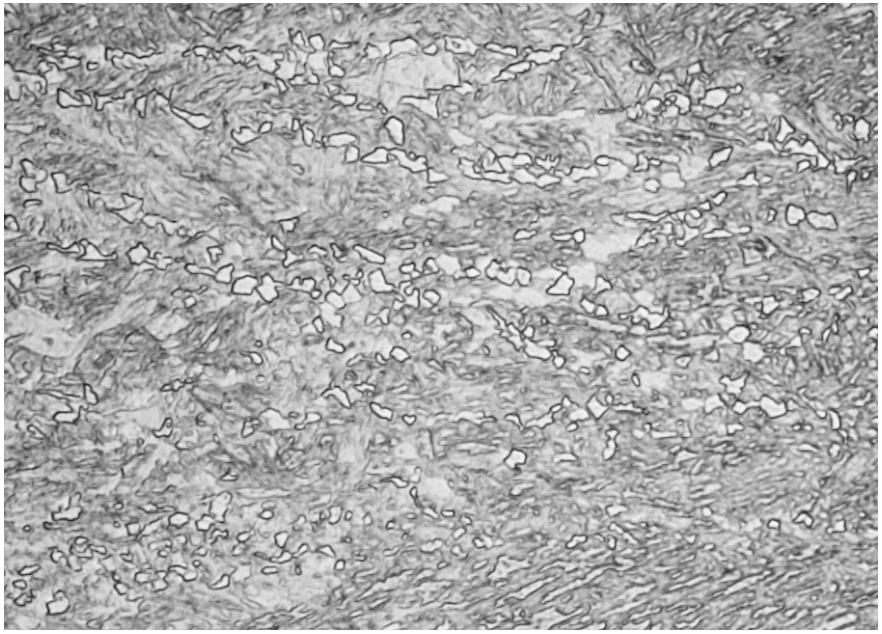
Optical microscopy and STEM-EDX analysis

Optical Microstructure



10 μm

(a)



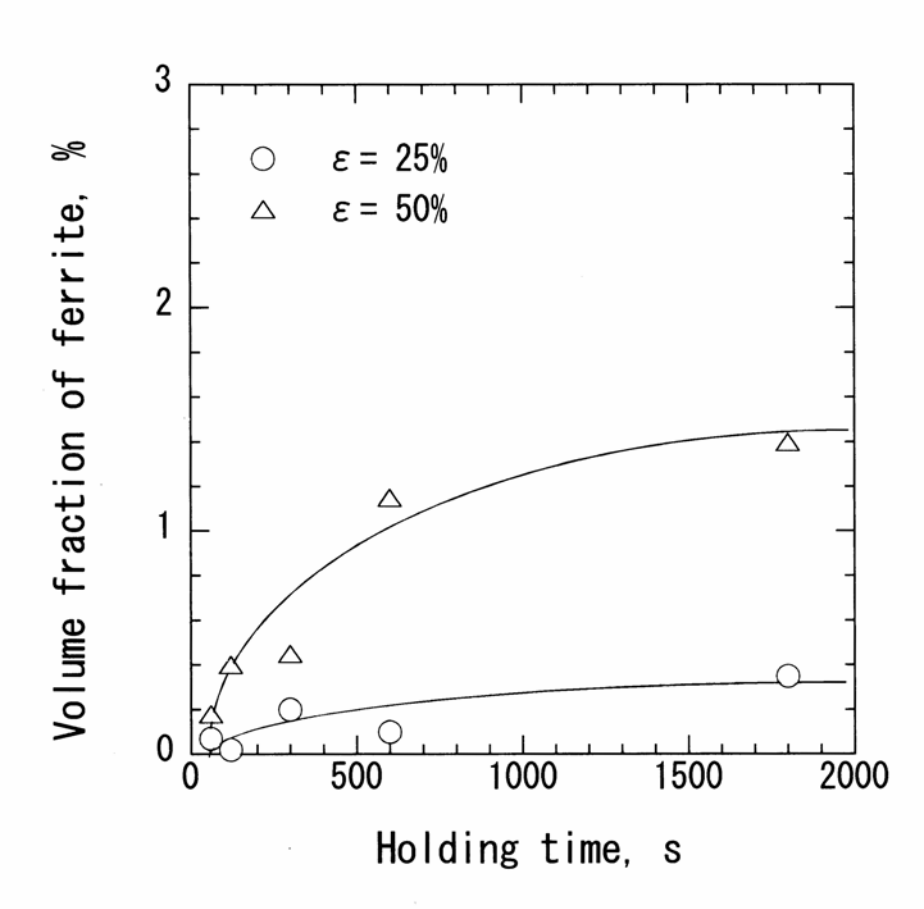
(b)

