合金元素分配和奥氏体热变形对铁素体相变动力学影响

Partition of alloy elements and deformation on the Kinetics of ferrite formation

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Outline

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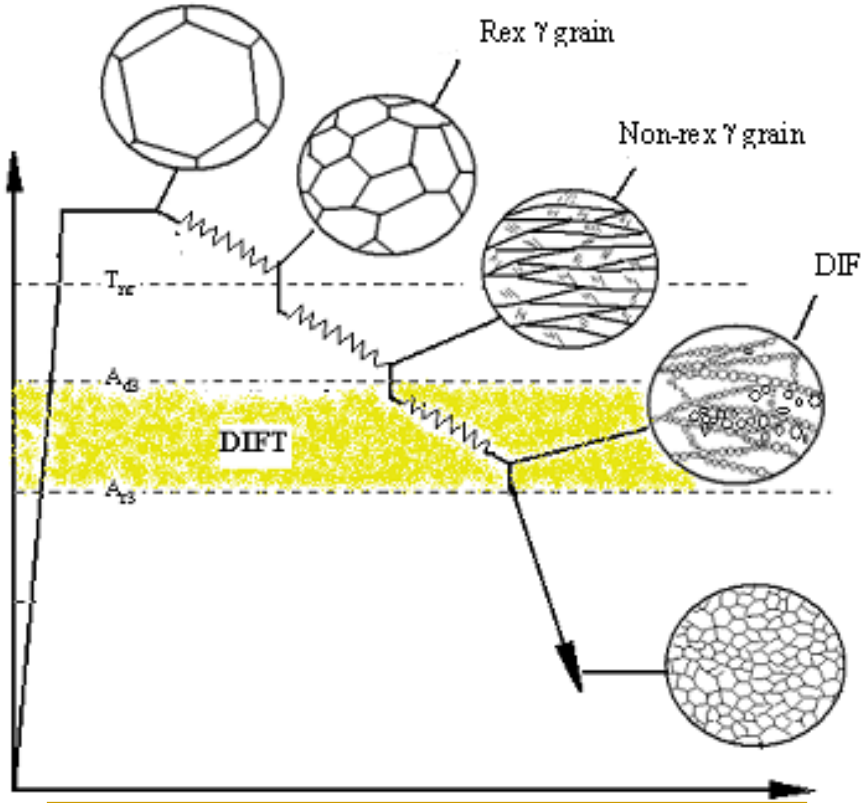
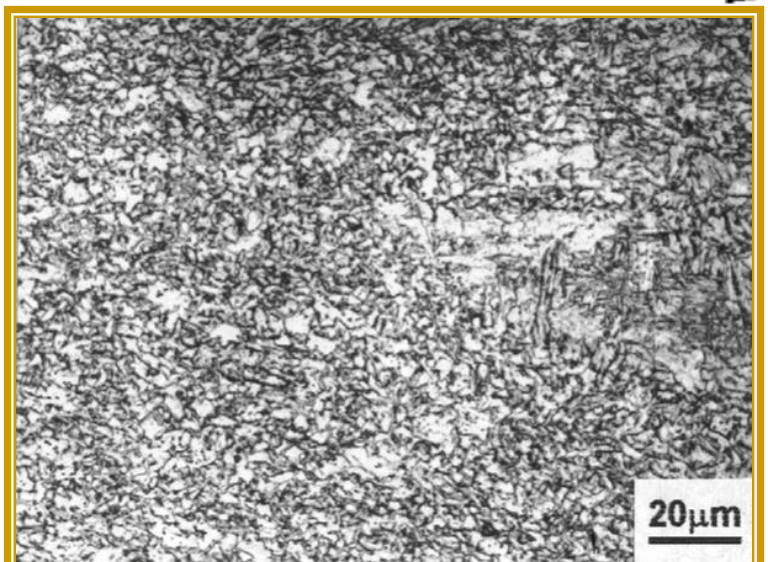
- Introduction
- Diffusion control growth by C or M? PLE/NPLE
- Stored deformation energy
- Deformation on PLE/NPLE
- Deformation on nucleation
- Summary

Introduction

- It is well known from experiments that the ferrite grains can be refined significantly by hot deformation of austenite
- The quantitative effect of deformation on growth of ferrite has not been fully understood, in Fe-C-M.
- Diffusion growth by C or M?

Fine grains in Fe-C-Mn

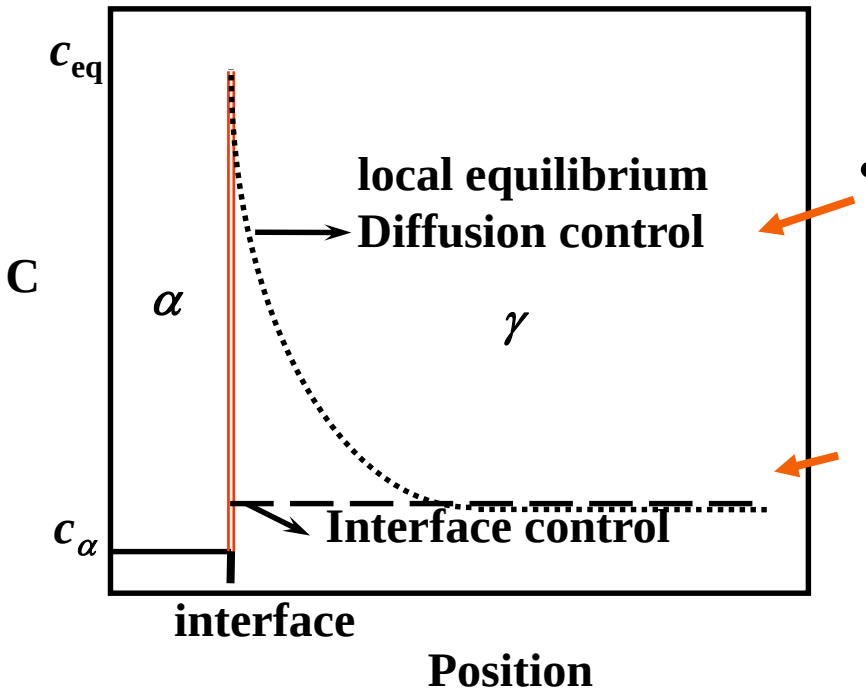




From γ to α, What changes?

