Kinetic of Martensite/austenite interface migration and carbon partitioning during the Q&P process

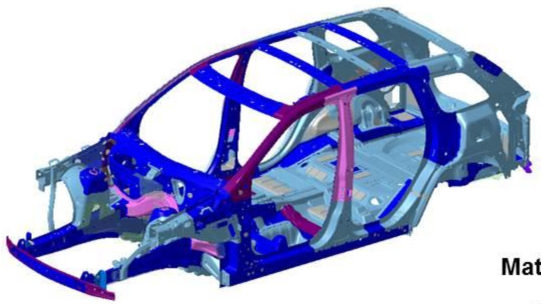
Zongbiao Dai, Ran Ding,
Zhigang Yang, Chi Zhang, Hao Chen

Key laboratory for Advanced Materials of Ministry of Education,
School of Materials Science and Engineering,
Tsinghua University, Beijing 100084, China

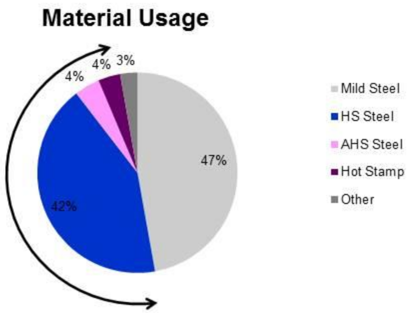
2017-06-27

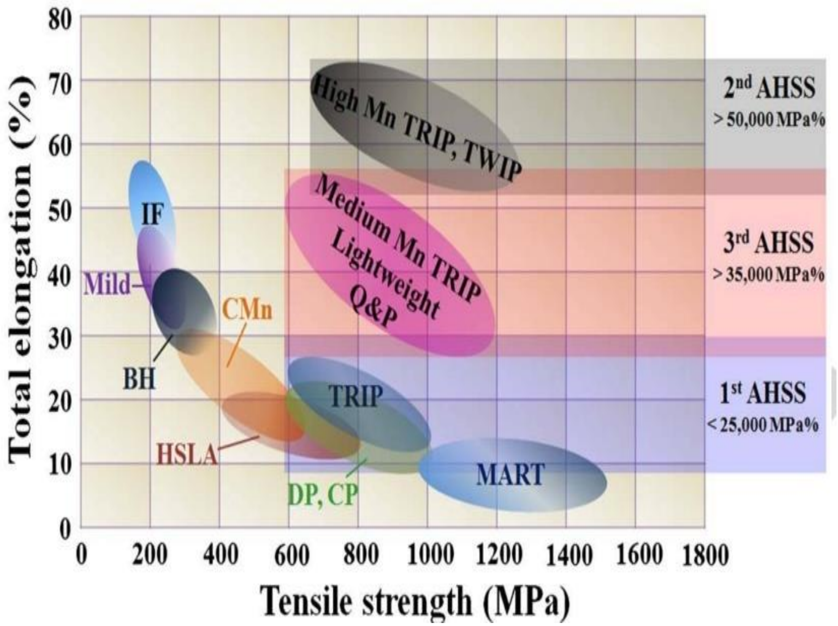
Introduction

- Vehicle emissions and exhaust
- Fuel consumption
- Safety and Lightweight



www.aotusteel.org





Y.-K. Lee et al. MST, 2015

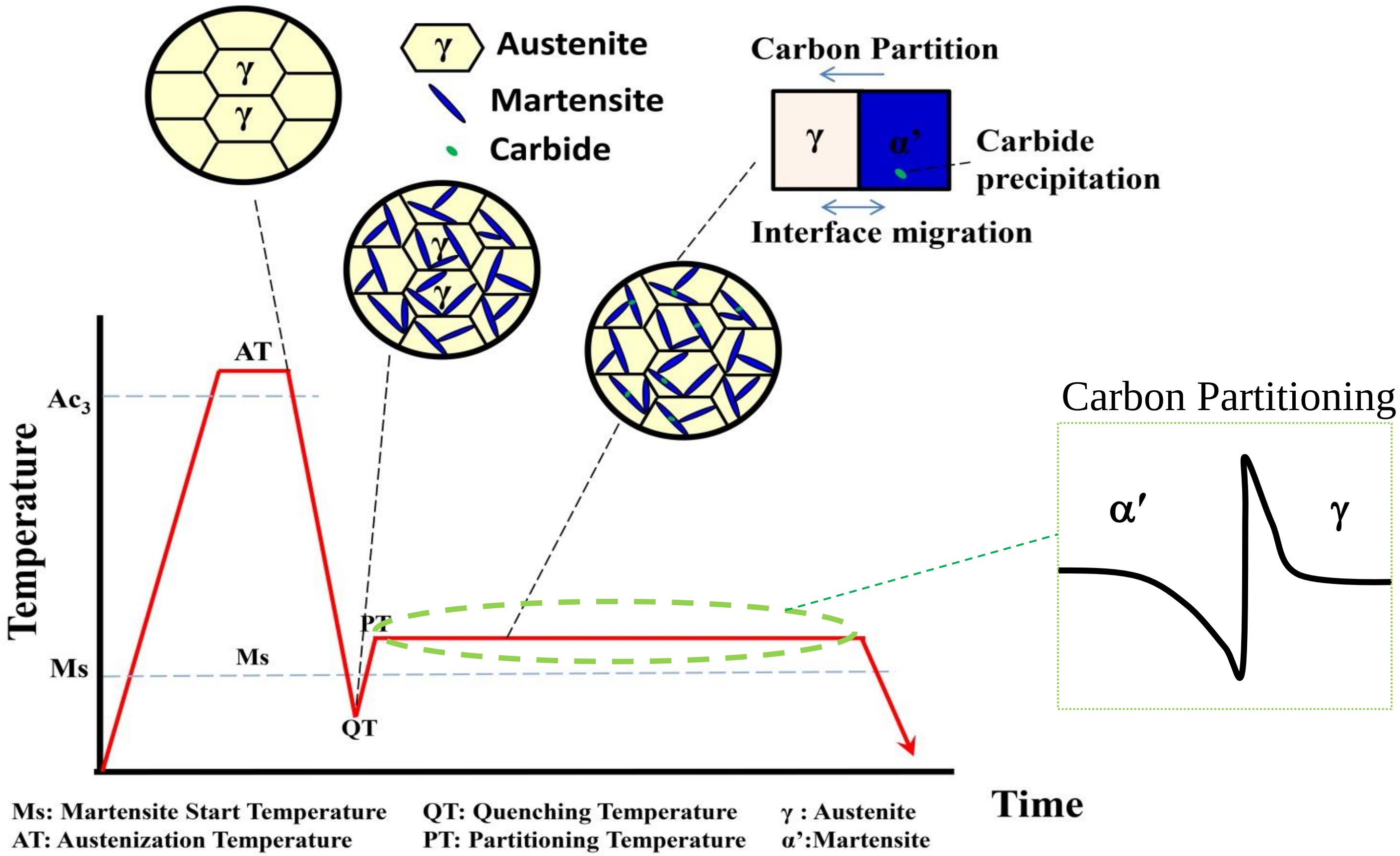
Retained Austenite

Retained Austenite + Martensite （Q&P）

Retained Austenite + Ferrite + Bainitic Ferrite

Ferrite + Martensite

Quenching & Partitioning Process



Scientific questions:

1. **Is the α′/γ interface mobile or not? How?**
2. **Is there partitioning of substitutional alloying elements during the Q&P process?**
3. **Will partitioning of substitutional alloying elements affect the interface migration and carbon partitioning?**

The Interface Migration or not?!

◻ Immobile Interface : *(CCE Theory)*

- Toji et al, Acta Mater., 65 (2014) 215 — Dilatometer
- Seo et al, Acta Mater., 107 (2016) 354 — Dilatometer
- Seo et al, Acta Mater., 113 (2016) 124 — Dilatometer
- Bigg et al, JAC, 577S (2013) 695 — In-situ Neutron diffractometry
- Thomas et al, MST, 30 (2014) 998 — EBSD

• • •

◻ Mobile Interface :

- Zhong et al, JMST, 22 (2006) 751. — Ex-situ TEM

◻ Interface migrates from BCC to FCC:

- Santofimia et al, MSEA, 527 (2010) — Dilatometer
- Santofimia et al, Acta Mater., 59 (2011) — Dilatometer
- Allain et al, Scripta Mater., 131 (2017) — In-situ HE-XRD

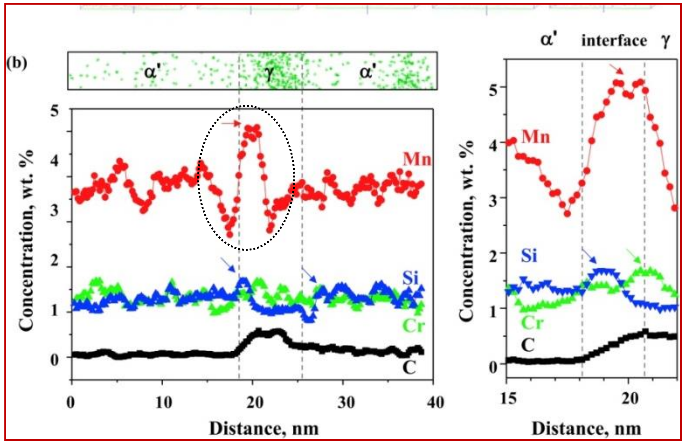
• • •

◻ Interface migrates from FCC to BCC:

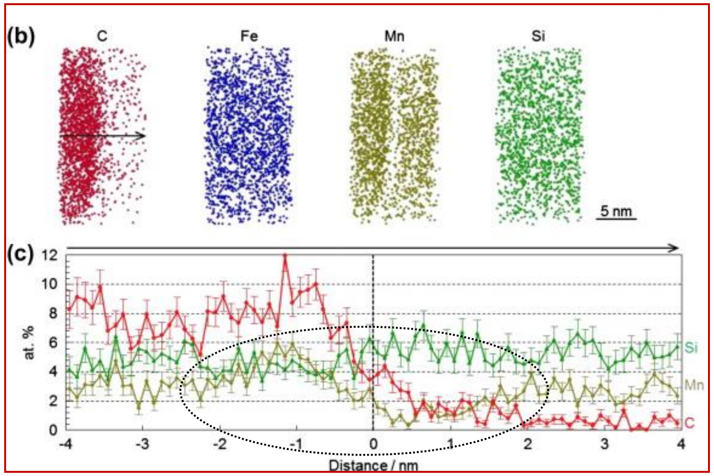
- De Knijf et al, Acta Mater., 90 (2015) — In-situ HR-TEM
- Thomas et al, MST, 30 (2014) 998 — EBSD

Complex and Controversial !

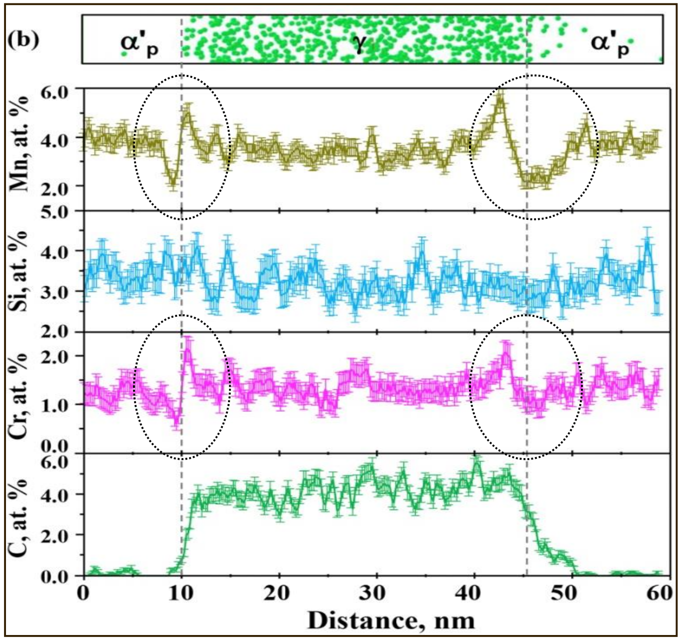
Mn and Cr Partition or not?!