790°C for 10min after 50% compression

730°C for 10min after 50% compression

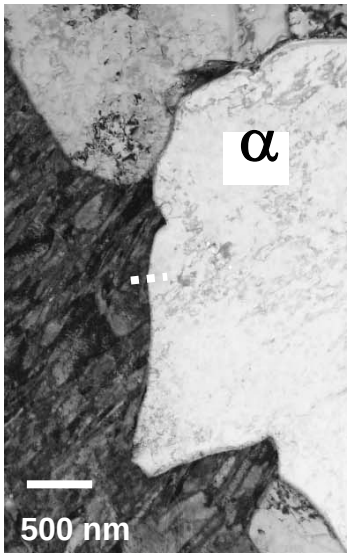
Ae_3 = 822 °C, Ae_3' = 778 °C, PLE/NPLE = 660 °C

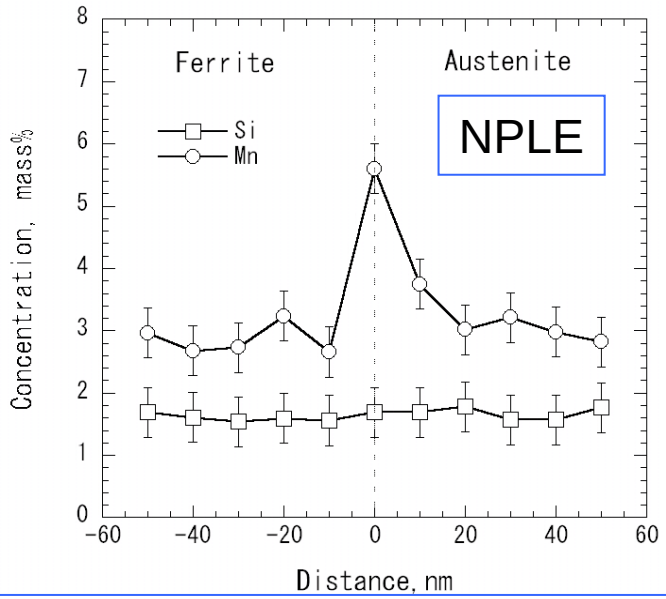
Ferrite volume fraction



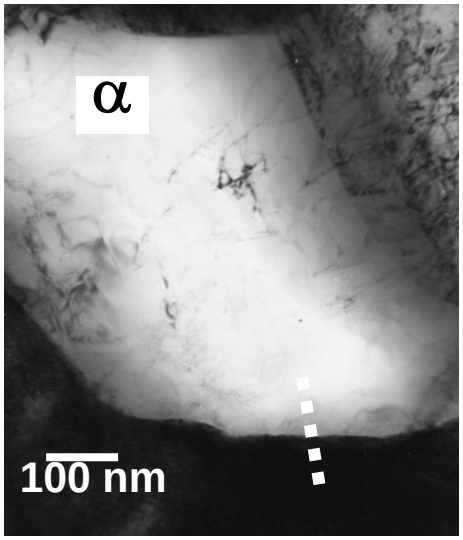
Variation of ferrite volume fraction with holding time at 710°C.

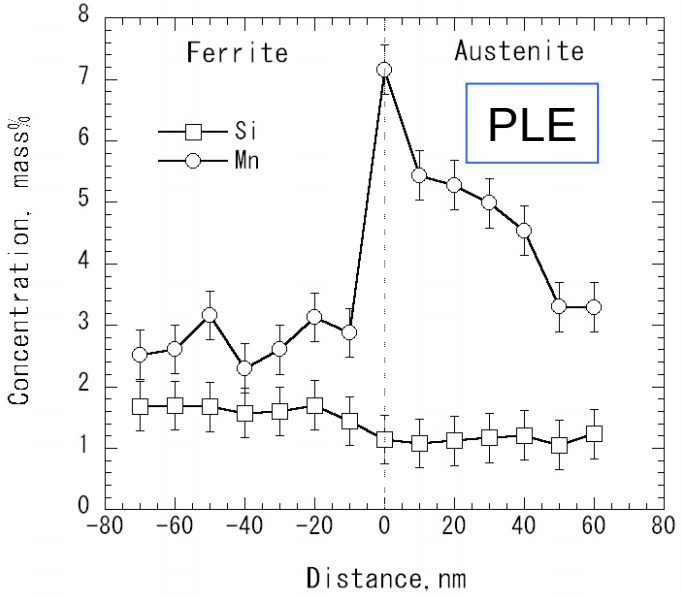
TEM micrograph and concentration profile at NPLE/PLE stage