Structure change: fcc to bcc → γ/α interface migration

Chemical change: → carbon/alloy diffusion from γ/α to γ



Interface reaction:

- **Fast enough**→ LE mode: C / M diffusion controlled ferrite growth
- **Slow enough**→ Interface control mode: negligible gradient of carbon/alloy concentration

Aaronson, 1962; Christian, 1981

Mixed Model control results

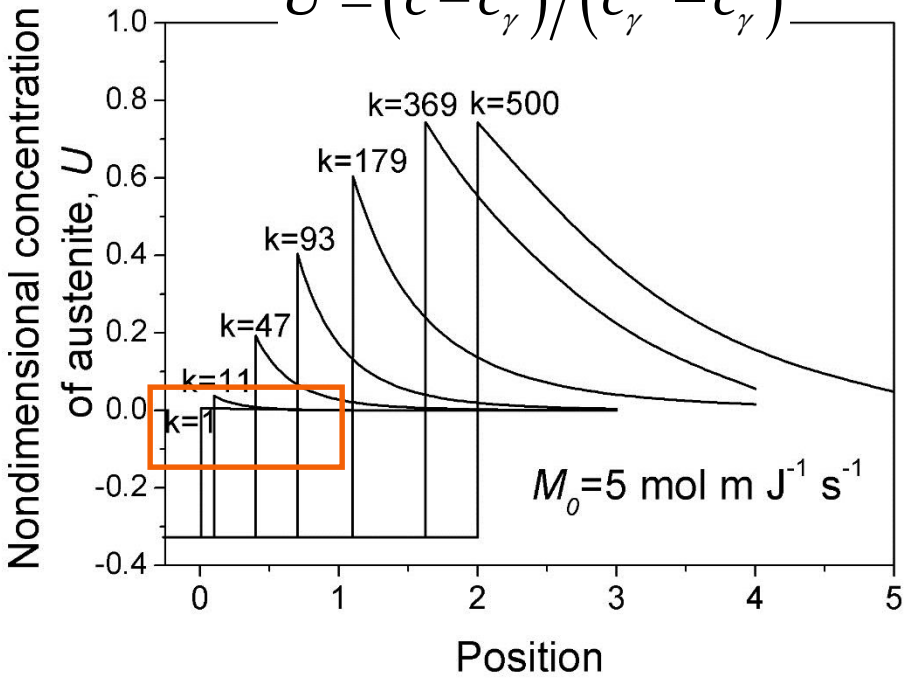
An example: Fe-0.22 wt% C, holding at 993 K