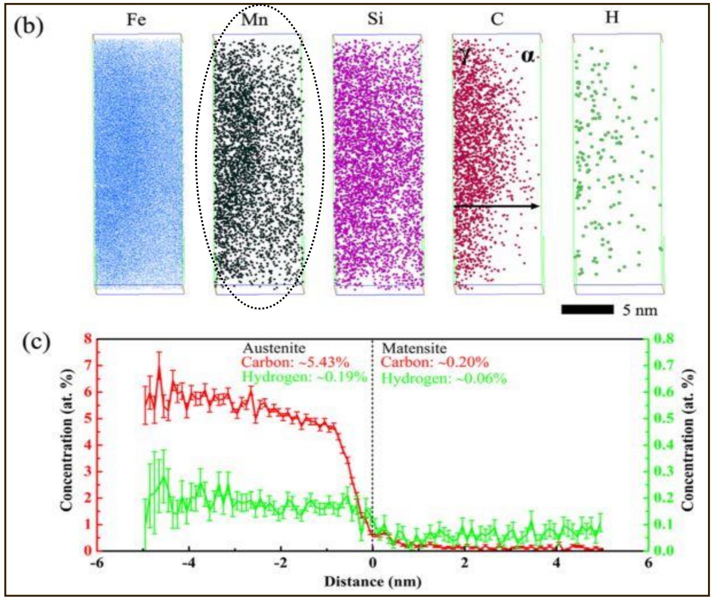
Seo et al. *Acta Mater.* ,2016



Toij et al. *Acta Mater.* , 2014



Seo et al. *Acta Mater.* ,2016



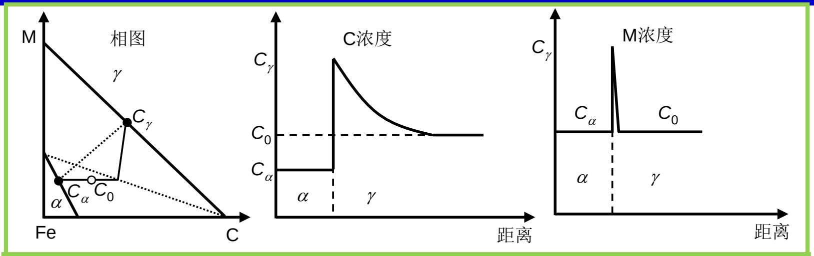
Zhu et al. *Int. J. Hydrogen Energy*, 2014

Models

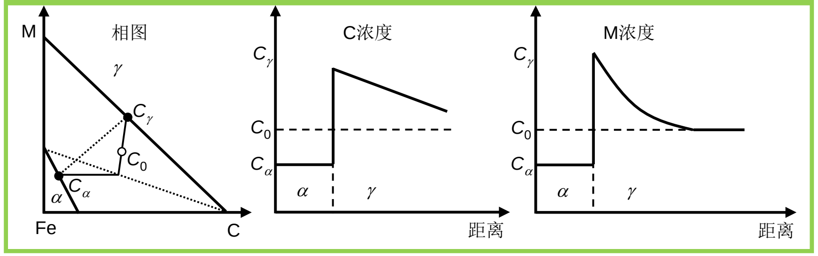
LE--Local equilibrium:

$$\mu_i^{\gamma} = \mu_i^{\alpha}$$

NP-LE :
C diffusion controlled



P-LE :
M diffusion controlled

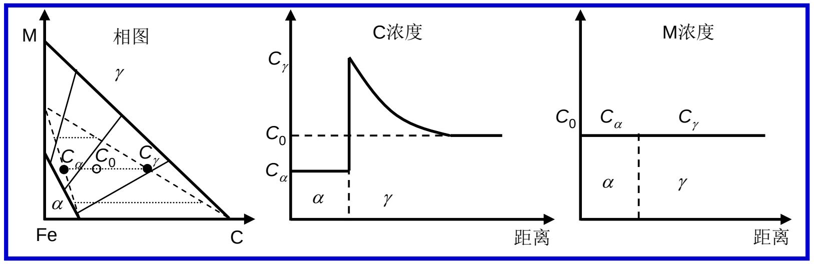


PE--Paraequilibrium:

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

$$\left(\mu_M^{\gamma} - \mu_M^{\alpha}\right) = -\frac{X_{Fe}}{X_M}\left(\mu_{Fe}^{\gamma} - \mu_{Fe}^{\alpha}\right)$$

PE :
C diffusion
Mn indiffusible



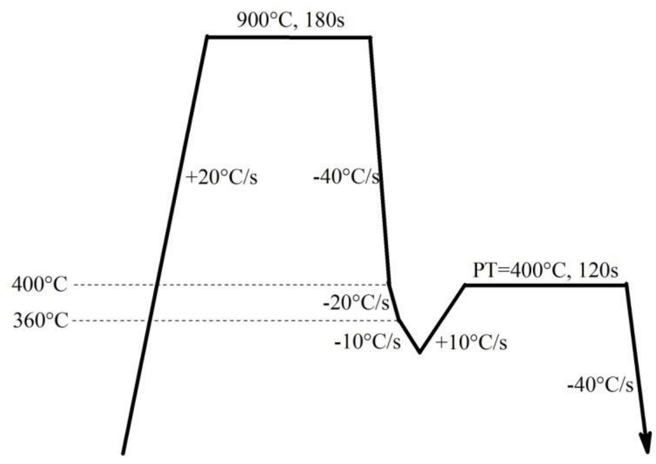
CCE—Constrain Carbon Equilibrium:

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

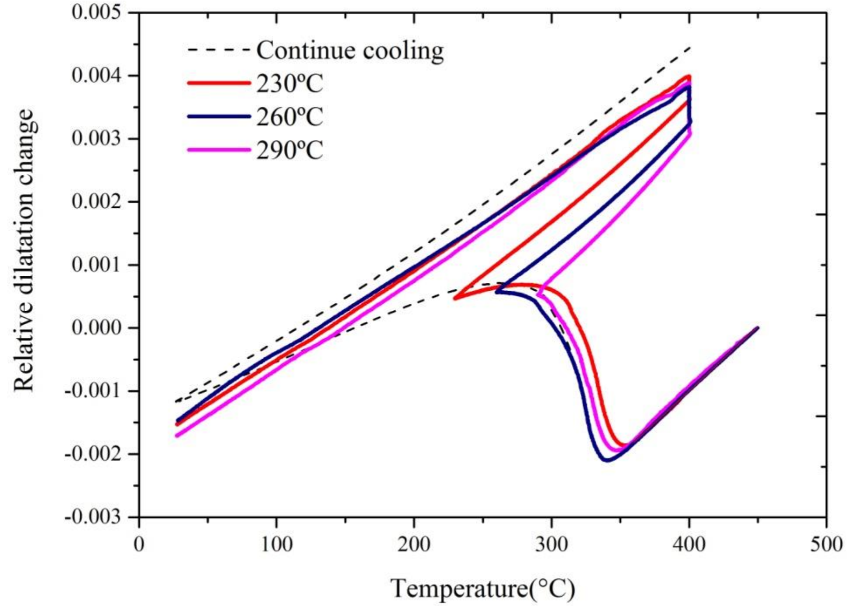
Martensite/austenite interface is immobile

Experiments

Fe-0.25C-2.1Mn-1.1Si（wt.%）



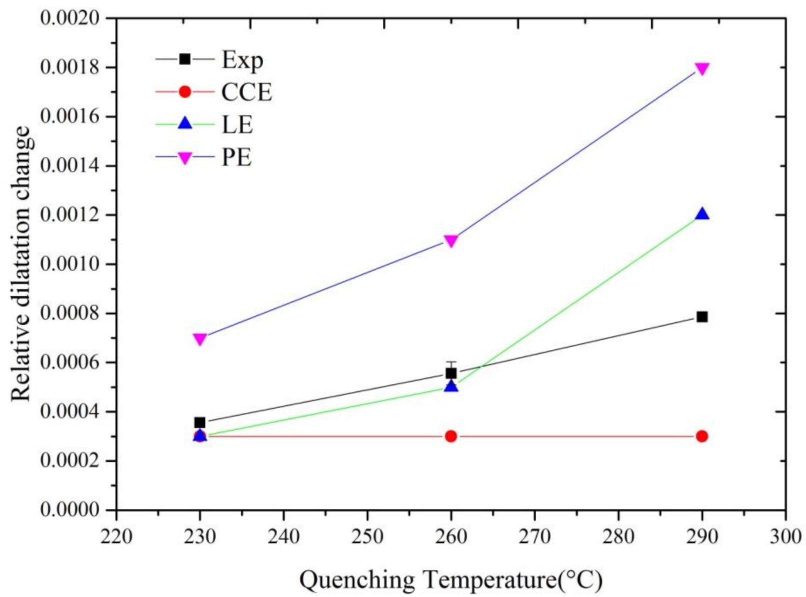
QT=230 °C   260 °C 290 °C



Calculation of relative dilatation strain:

$$\frac{\Delta L}{L_0}=\frac{L-L_0}{L_0}\approx\frac{1}{3}\frac{V-V_0}{V_0}$$

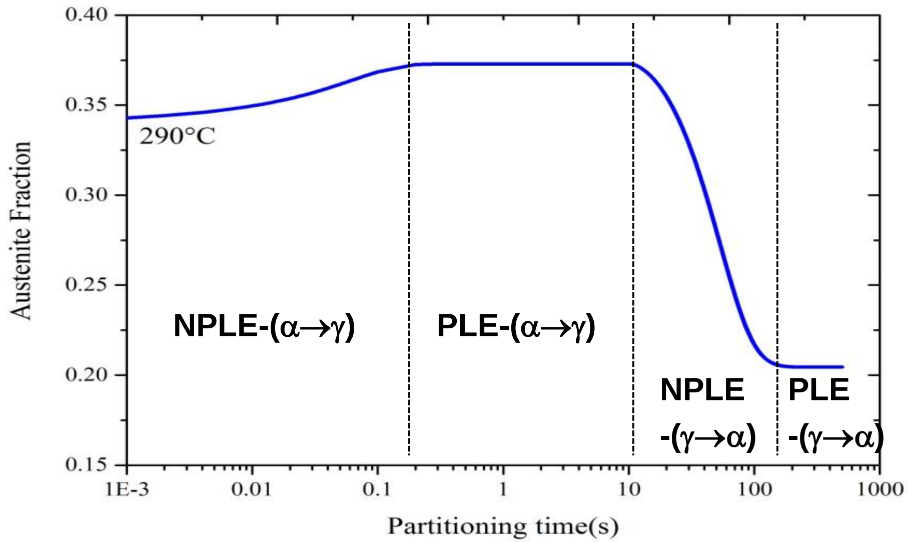
$$\frac{\Delta L}{L_0}=\frac{2V_{\alpha'}(1-x_C^{\alpha'})a_{\alpha'}^2c_{\alpha'}+[1-V_{\alpha'}-(x_{C0}^{\gamma}-V_{\alpha'}x_C^{\alpha'})]a_{\gamma}^3-(1-x_{C0}^{\gamma})a_{\gamma0}^3}{3(1-x_{C0}^{\gamma})a_{\gamma0}^3}$$