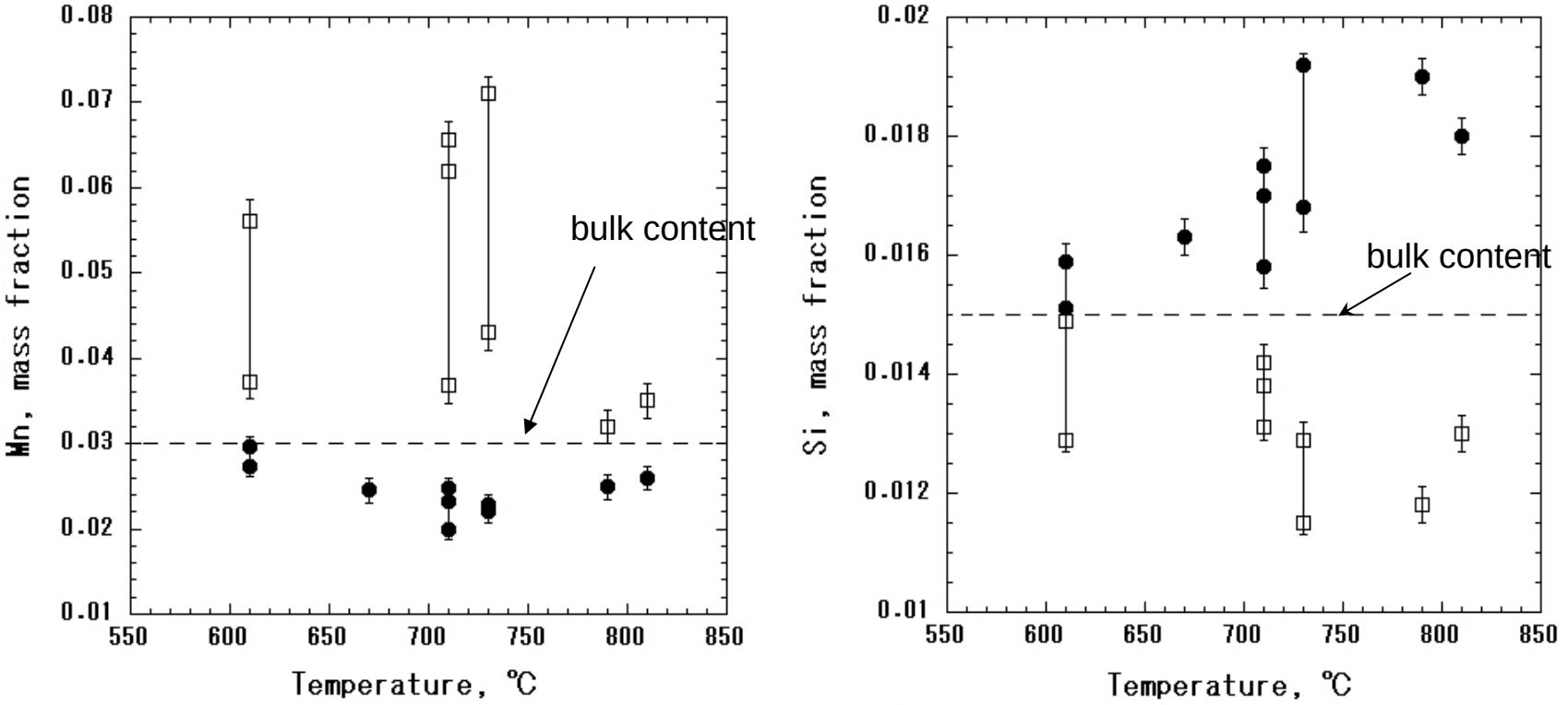
610°C for 5min under 25% deformation





730°C for 10min under 50% deformation.

Concentration profile measured by STEM-EDX



Mn and Si concentrations in ferrite (open circles) austenite (open squares, transformed to martensite upon cooling).

Coates equations

The i-th species (i=0, 1, 2, and 3 for Fe, C, Mn and Si)

NPLE Ω_2~1, and Ω_3~1

$$\Omega_1 = f(\eta_1) + \left(m_{21} D_{21}^{12} + m_{31} D_{31}^{13}\right)\left\{1 - f(\eta_1)\right\}$$

$$\Omega_i = \frac{x_i^{\gamma} - x_i^{0}}{x_i^{\gamma} - x_i^{\alpha}}$$ supersaturation