M_0=5 mol m J^{-1} s^{-1} $D=8.114\times10^{-13}m^2/s$,

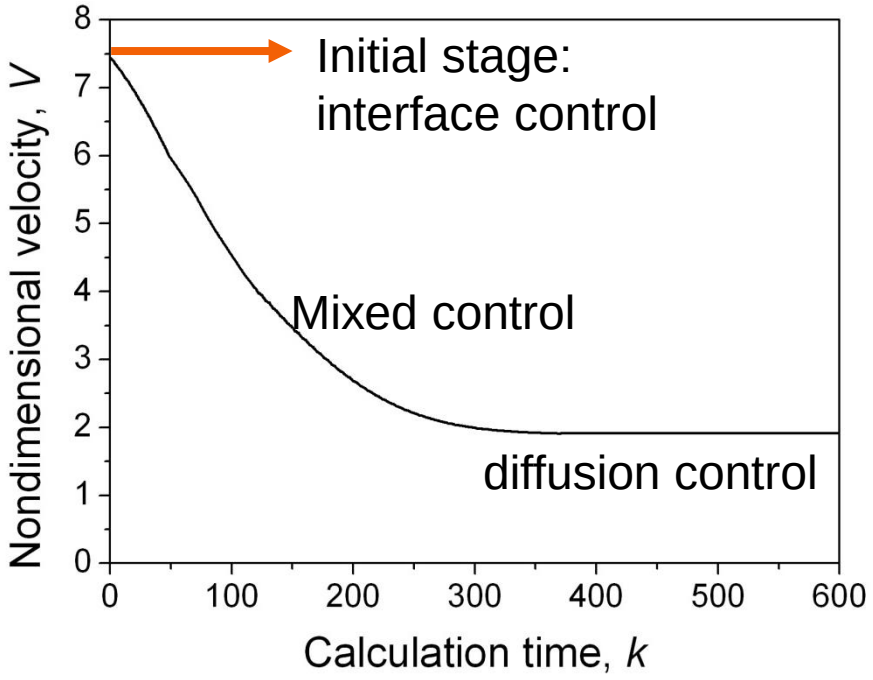
$a=0.066\mu m$, $\chi=110J/mol$

Development of carbon profile

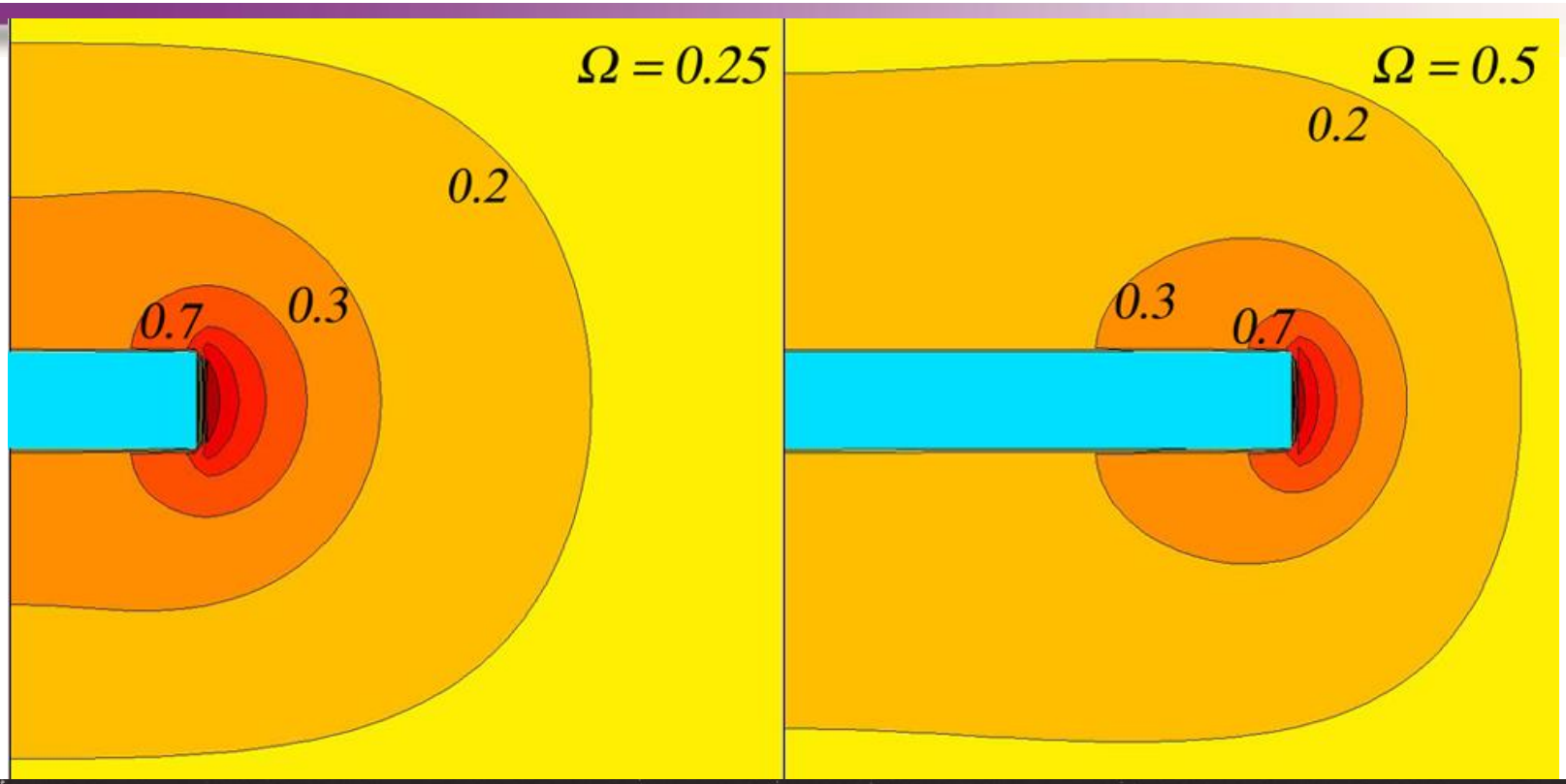
$$U=\left(c-c_\gamma^0\right)/\left(c_\gamma^{eq}-c_\gamma^0\right)$$

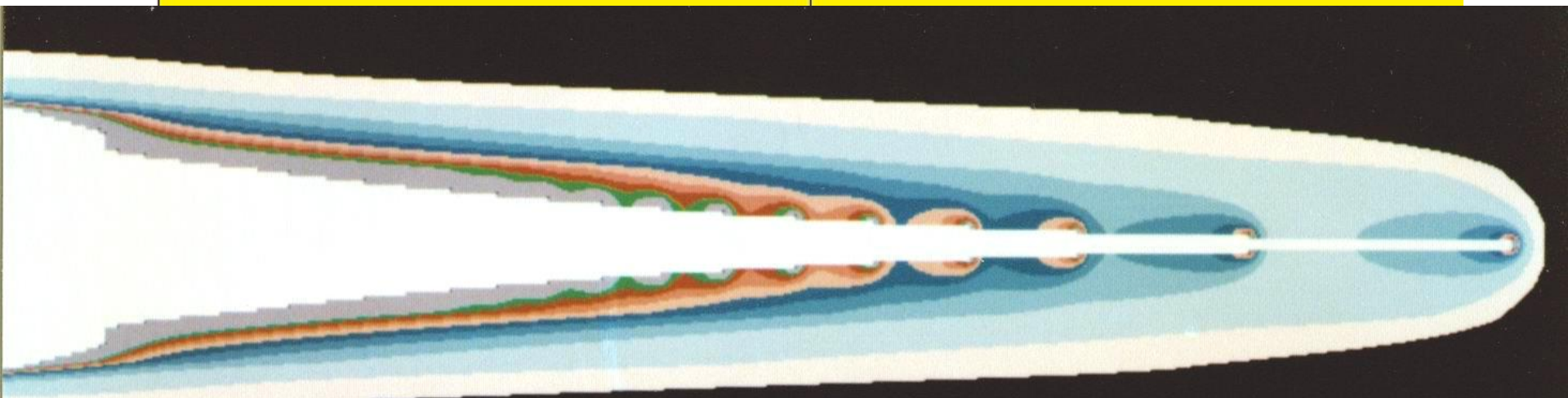


$$V=\frac{M_0}{D}a\chi\cdot(c_\gamma^{eq}-c_\gamma^{\gamma\alpha})\cdot\exp(-\frac{E}{RT})$$