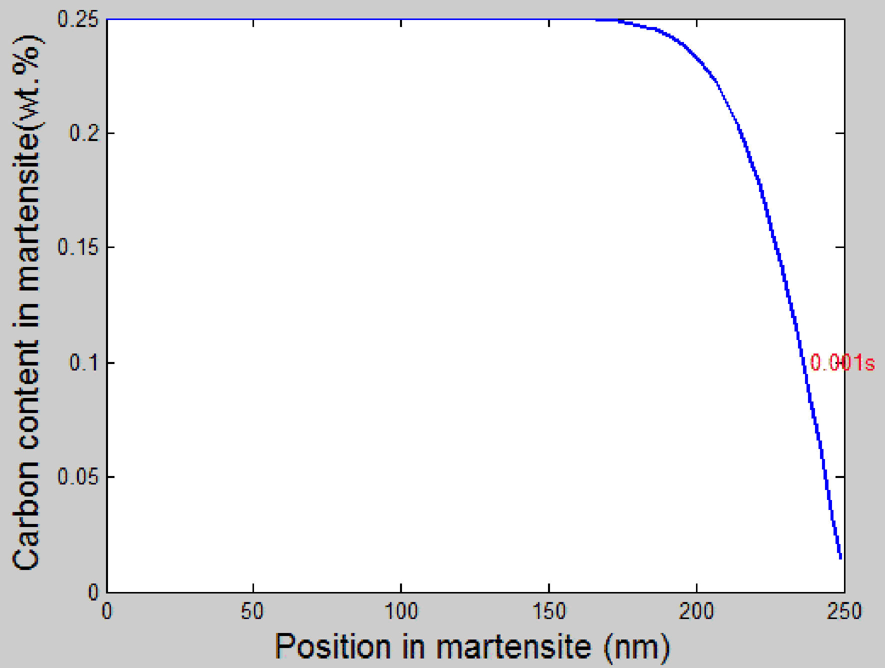


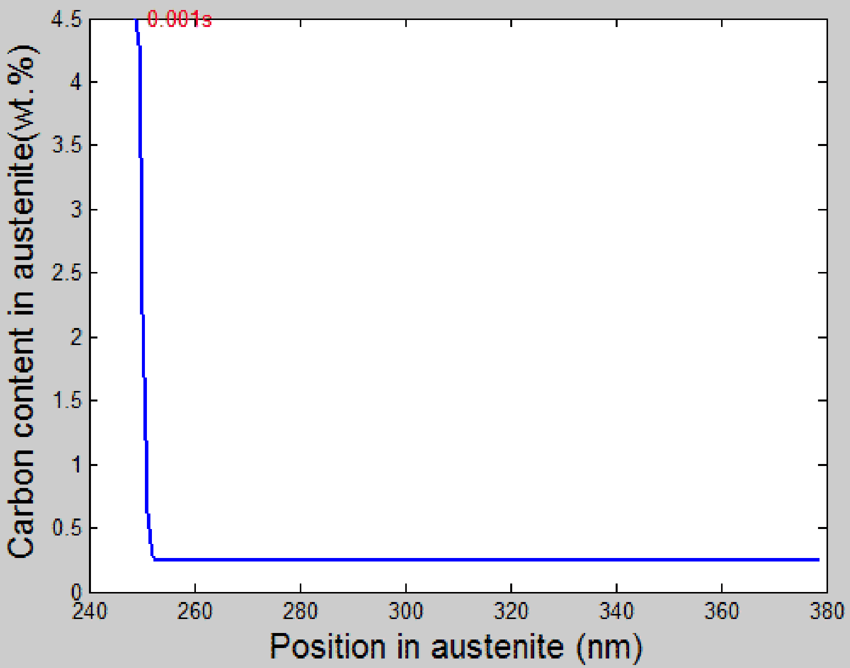
Case for martensite growth

QT=290°C

PT=400°C

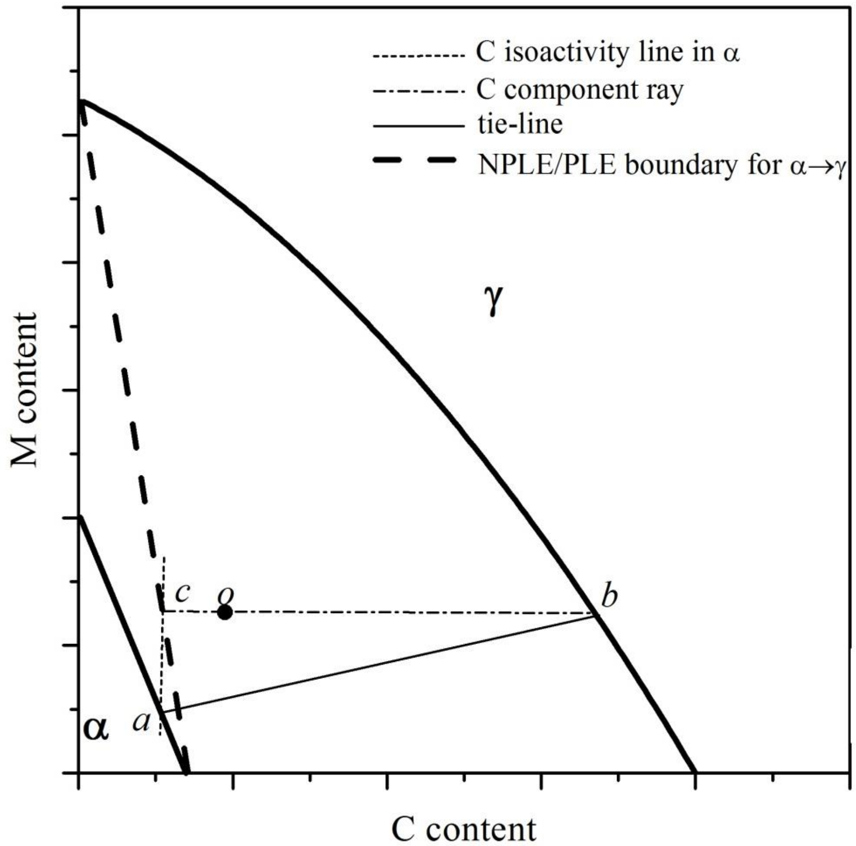




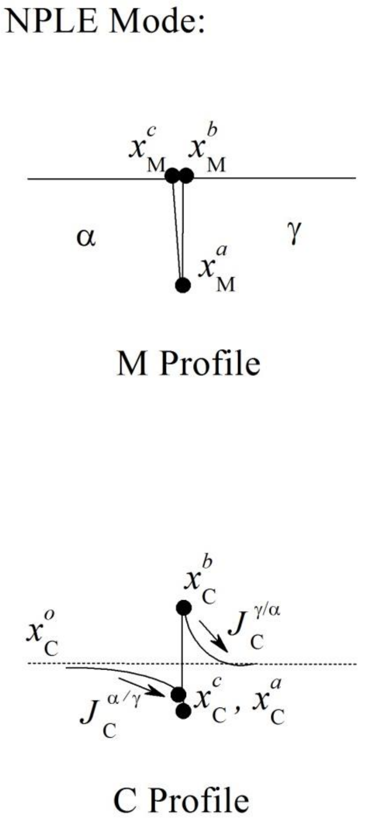


Case for martensite growth

Stage I: NPLE-(α→γ)



a)



$$v = \frac{J_C^{\gamma/\alpha} - J_C^{\alpha/\gamma}}{x_C^{\gamma/\alpha} - x_C^{\alpha/\gamma}}$$

$$J_i^{\phi} = -\frac{D_i^{\phi} x_i^{\phi}}{RT} \nabla \mu_i^{\phi}$$

$$x_C^{\alpha'} = x_C^{\gamma} = x_{C0}$$

$$\nabla \mu_C^{\alpha} > \nabla \mu_C^{\gamma}$$

$$D_C^{\alpha} \gg D_C^{\gamma}$$

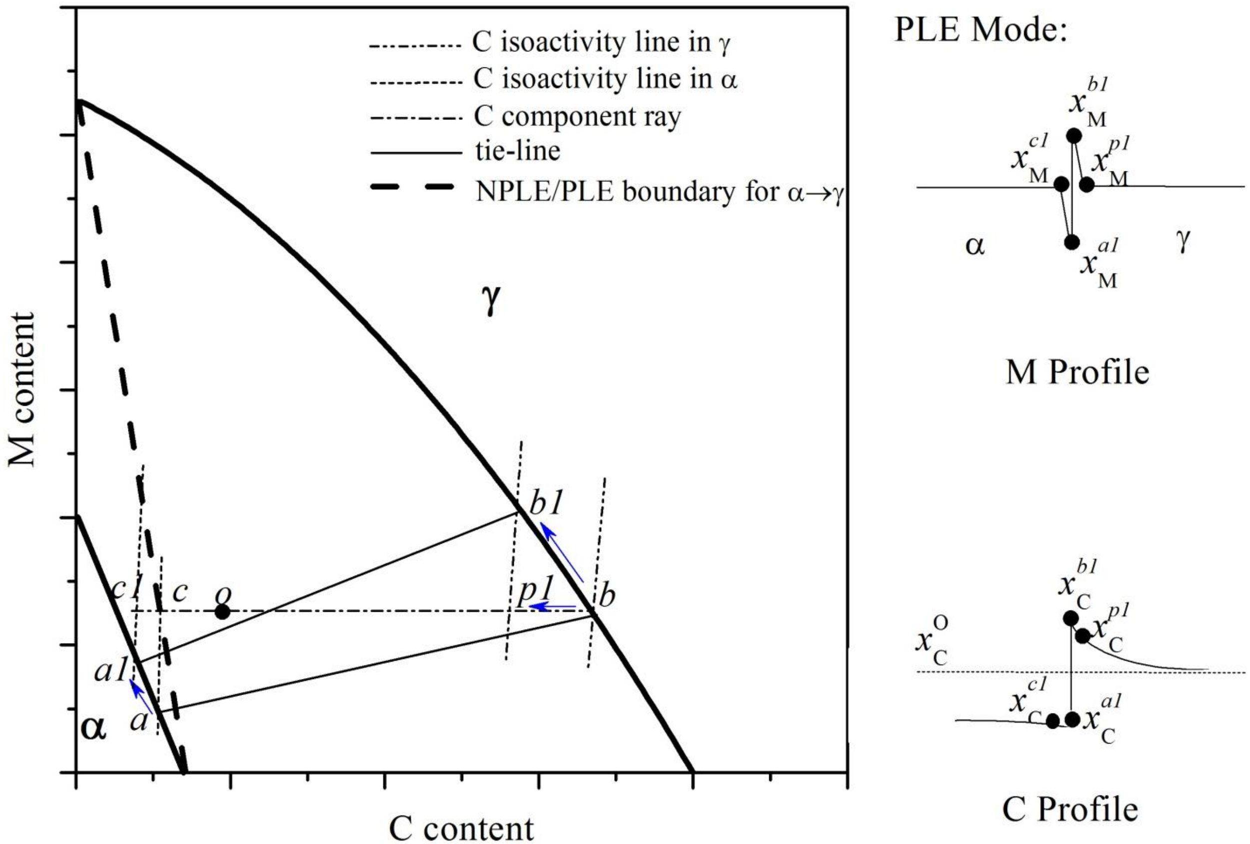
$$J_C^{\alpha/\gamma} \gg J_C^{\gamma/\alpha}$$

$$v = \frac{J_C^{\gamma/\alpha} - J_C^{\alpha/\gamma}}{x_C^{\gamma/\alpha} - x_C^{\alpha/\gamma}} \approx -\frac{J_C^{\alpha/\gamma}}{x_C^{\gamma/\alpha}}$$

Controlled by Carbon diffusion in martensite

Case for martensite growth

Stage II: PLE-(α→γ)



b)

$$J_{\mathrm{C}}^{\alpha/\gamma} \downarrow$$

$$J_{\mathrm{C}}^{\gamma/\alpha} - J_{\mathrm{C}}^{\alpha/\gamma} \approx 0$$

$$v = \frac{J_{\mathrm{C}}^{\gamma/\alpha} - J_{\mathrm{C}}^{\alpha/\gamma}}{x_{\mathrm{C}}^{\gamma/\alpha} - x_{\mathrm{C}}^{\alpha/\gamma}} \approx 0$$

$$v \approx 0$$

$$D_{\mathrm{Mn}}^{\alpha} \ll D_{\mathrm{Mn}}^{\gamma}$$

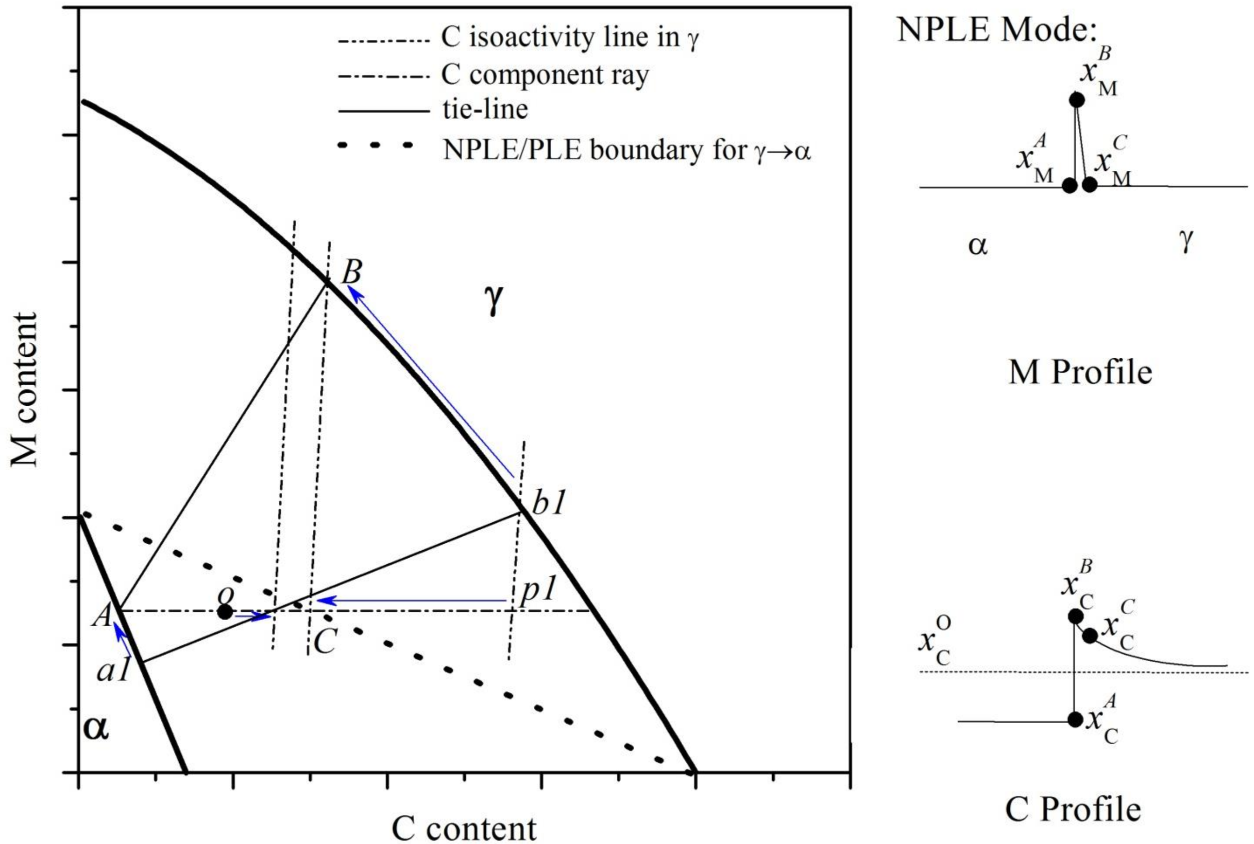
$\longrightarrow$

Mn spike in martensite decrease： *aa1* line

Mn spike in austenite is built up ： *bb1* line

Case for martensite growth

Stage III: NPLE-(γ→α)