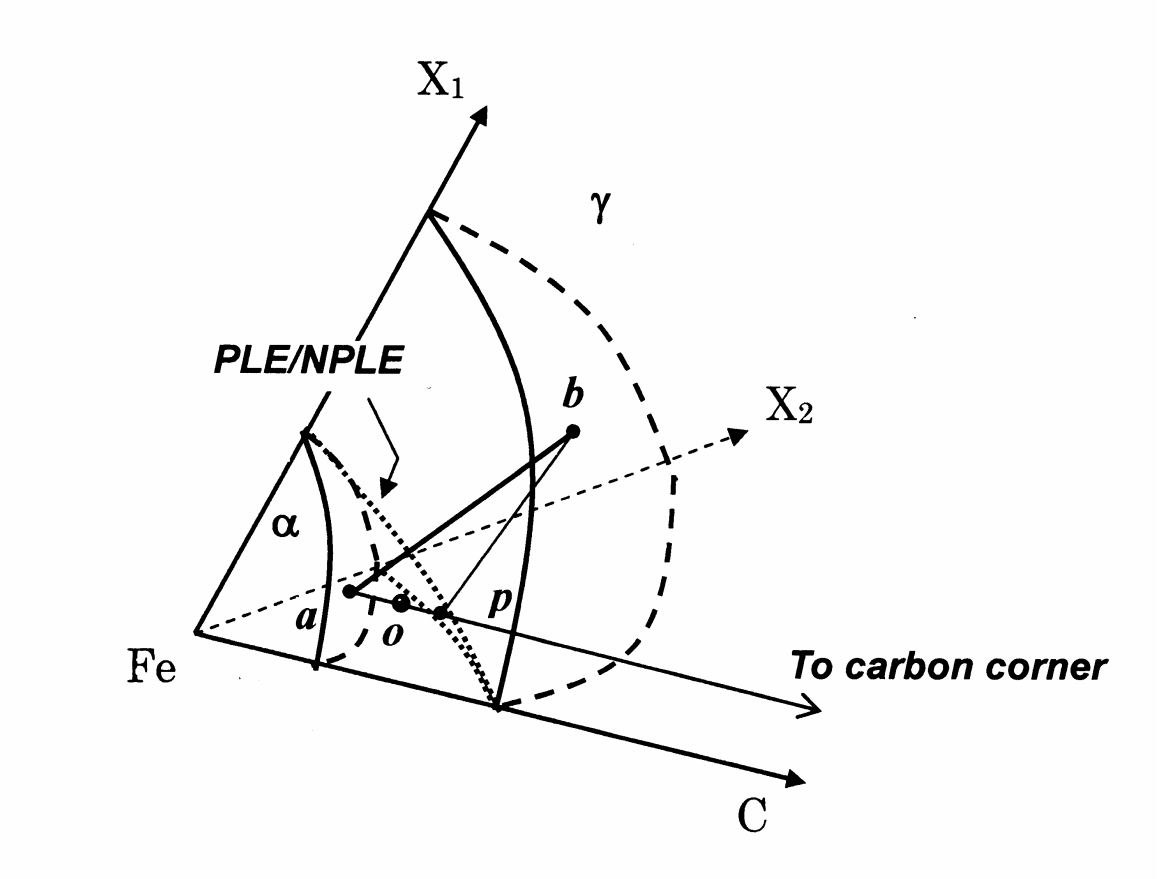
$$m_{ji} = \frac{x_j^{\gamma} - x_j^{\alpha}}{x_i^{\gamma} - x_i^{\alpha}}$$ slope of the tie-line

$$D_{ji}^{ij} = \frac{D_{ij}^{\gamma}}{D_{jj}^{\gamma} - D_{ii}^{\gamma}}$$ cross-diffusion coefficient

$$f(\eta_i) = \frac{\eta_i^2}{2}\left[1 - \sqrt{\pi}\,\frac{\eta_i}{2}\exp\left(\frac{\eta_i^2}{2}\right) erfc\left(\frac{\eta_i}{2}\right)\right]$$ spherical

Interfacial tie-line in NPLE

NPLE



Approximate calculation

- Ignore the differences in diffusion coefficients between X_1 and X_2

→ $D_2 \sim D_3$ $\qquad \eta_2 = \dfrac{\alpha}{\sqrt{D_2}} = \eta_3 = \dfrac{\alpha}{\sqrt{D_3}} \qquad \Omega_2 = \Omega_3$

PLE

Coates equations

$$\begin{cases} \Omega_1 = m_{21}\Omega_2 D_{21}^{12} + m_{31}\Omega_3 D_{31}^{13} \\ \Omega_2 = f(\eta_2) + m_{32}\Omega_3 D_{32}^{23}\left\{1 - \dfrac{f(\eta_2)}{f(\eta_3)}\right\} \\ \Omega_3 = f(\eta_3) + m_{23}\Omega_2 D_{23}^{32}\left\{1 - \dfrac{f(\eta_3)}{f(\eta_2)}\right\} \end{cases}$$

Approximate method

$$\begin{cases} \Omega_1 = m_{21}\Omega_2 D_{21}^{12} + m_{31}\Omega_3 D_{31}^{13} \\ \Omega_2 = \Omega_3 = f(\eta) \end{cases}$$