Ledge growth of ferrite by diffusion of carbon





What dominate Microstructure of (α)+ (γ)

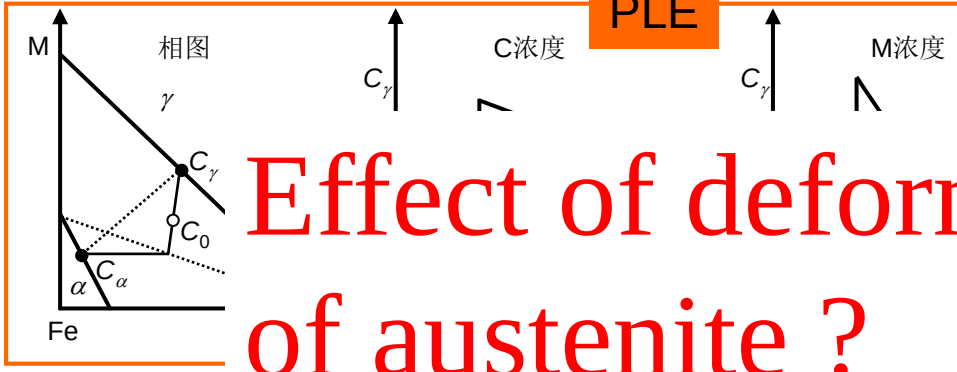
- Equilibrium: By Phase diagram (Thermodynamics)
- Always Non Equilibrium: By Kinetics

Alloy elements' (such as Mn) diffusivity is several orders smaller than carbon, thus, it is difficult to reach equilibrium by partition between α and γ.

- PLE：Partition local equilibrium, slow, by M diffusion
- NPLE：Non-Partition local equilibrium, fast, by C diffusion
- PE：para-equlibrium, C diffusion, neglect M, fast

More than C, Alloy element diffusion or not?

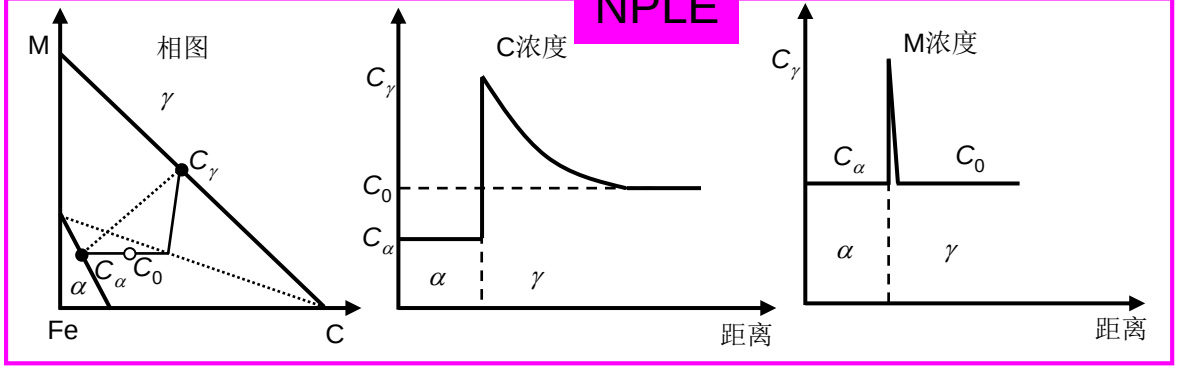
PLE



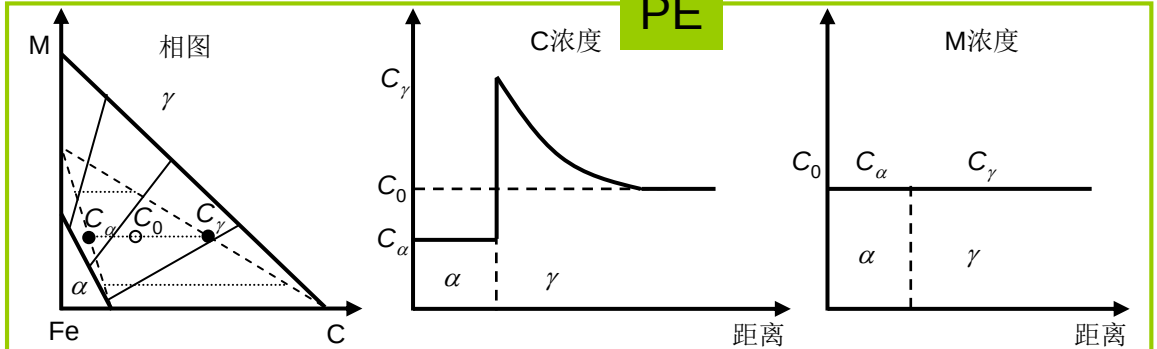
Effect of deformation of austenite ?