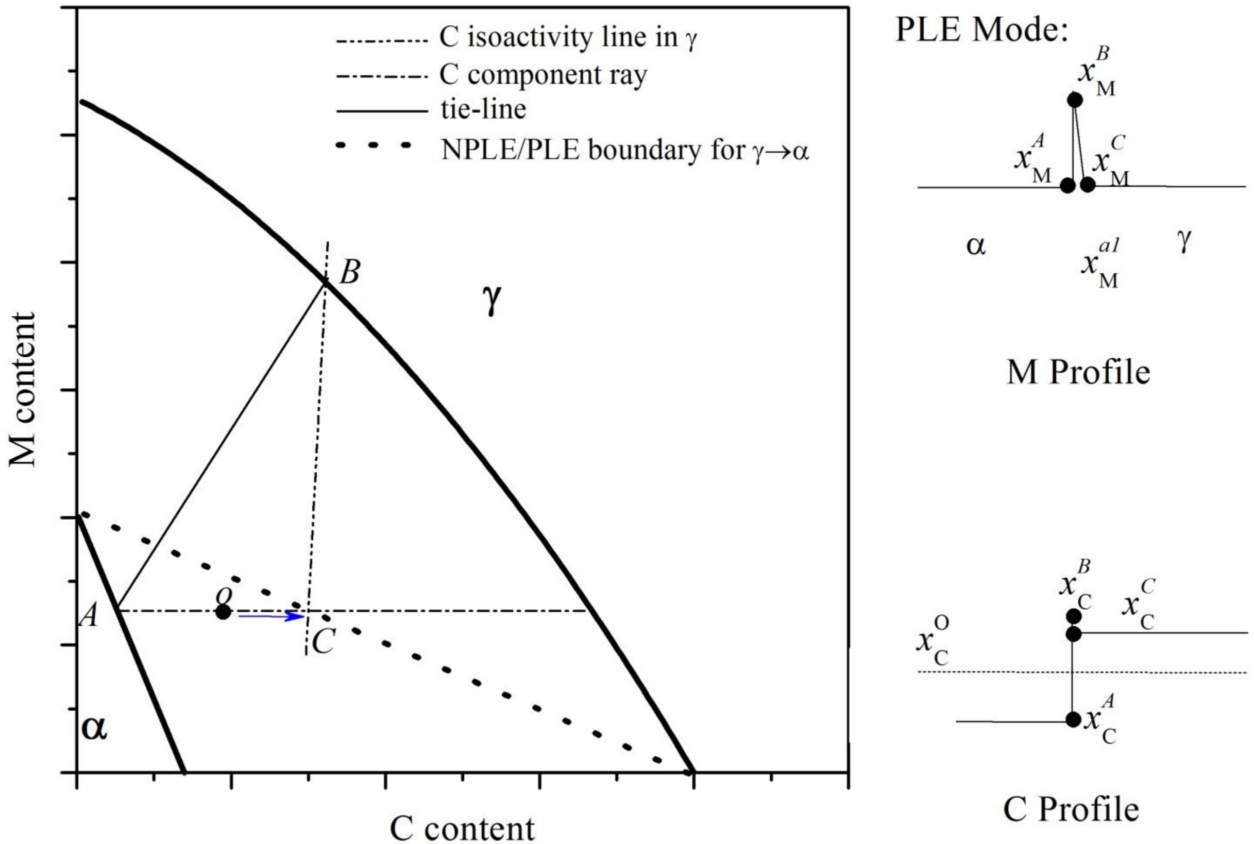
c)

$$v = \frac{J_C^{\gamma/\alpha} - J_C^{\alpha/\gamma}}{x_C^{\gamma/\alpha} - x_C^{\alpha/\gamma}} \approx \frac{J_C^{\gamma/\alpha}}{x_C^{\gamma/\alpha}}$$

Controlled by Carbon diffusion in austenite

Case for martensite growth

Stage IV: PLE-(γ→α)



d)

$$J_C^{\gamma/\alpha} \downarrow$$

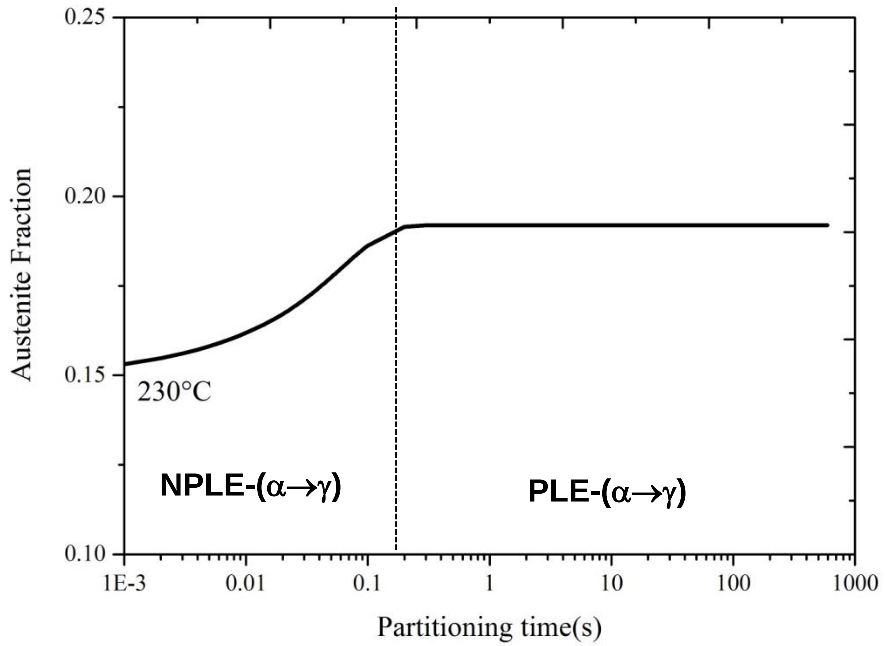
$$J_C^{\gamma/\alpha} \approx 0$$

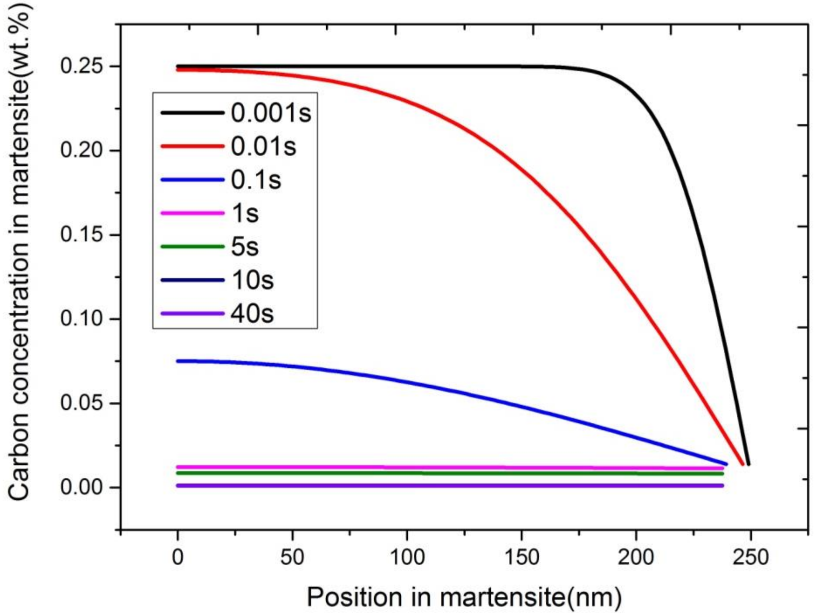
$$v = \frac{J_C^{\gamma/\alpha} - J_C^{\alpha/\gamma}}{x_C^{\gamma/\alpha} - x_C^{\alpha/\gamma}} \approx 0$$

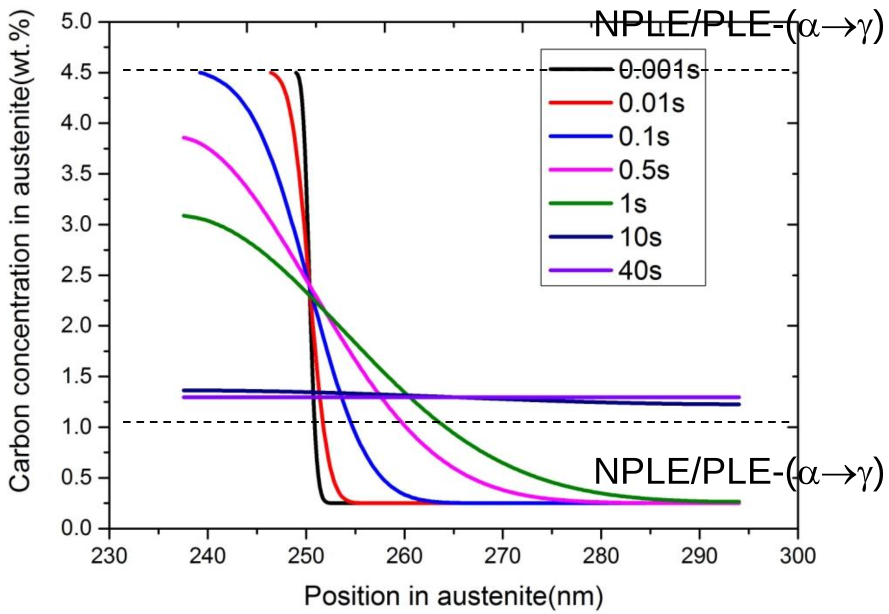
Carbon concentration in austenite will be determined by NPLE/PLE-(γ→α) (i.e. *Point C*)