$$\alpha = \eta\sqrt{D_{22}}, \qquad \alpha = \eta\sqrt{D_{33}}$$

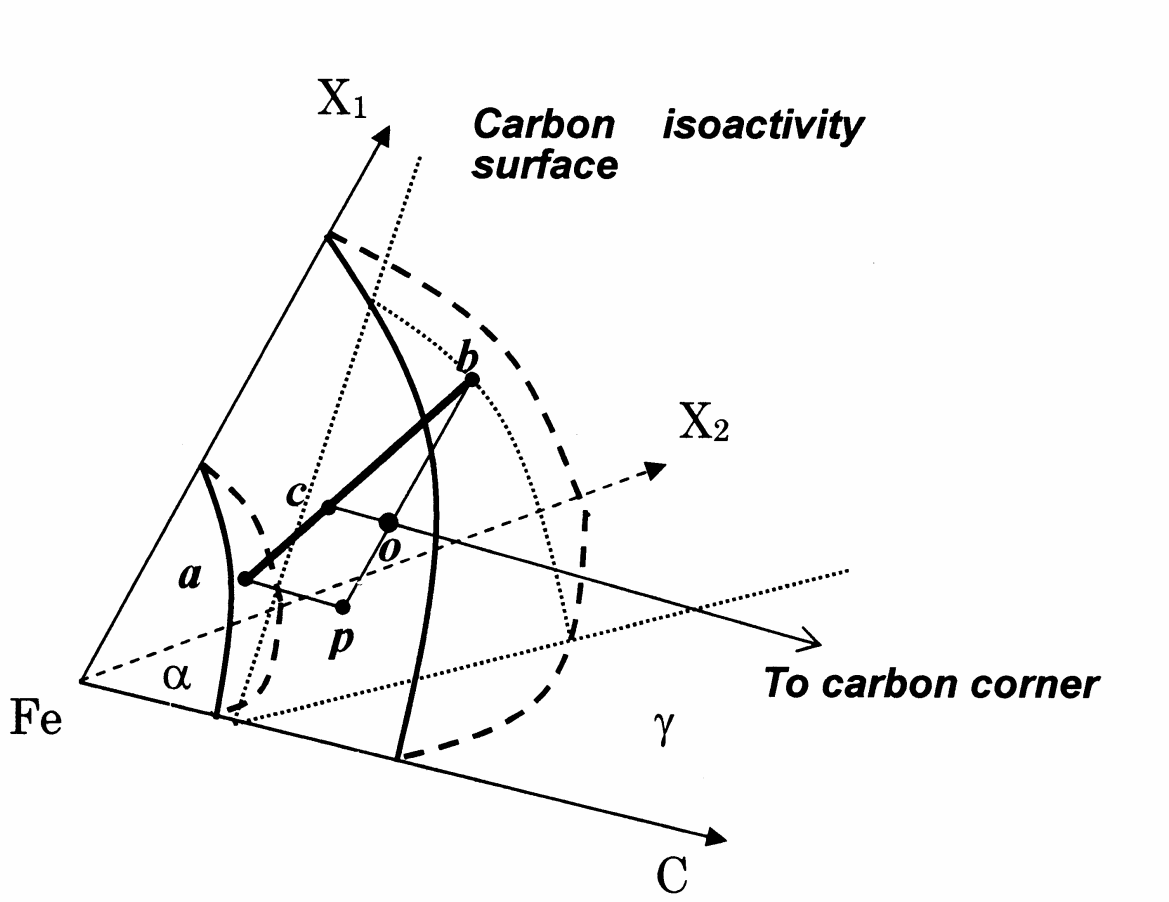
To use Coates equation, multiple regression of equilibrium phase boundary composition

$$x_k^{\alpha \ or \ \gamma} = a_{00} + a_{10}x_2^{\gamma} + a_{01}x_3^{\gamma} + a_{20}\left(x_2^{\gamma}\right)^2 + a_{11}x_2^{\gamma}x_3^{\gamma} + a_{02}\left(x_3^{\gamma}\right)^2 + \cdots$$

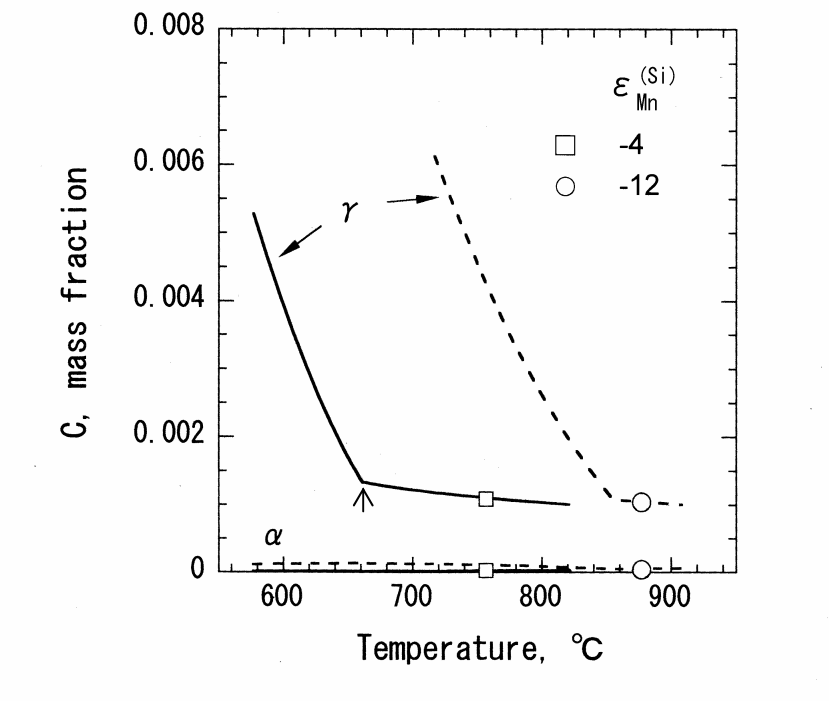
- This method is supposed to yield an exact tie-line composition and a growth rate.