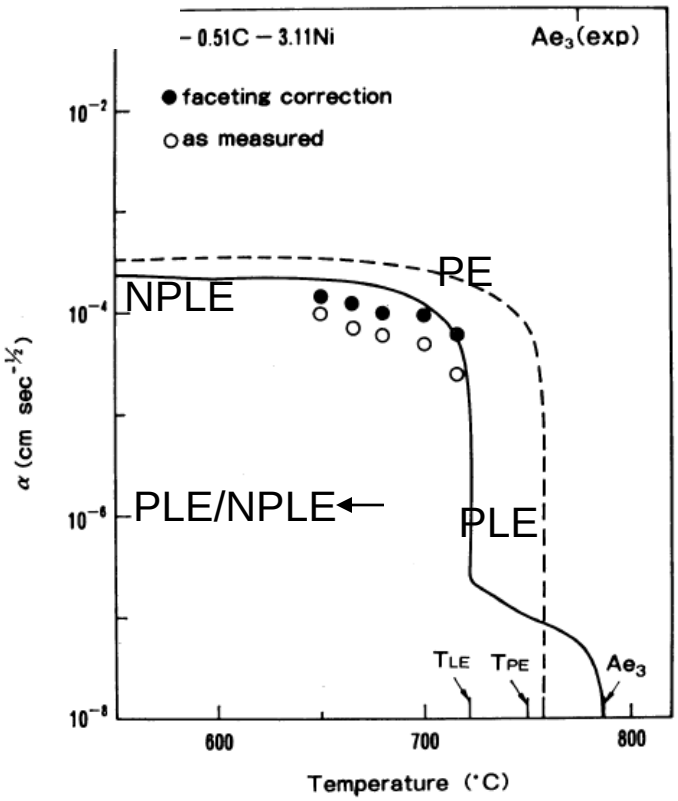
- **PLE：Partition local equilibrium, slow, by M diffusion**
- **Non-Partition local …m, fast, by C diffusion**
- **…a-equlibrium, C diffusion**

NPLE



PE

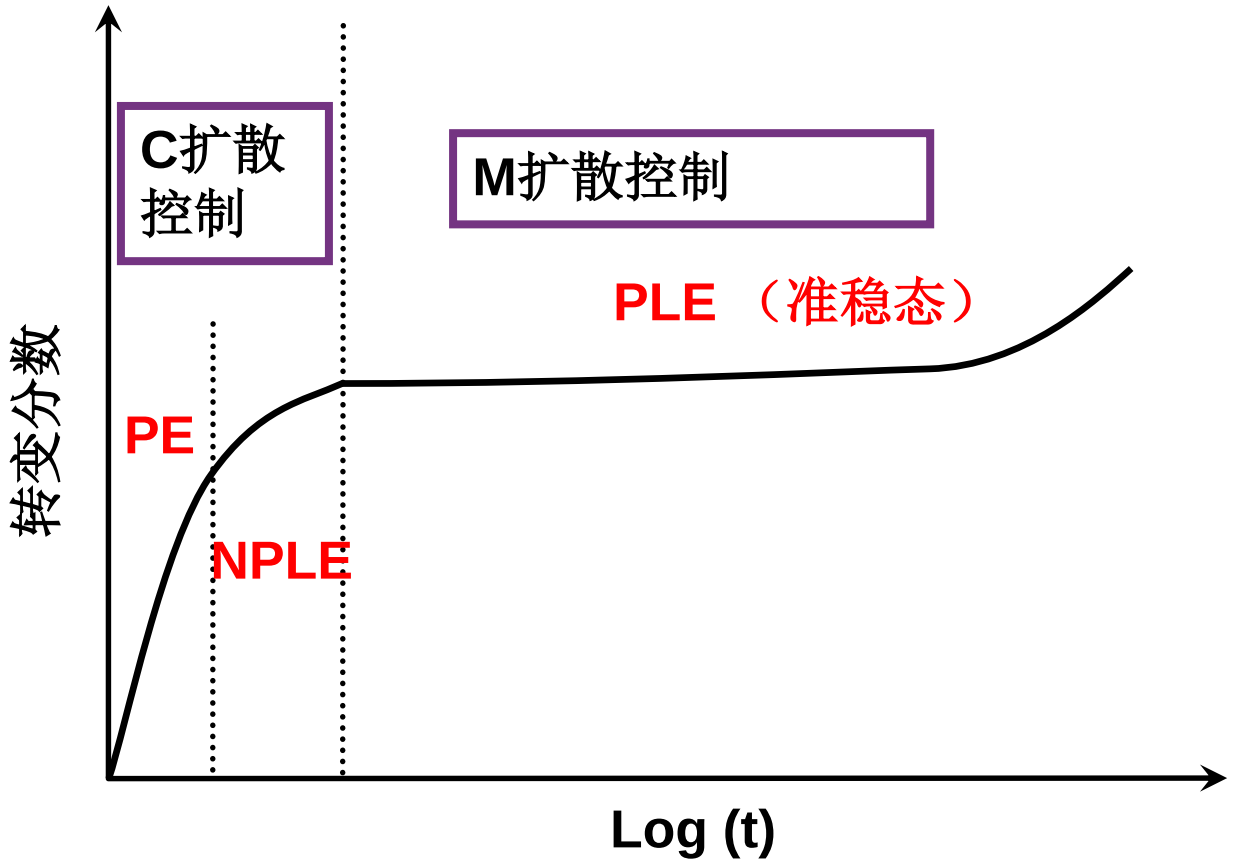




Growth rate vs diffusion mode

From initial PE to later NPLE with time

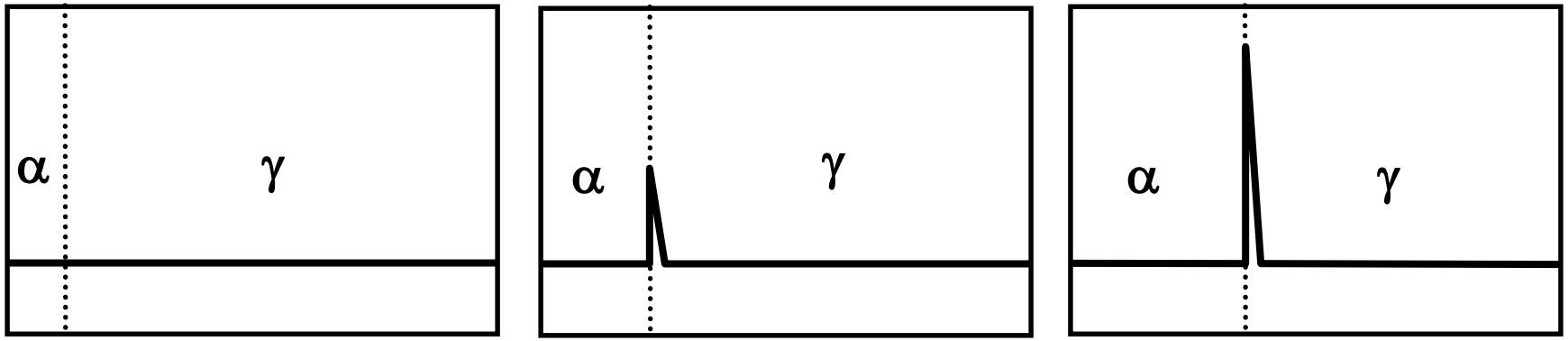
Ferrite Transformation fraction with time