Case for Immobile interface

QT=230°C

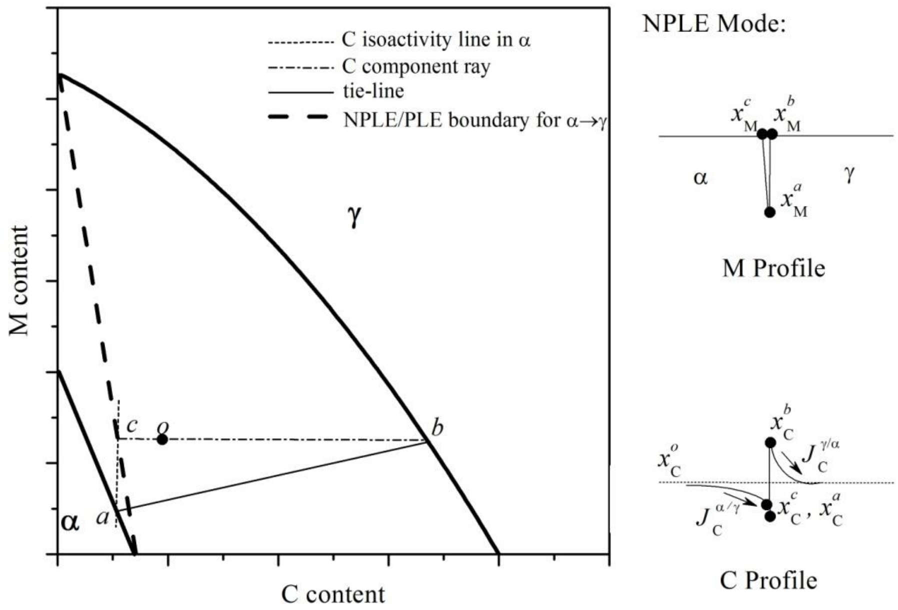






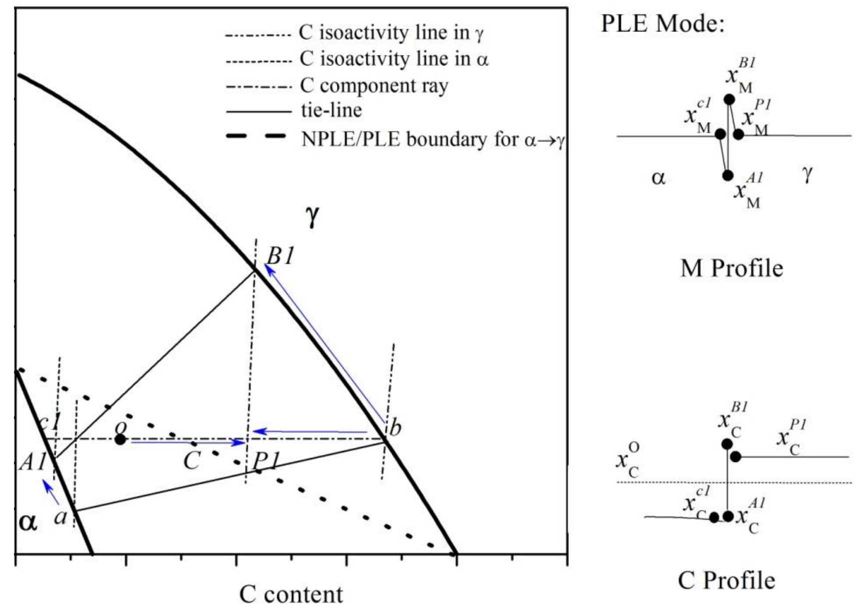
Case for Immobile interface

Stage I: NPLE-($\alpha\rightarrow\gamma$)



a)

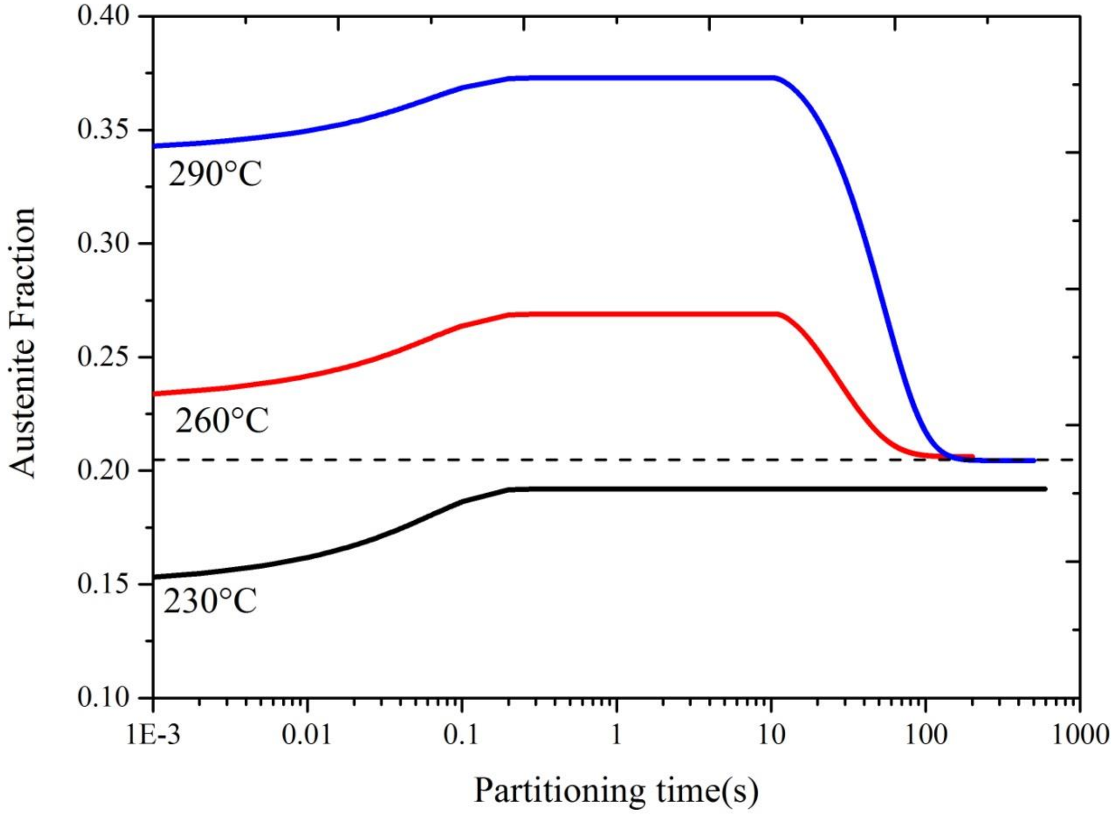
Stage II: PLE-($\alpha\rightarrow\gamma$)



b)

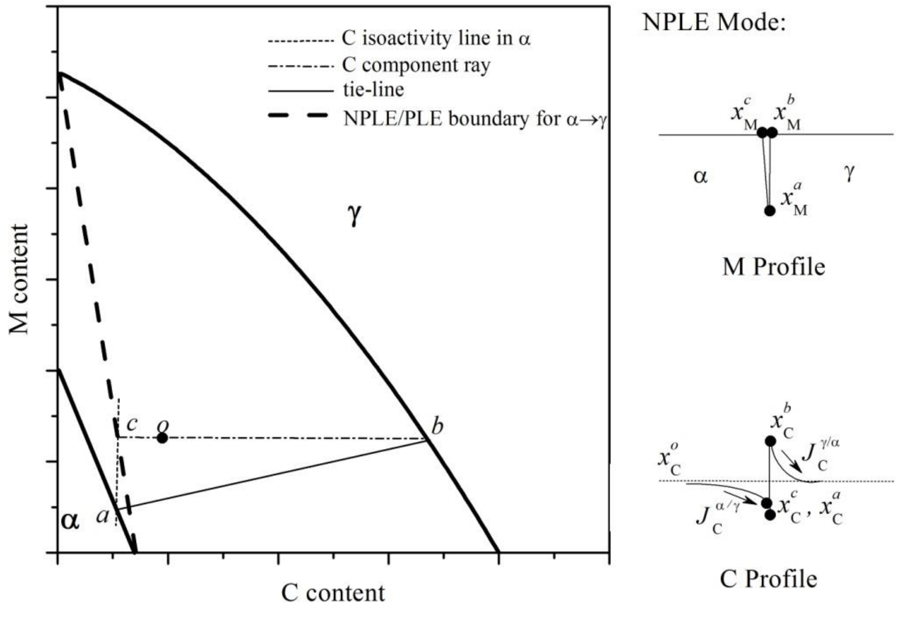
Carbon concentration in austenite (*Point P1*) will be located between NPLE/PLE-($\alpha\rightarrow\gamma$) (i.e. *Point b*) and NPLE/PLE-($\gamma\rightarrow\alpha$) (i.e. *Point C*)

Effect of QT on Interface migration



Extreme cases for austenite growth

Stage I: NPLE-(α→γ)

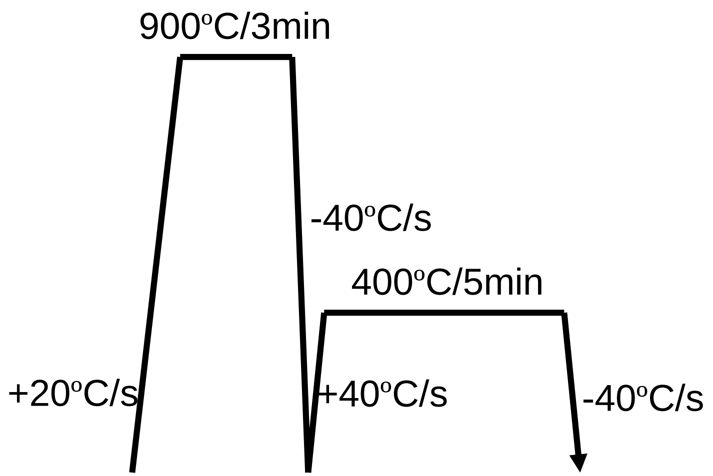


a)

$$v=\frac{J_C^{\gamma/\alpha}-J_C^{\alpha/\gamma}}{x_C^{\gamma/\alpha}-x_C^{\alpha/\gamma}}\approx-\frac{J_C^{\alpha/\gamma}}{x_C^{\gamma/\alpha}}$$