Interfacial tie-line in PLE

PLE



Comparison between Coates and approximate (c.c. ray) solution



—— **Fe-0.1C-3Mn-1.5Si**

····· **Fe-0.1C-1.0Mn-1.5Si**

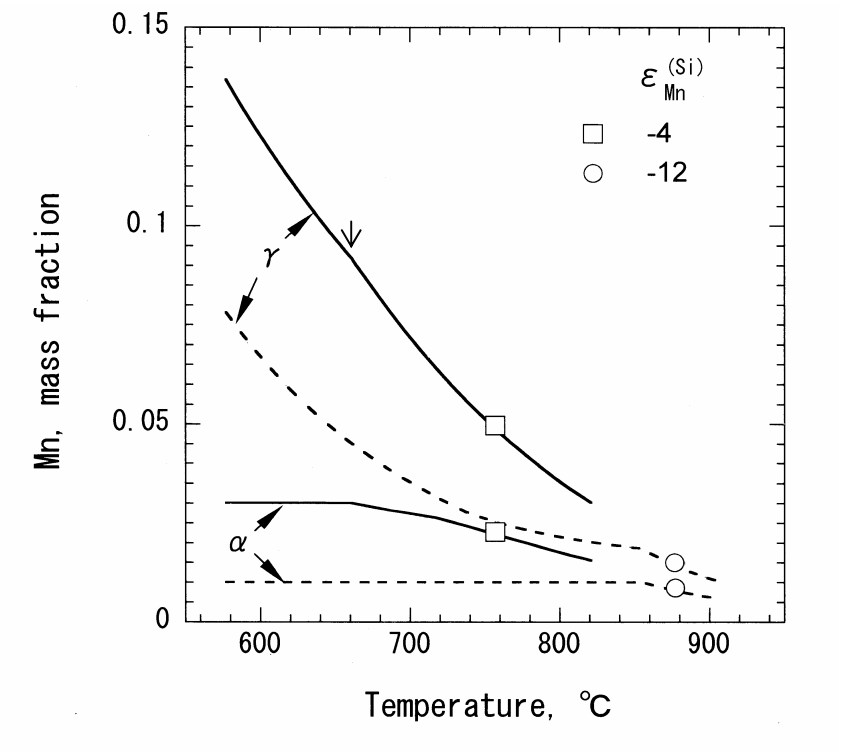
ε_{MnSi}=-12

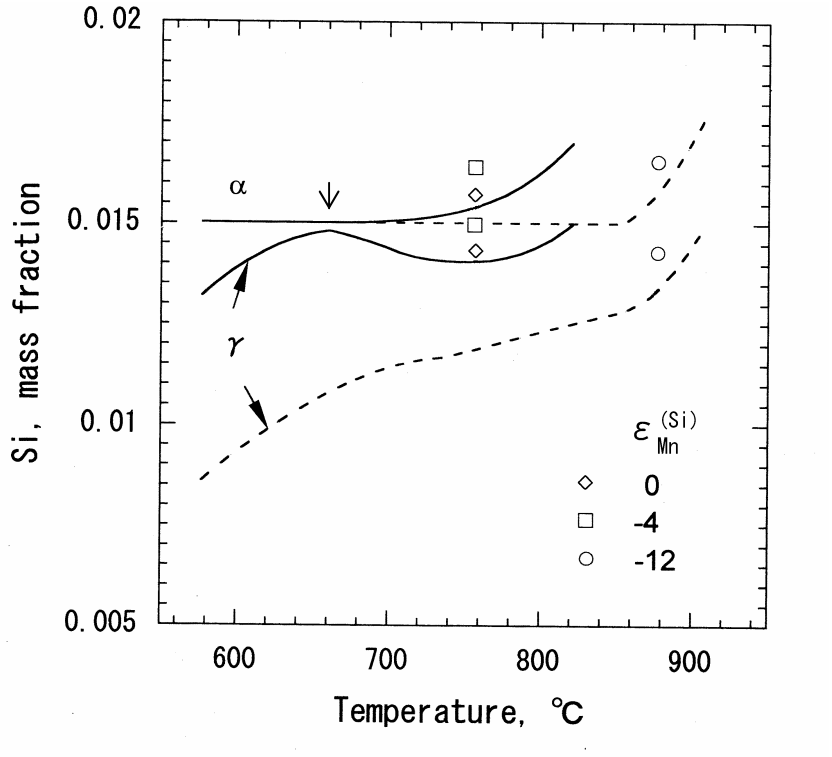
$D_{Si} \sim 5\, D_{Mn}$

Solutions for the 3Mn-1.5Si alloy only at small ε_{MnSi} .

Lower Mn content alloy at all ε_{MnSi} values.