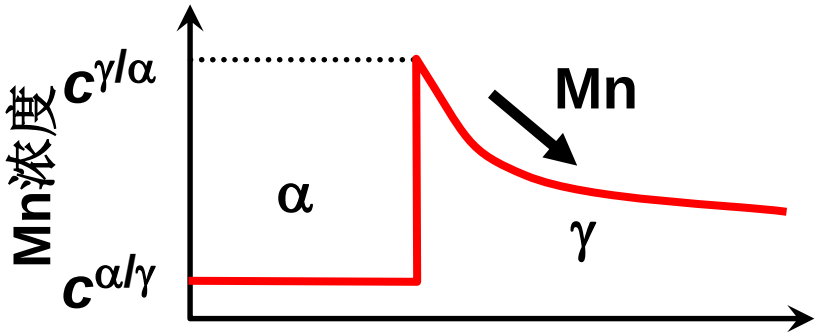


铁素体长大过程元素配分模式转换（前期 PE → 中期 NPLE → 后期 PLE）

Mn浓度分布

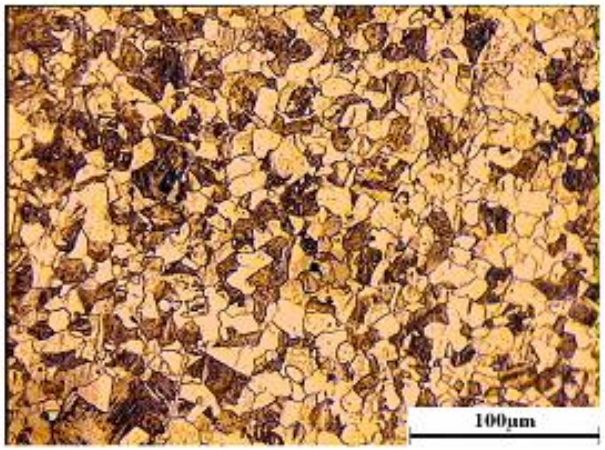
前期: *PE*　　过渡　　中期: *NPLE*



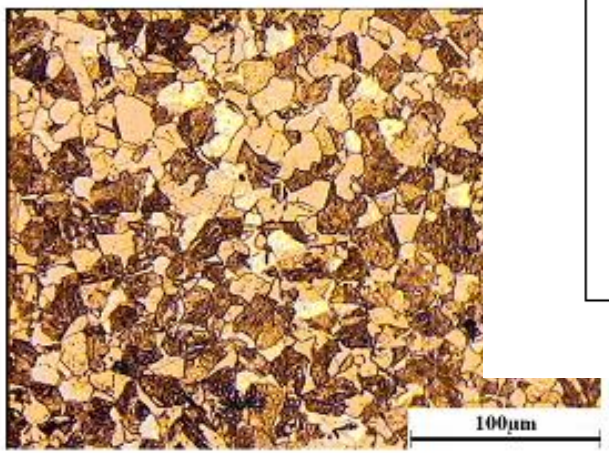


最后：PLE：合金元素配分，Mn扩散控制

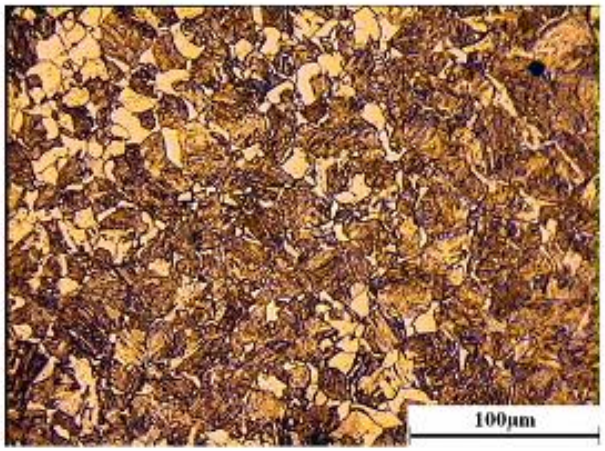
Fe-0.07C-2.2Mn-0.8Si-0.9Cr



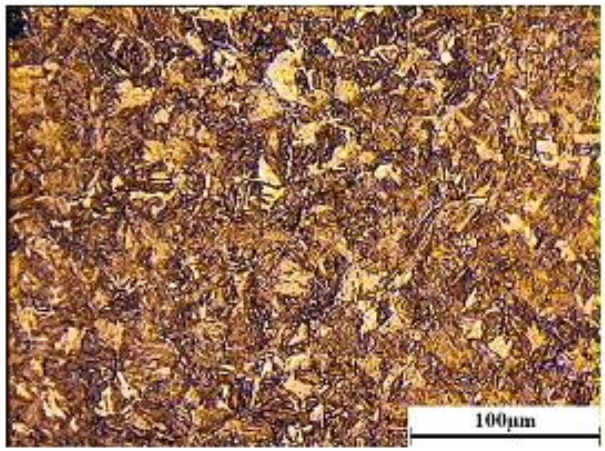
(a)



(b)