Controlled by Carbon diffusion in martensite

Fe-0.59C-2.9Mn-2.0Si（wt.%）

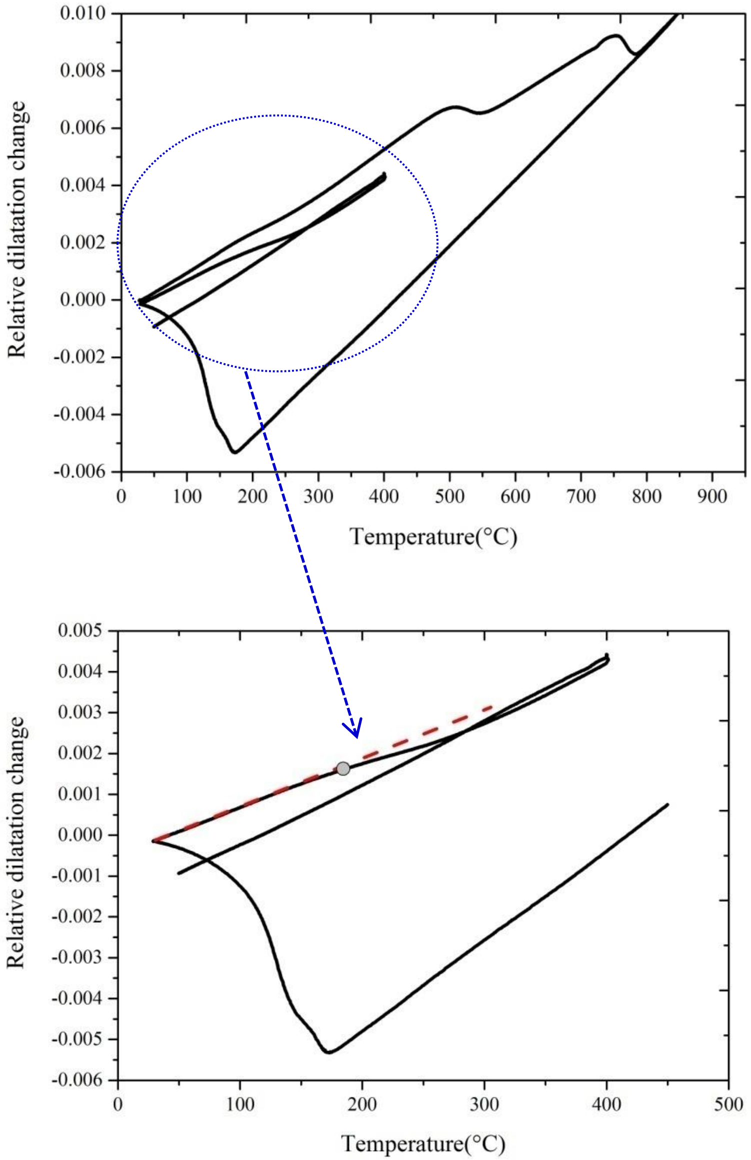


QT=Room temperature

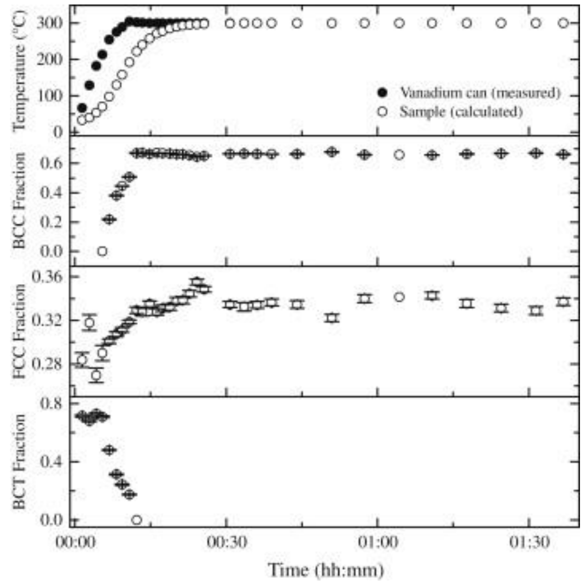
Vγ≈ 8% at QT

Extreme cases for austenite growth

Fe-0.59C-2.9Mn-2.0Si（wt.%）

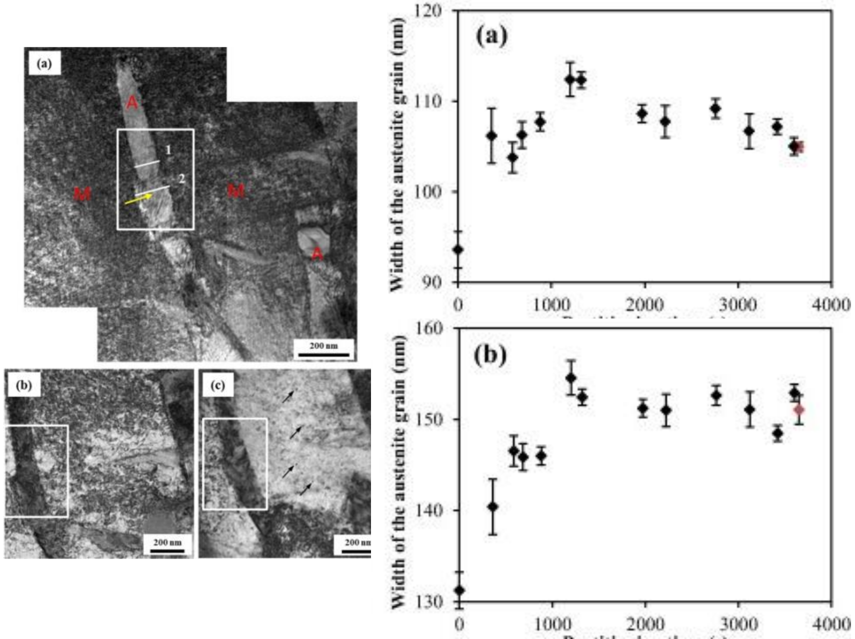


Fe-0.64C-4.57Mn-1.3Si（wt.%）



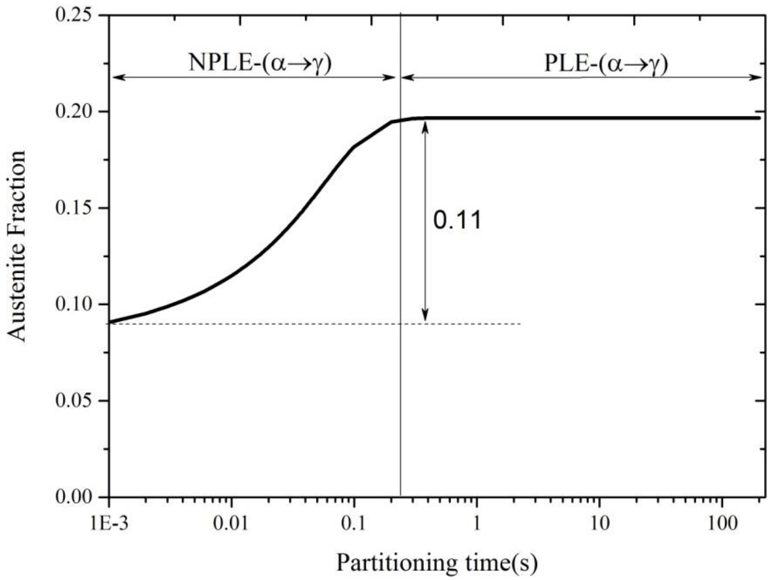
Bigg et al.
JAC
2013

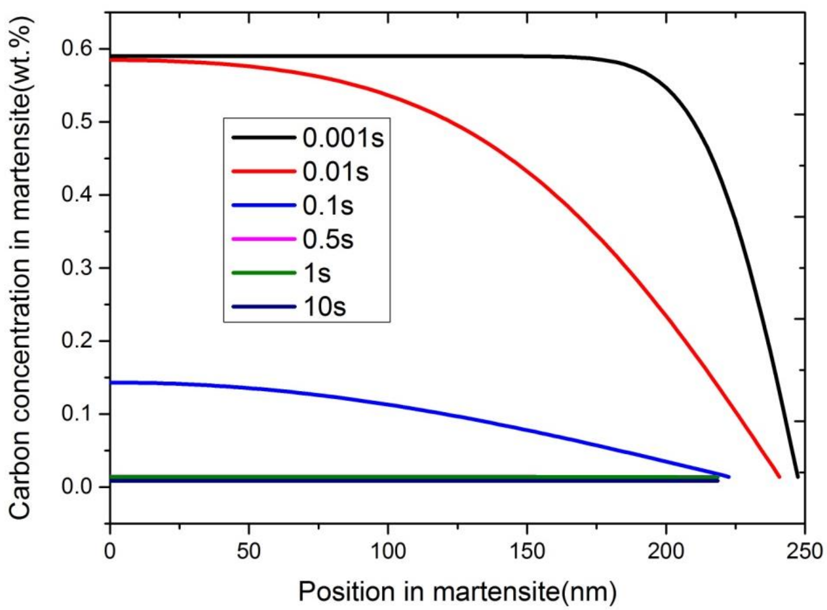
Fe-1.0C-3.0Mn-1.5Si（wt.%）

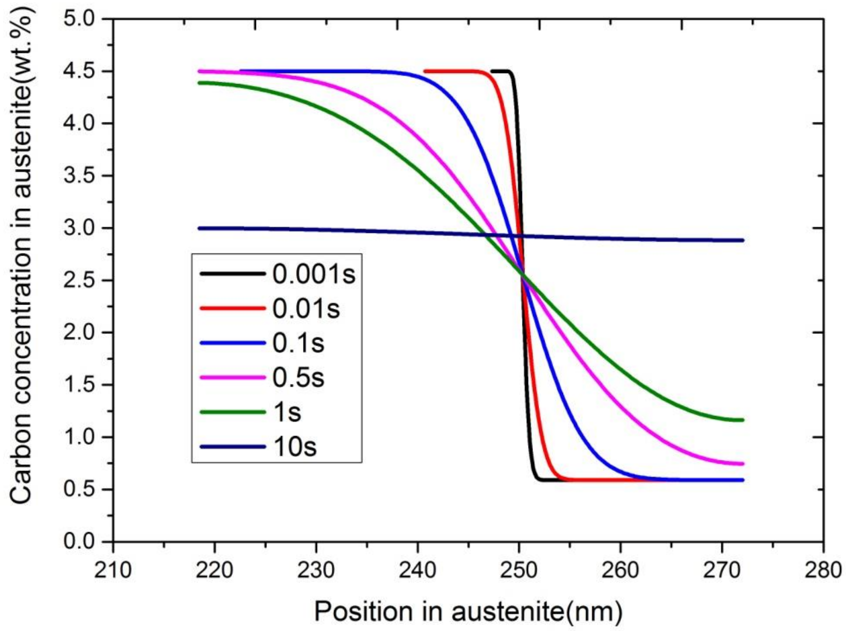


De Knijf et al.
Acta Mater.
2015

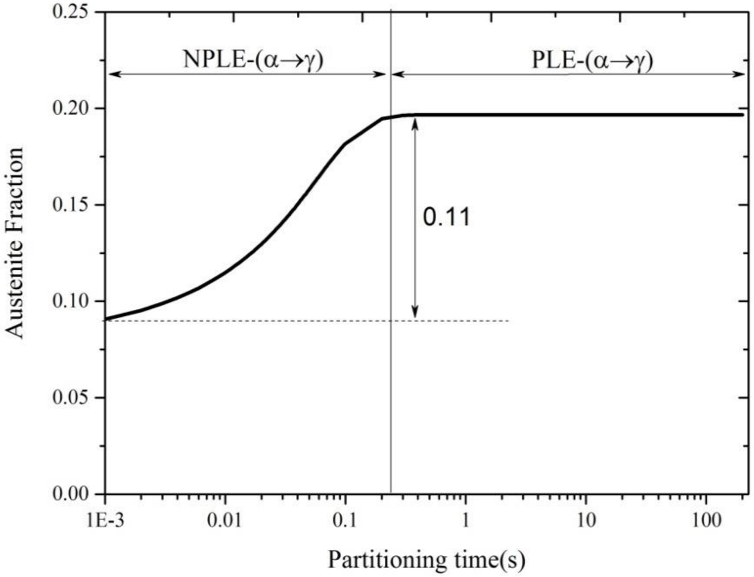
Extreme cases for austenite growth

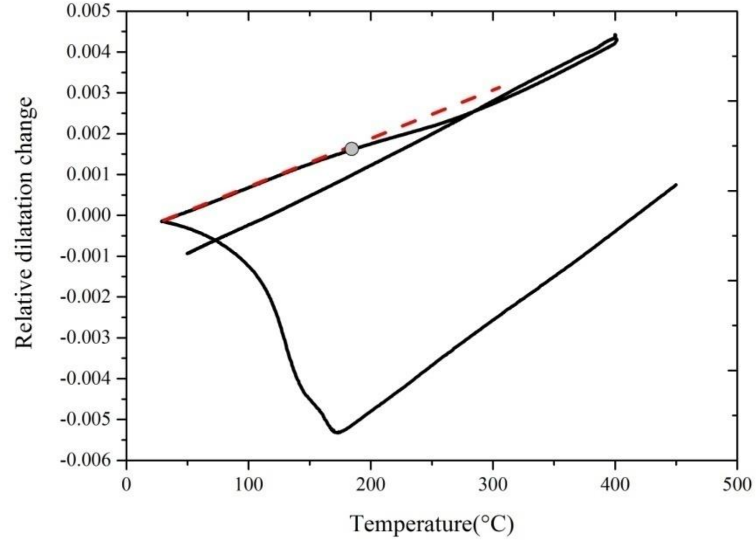


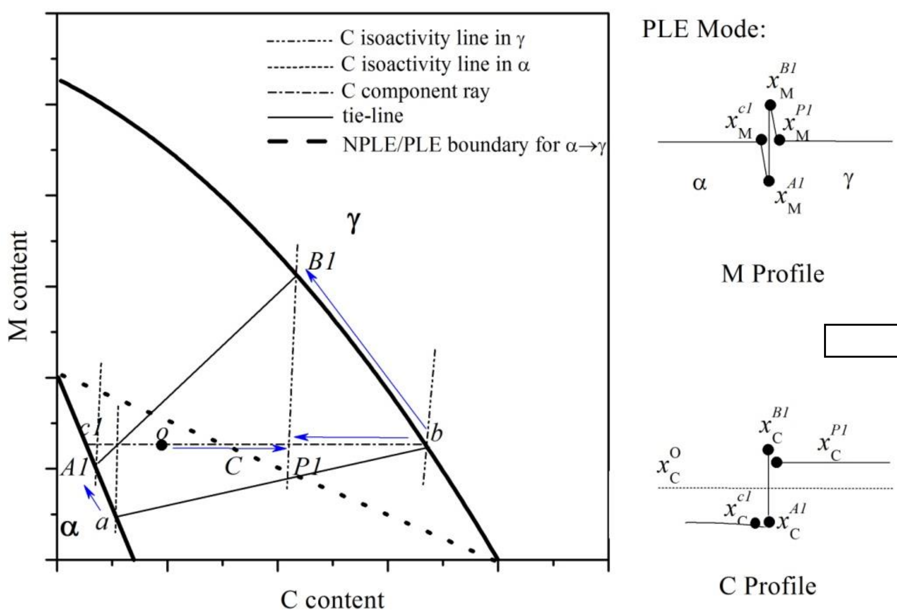


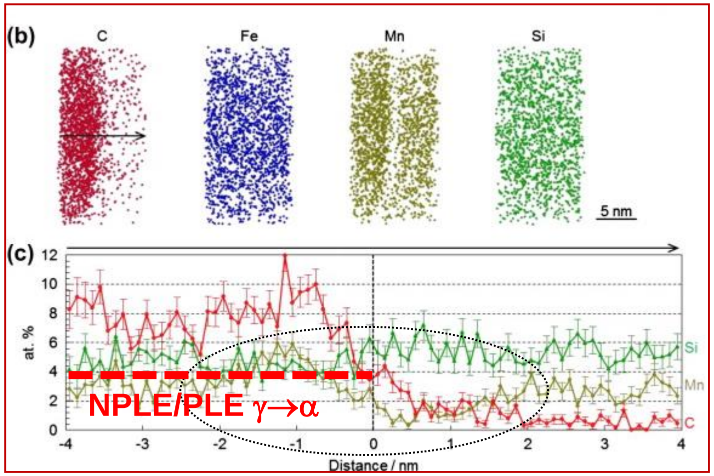


Extreme cases for austenite growth









Y. Toji et al. / Acta Materialia 65 (2014) 215–228

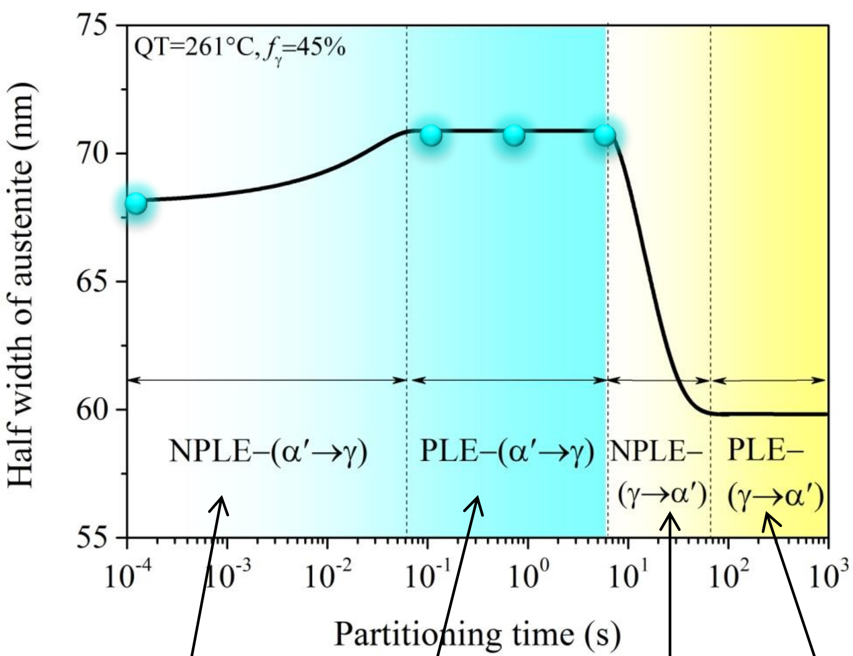
Conclusion

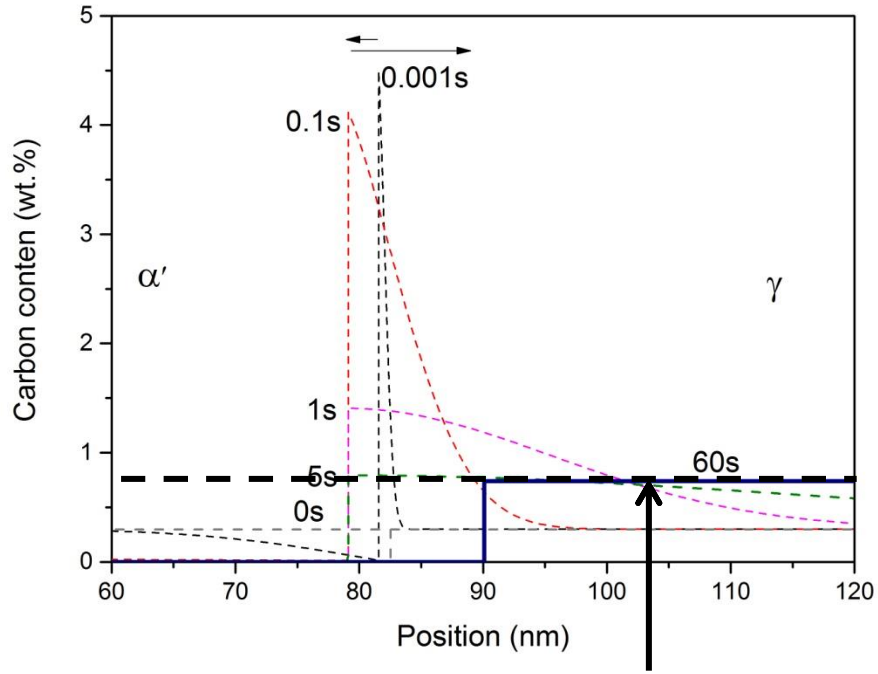
- **Interfacial partitioning of substitutional alloying elements plays a significant role in interface migration behavior and C content in austenite.**