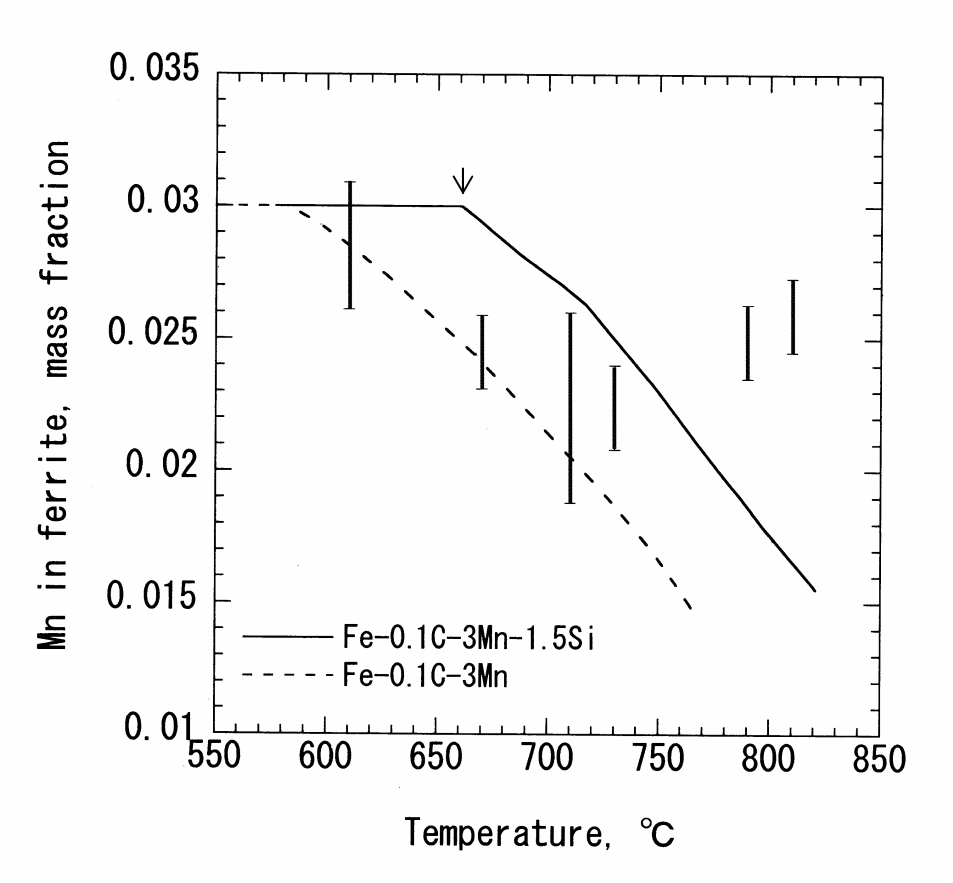
Comparison between Coates and approximate (c.c.ray) solutions





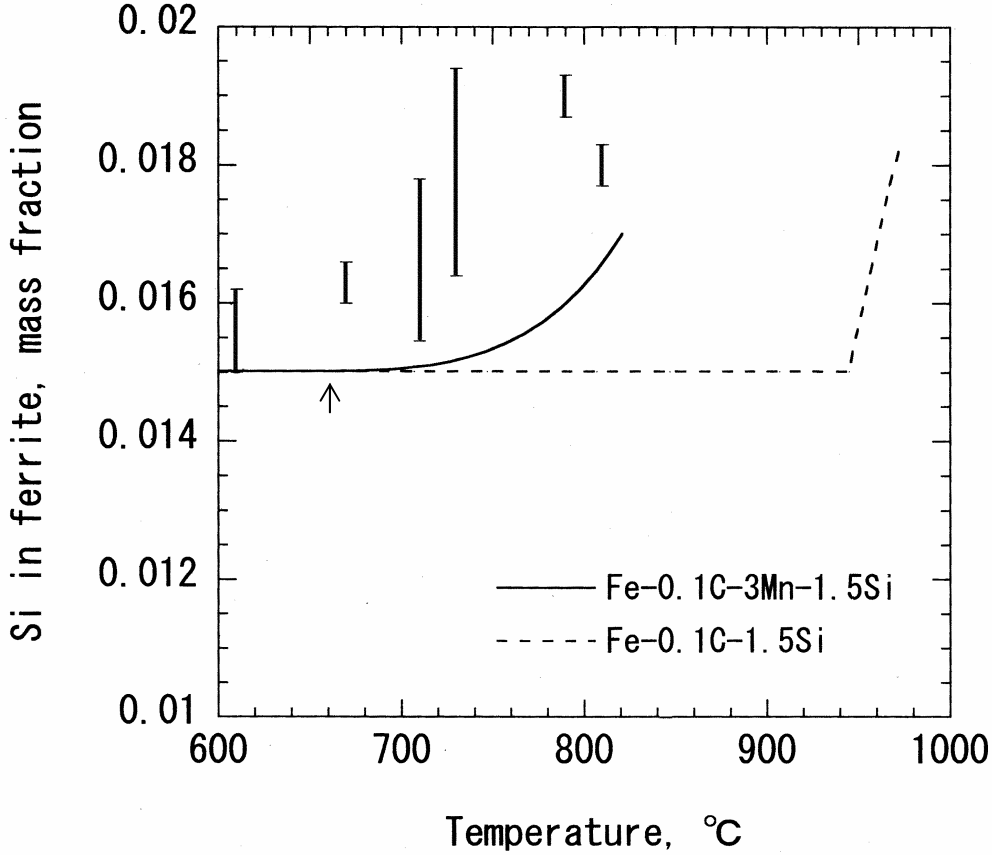
Errors are small for C and Mn concentrations, but is large for Si concentration.