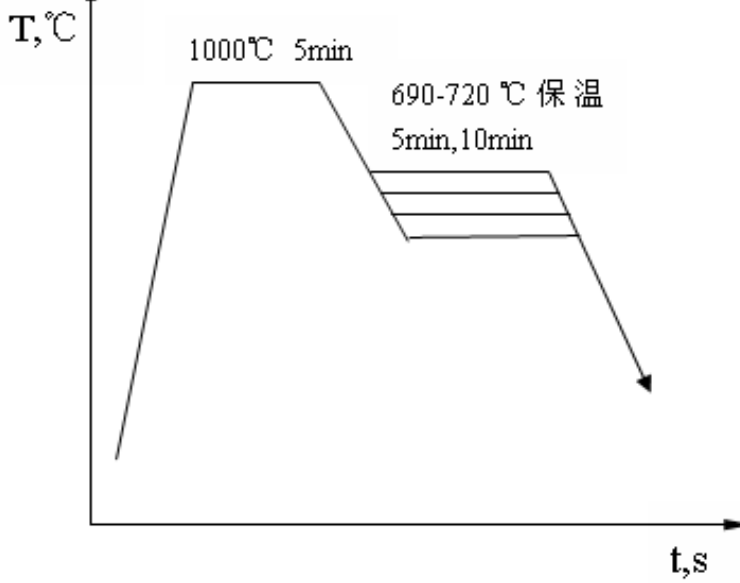


(c)



(d)