- **Kinetics of interface migration. Based on the LE model, the kinetics of interface migration can be generally divided into four stages: NPLE-($\alpha' \rightarrow \gamma$) $\rightarrow$PLE-($\alpha' \rightarrow \gamma$) $\rightarrow$NPLE-($\gamma \rightarrow \alpha'$) $\rightarrow$PLE-($\gamma \rightarrow \alpha'$). Presence of the $\gamma \rightarrow \alpha'$ stages or not depends on QT.**
- **Alloying elements partitioning. After the partitioning process, C content in austenite could be located between the NPLE/PLE boundaries for the $\gamma \rightarrow \alpha'$ and $\alpha' \rightarrow \gamma$ transformation. Substitutional alloying elements partitioning across the interface is predicted to occur.**

Thank You !

Simulations by the QP-LE Model

QT=261℃ (f_γ=45%), PT=400 ℃



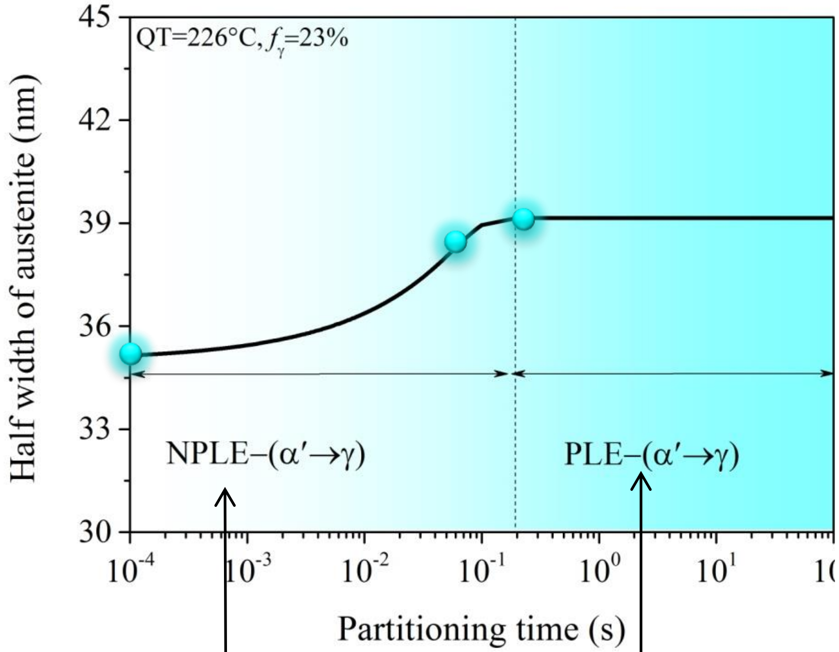


$C_{\gamma}^{NPLE/PLE\gamma\rightarrow\alpha'}$

C diffusion in α′ controlled | **Mn/Si diffusion in α′ controlled** | **C diffusion in γ controlled** | **Mn/Si diffusion in γ controlled**

Simulations by the QP-LE Model

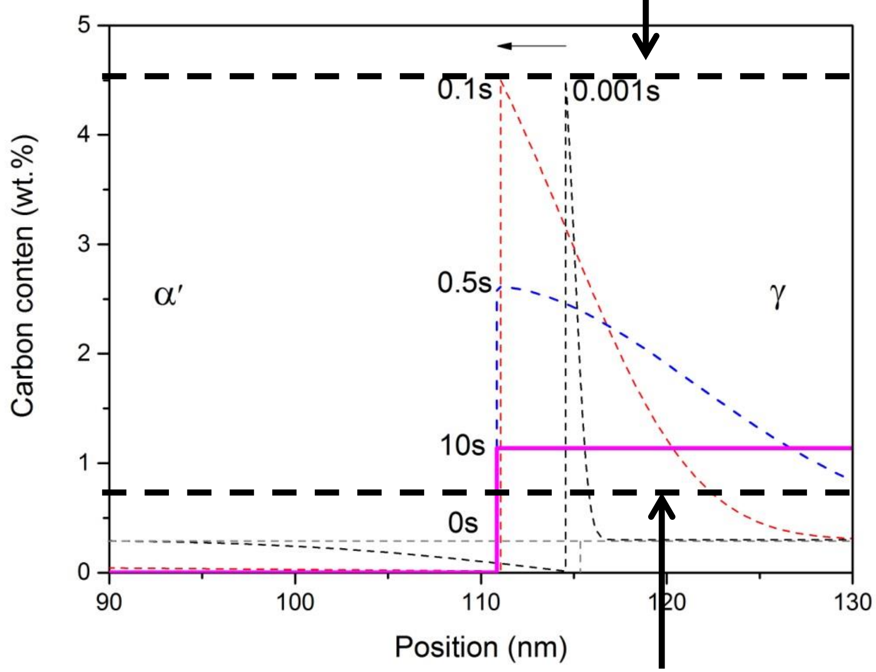
QT=226℃ (f_γ=23%), PT=400 ℃



C diffusion in α′ controlled

Mn/Si diffusion in α′ controlled

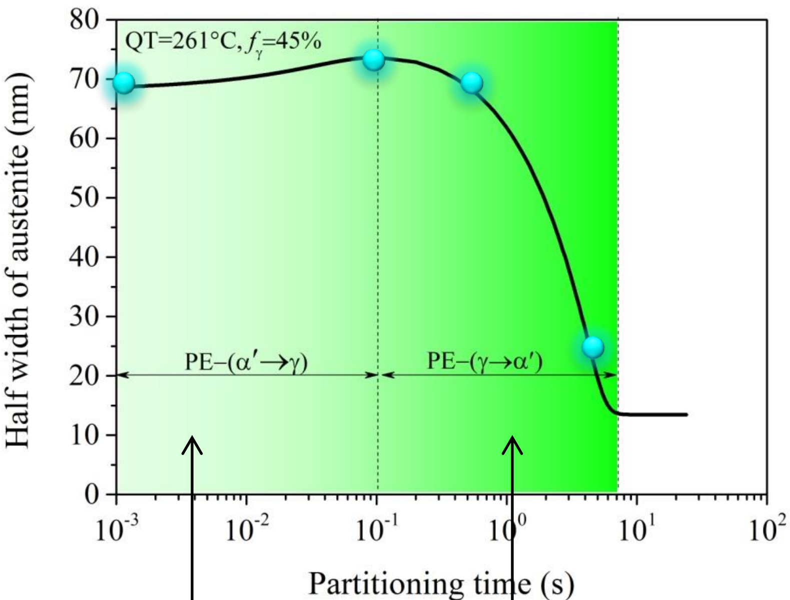
$C_\gamma^{NPLE/PLE\alpha'\rightarrow\gamma}$