Comparison with experiment and (approximate) calculation — Mn

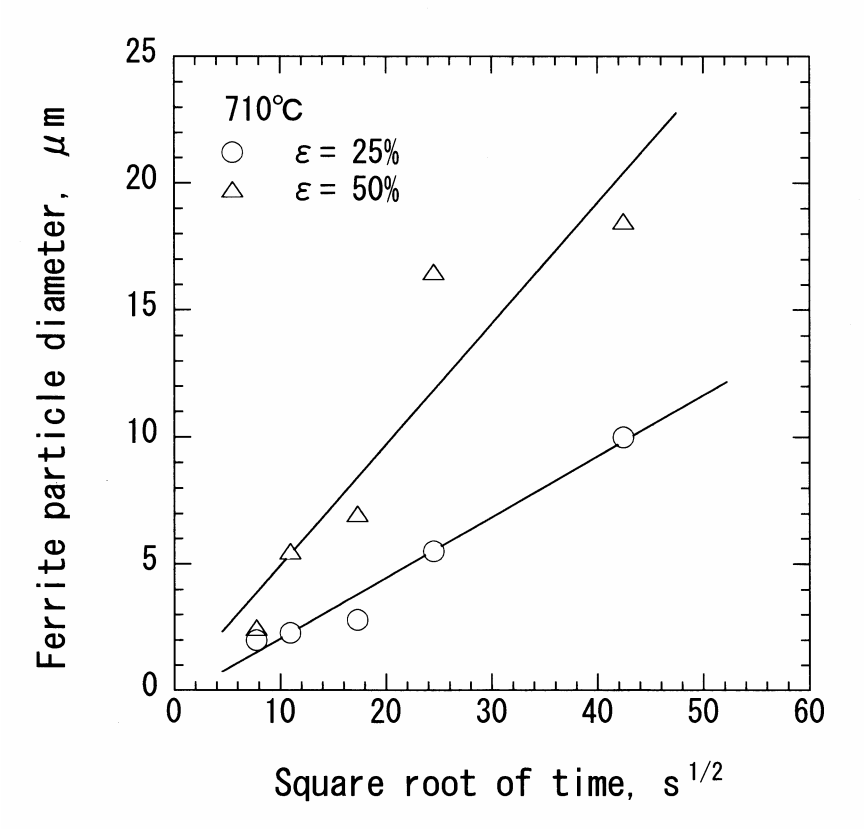


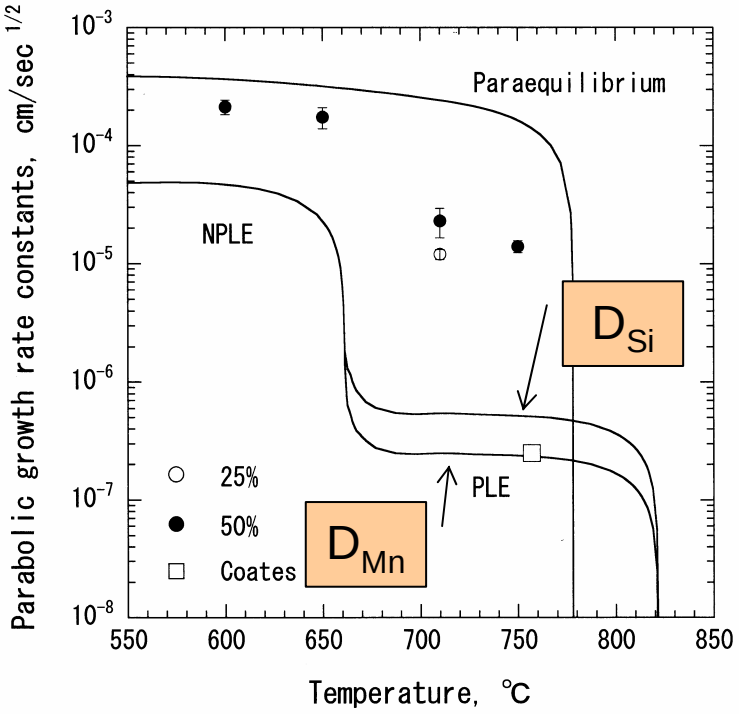
Mn concentration increases at high temperature, probably because the particles are small and fewer.

Comparison with experiment and (approximate) calculation — Si



Comparison of growth rate between experiment and calculation





The rate constant lies between para and local equilibrium (PLE).
We are comparing with DICTRA.

Summary

The compositions of within and near ferrite particles were analyzed by STEM-EDX in a Fe-0.1C-1.5Si-3Mn alloy deformed and isothermally reacted at temperatures between Ae_3 (822 °C) and 600°C.

Fine ferrite particles were formed with partitioning of Mn and Si at temperatures down to ~150°C below Ae_3. Si was partitioned between ferrite and austenite at much lower temperatures than in a Fe-C-Si ternary alloy.

Summary (cont'd)

- The partitioning of Mn and Si was calculated using carbon component ray. The PLE/NPLE transition temperature was ~660°C. Mn appeared to dictate partitioning of two elements.

- Experimentally observed temperature of cessation of partitioning was somewhat smaller than the calculated PLE/NPLE temperature.

- The parabolic growth rate constant was greater than local equilibrium in the PLE. Vacancy-enhanced diffusion, dislocation pipe diffusion and grain boundary diffusion-assisted solute transport can account for the differences.

For full details readers are referred to Metall.Mater.Trans. A, in press.