$C_\gamma^{NPLE/PLE\gamma\rightarrow\alpha'}$

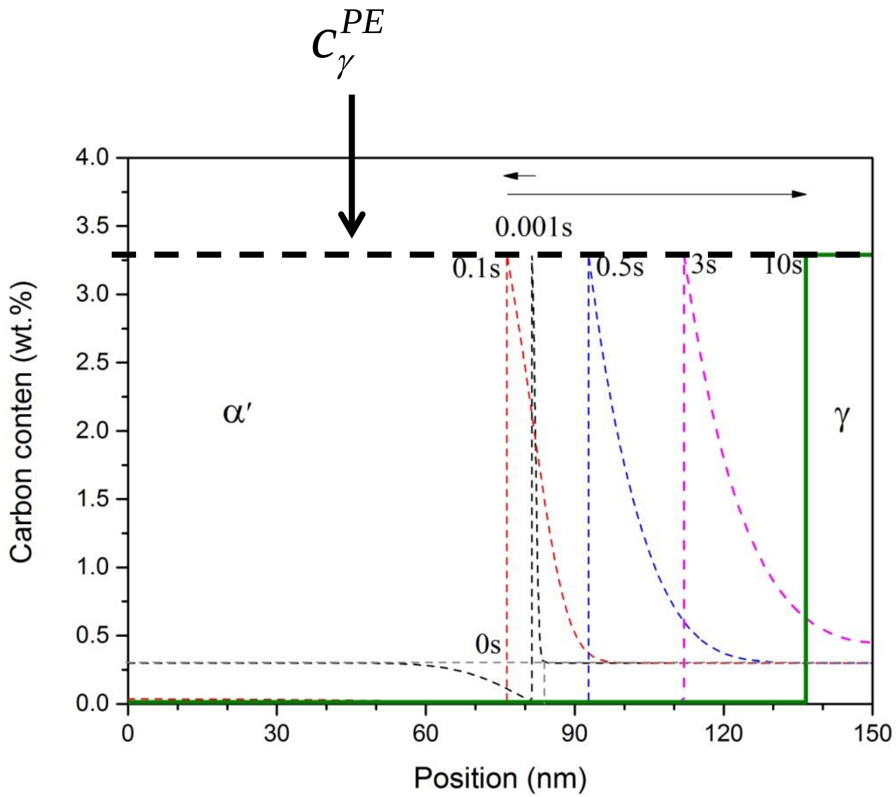
Simulations by the QP-PE Model

QT=261 ℃,PT=400 ℃



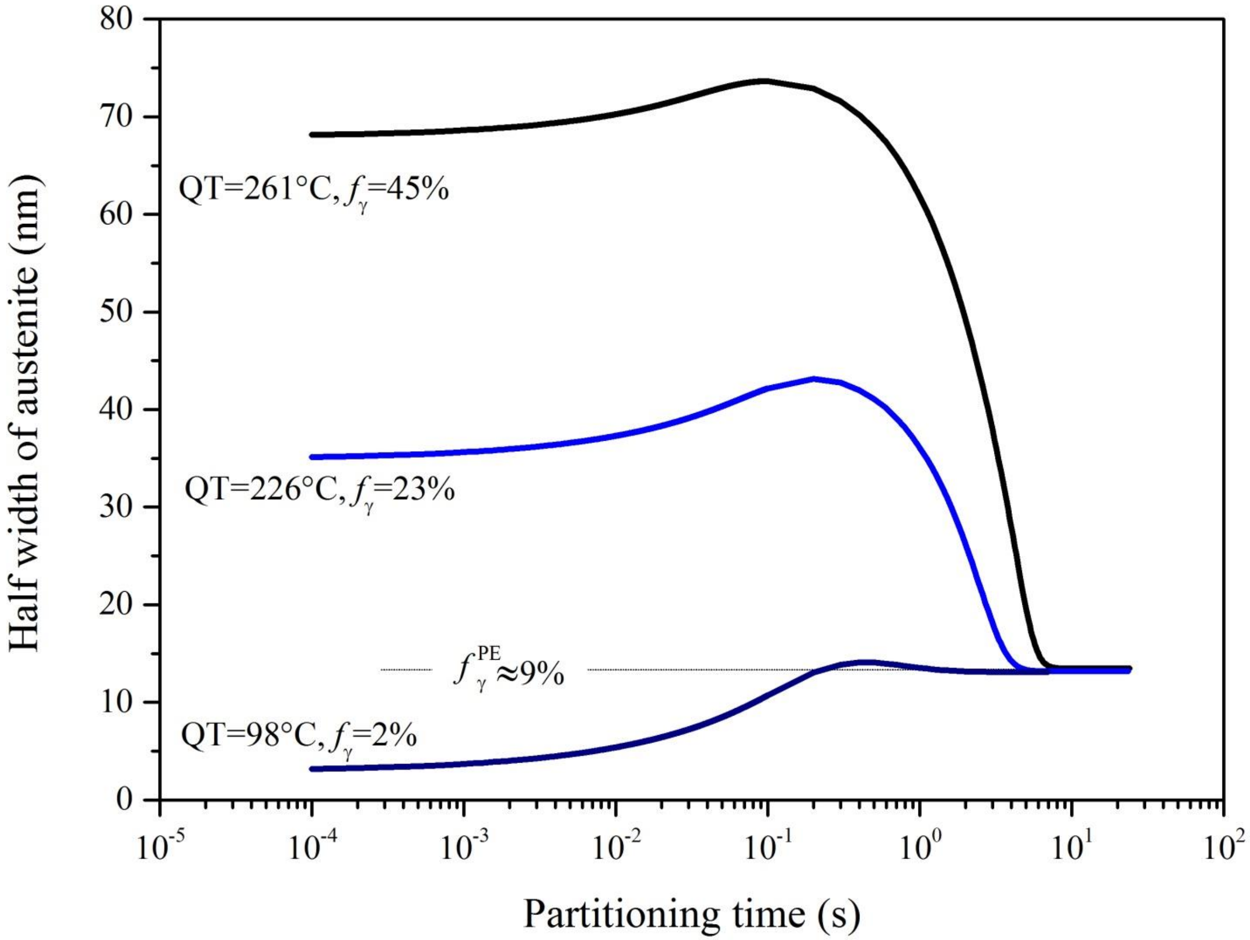
C diffusion
in α′ controlled

C diffusion
in γ controlled



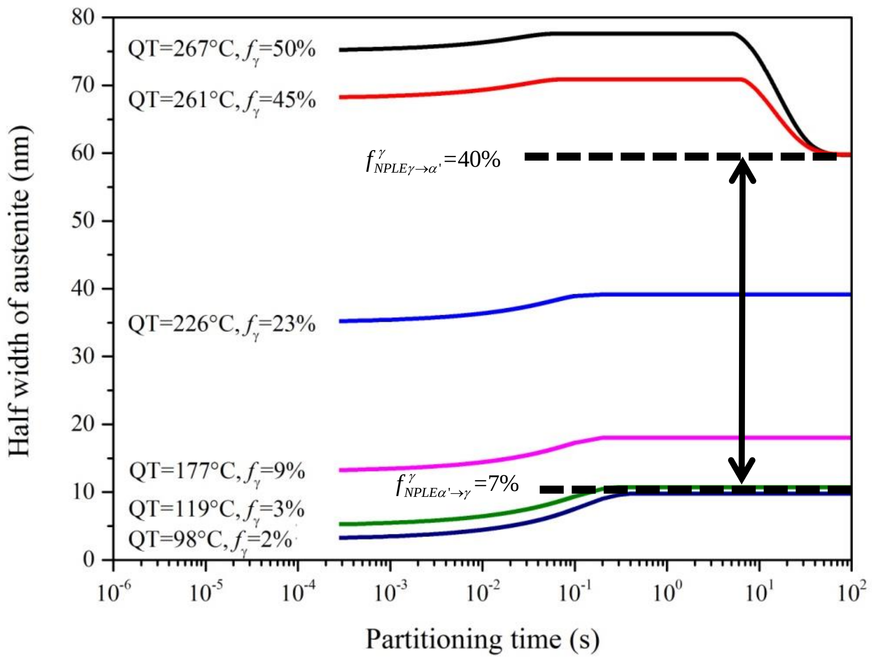
Simulations by the QP-PE Model

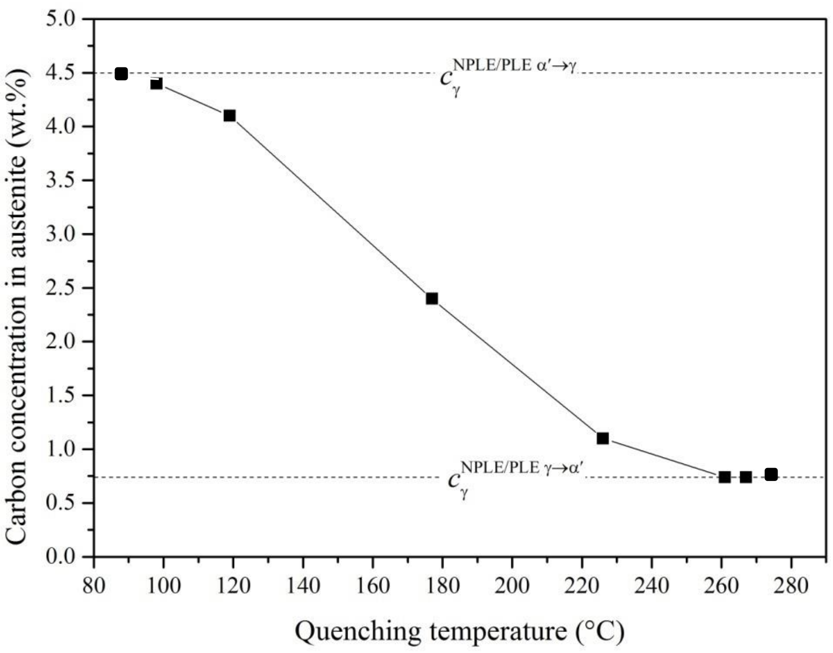
QT=261 / 226 / 98 ℃, PT=400 ℃



Simulations by the QP-LE Model

QT=267 ~ 98 ℃, PT=400 ℃





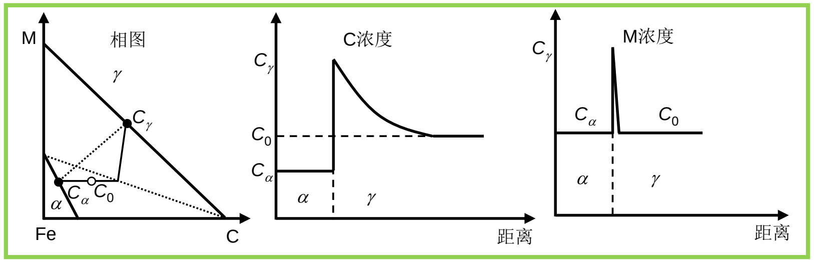
C content in austenite is between $c_\gamma^{NPLE/PLE\gamma\to\alpha'}$ and $c_\gamma^{NPLE/PLE\alpha'\to\gamma}$!

QP-LE Model

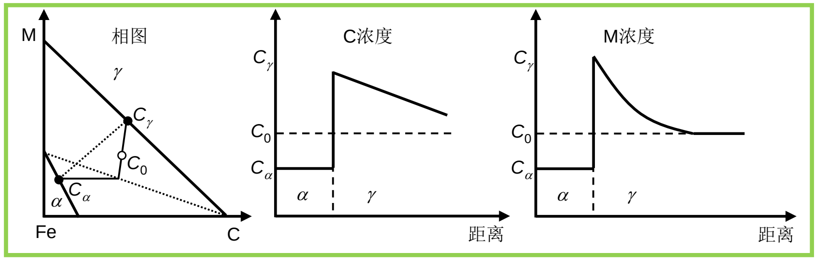
QP-LE--Local equilibrium:

$$\mu_i^{\gamma} = \mu_i^{\alpha}$$

Negligible Partitioning-Local Equilibrium (NP-LE) : C diffusion controlled



Partitioning-Local Equilibrium (P-LE) : M diffusion controlled

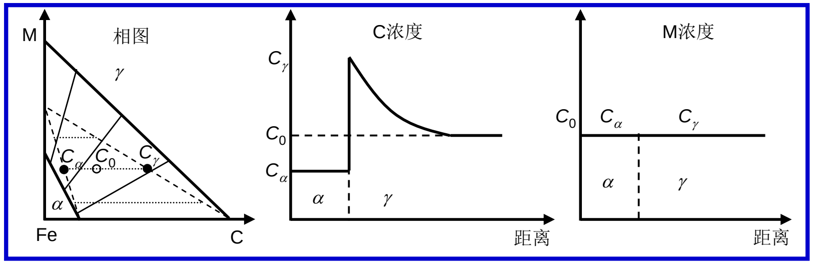


QP-PE--Paraequilibrium:

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

$$\left(\mu_M^{\gamma} - \mu_M^{\alpha}\right) = -\frac{X_{Fe}}{X_M}\left(\mu_{Fe}^{\gamma} - \mu_{Fe}^{\alpha}\right)$$

PE : C diffusion *AND* Mn indiffusible



Diffusion Controlled Kinetic Process :

$$\frac{\partial c}{\partial t} = \nabla \cdot \left(D \nabla c\right) \qquad (1)$$

$$\frac{c_{i,j+1} - c_{i,j}}{\Delta t} = D\frac{c_{i-1,j} - 2c_{i,j} + c_{i+1,j}}{\Delta x^2} + v\frac{N-i}{N-1}\frac{c_{i+1,j} - c_{i-1,j}}{2\Delta x} \qquad (2)$$

$$v = \left(D^{\alpha'}\frac{\partial c^{\alpha'}}{\partial x} - D^{\gamma}\frac{\partial c^{\gamma}}{\partial x}\right) / \left(c^{\gamma/\alpha'} - c^{\alpha'/\gamma}\right) \qquad (3)$$