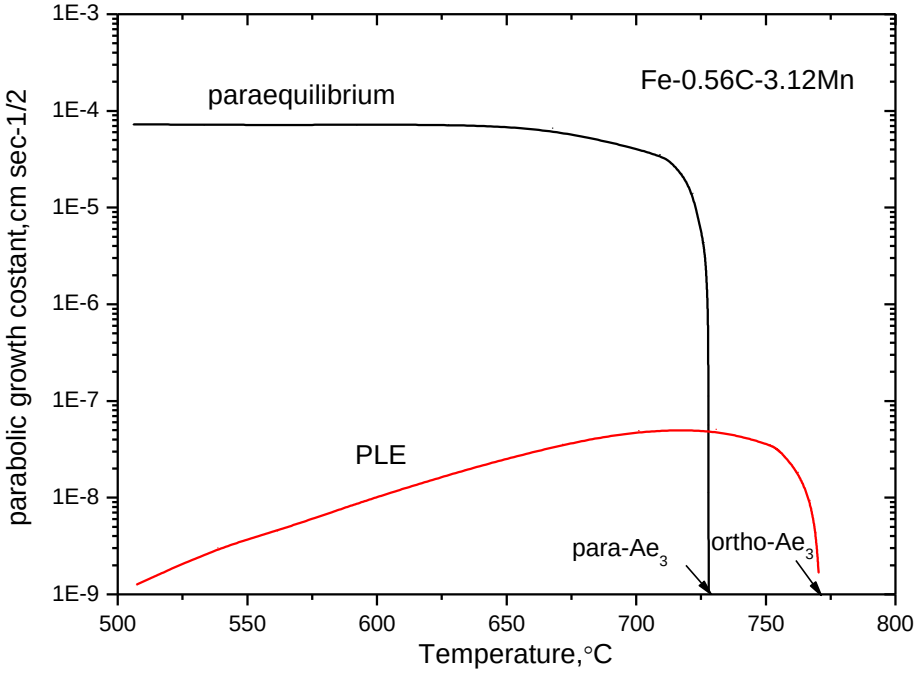
a)690C, b)700C, c)710C, d)720C

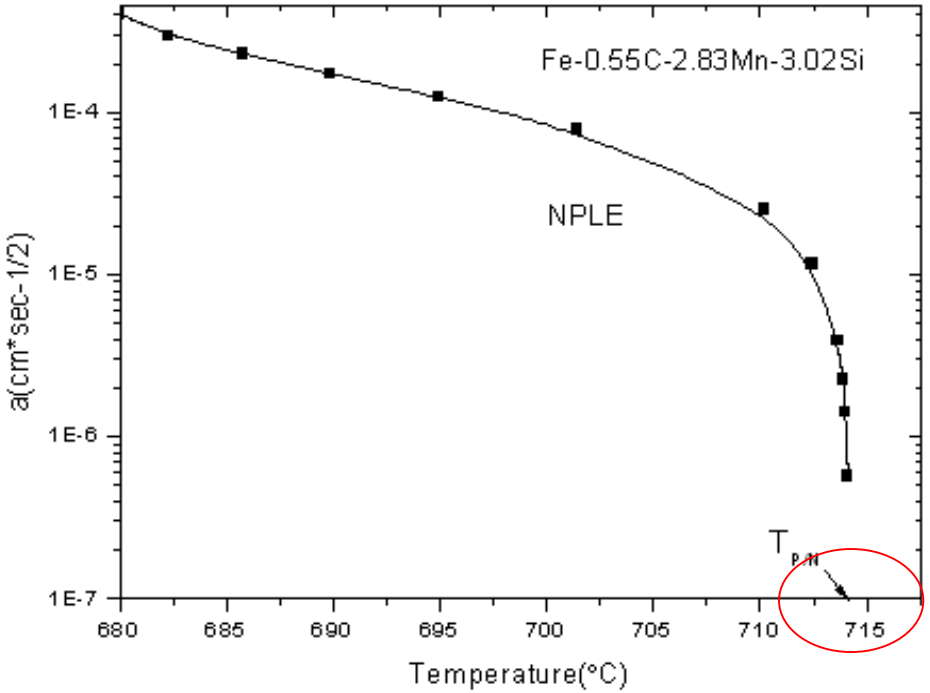


Ae3＝811℃

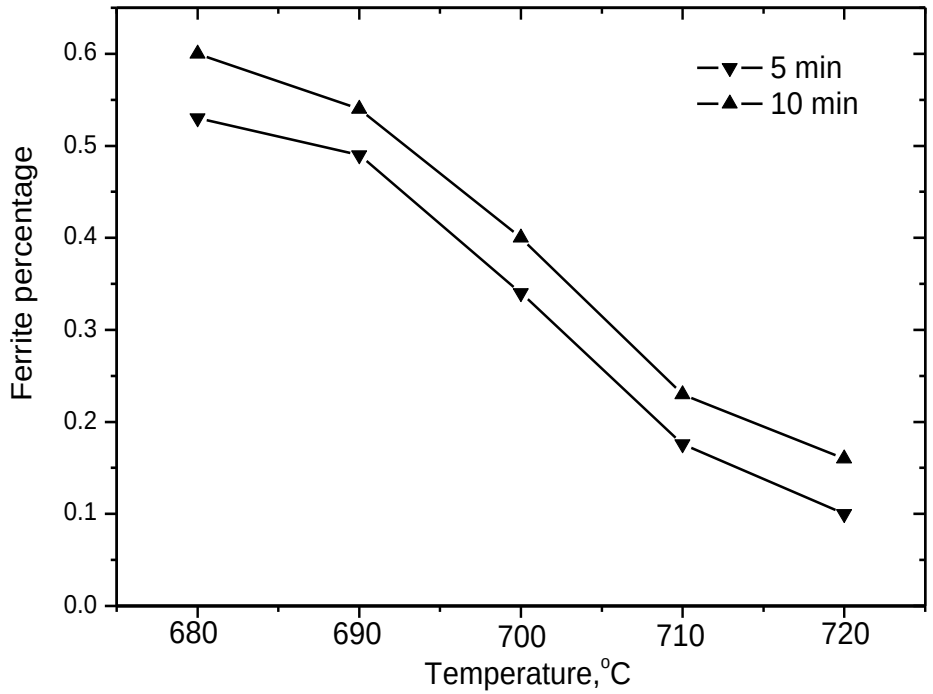
PLE/NPLE≈
(700~710℃)

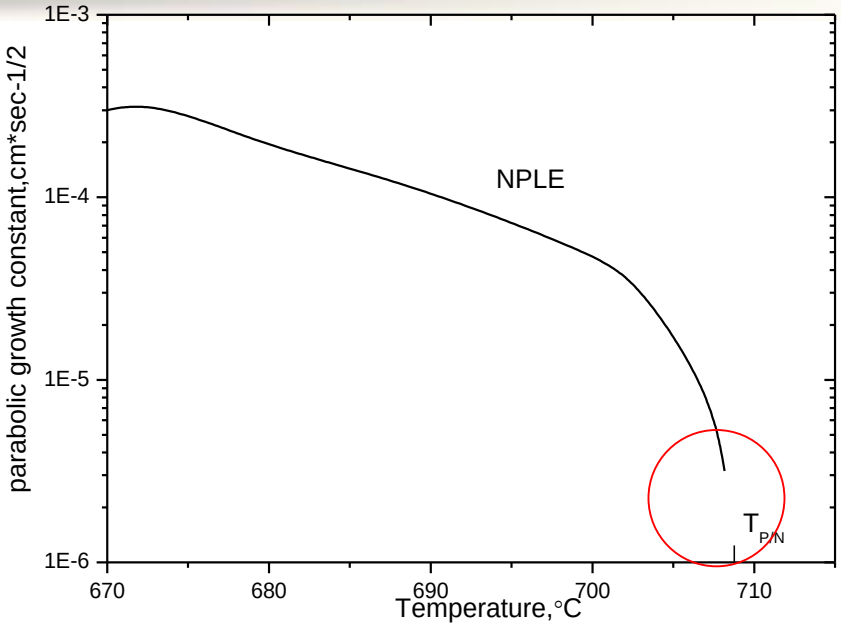
Calculation of parabolic growth rate (α) of ferrite by diffusion control, PLE & NPLE





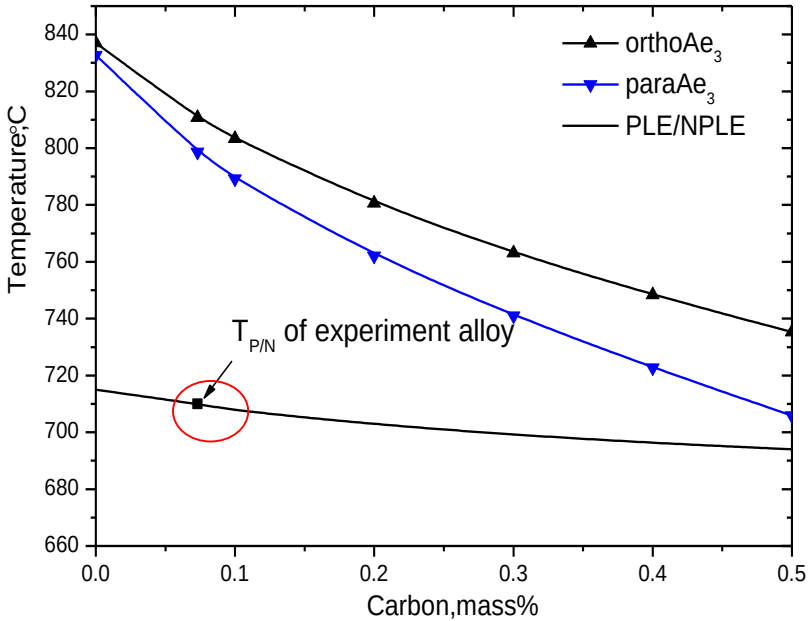
Temp of PLE/NPLE in Fe-0.07C-2.2Mn-0.8Si-0.9Cr,wt%





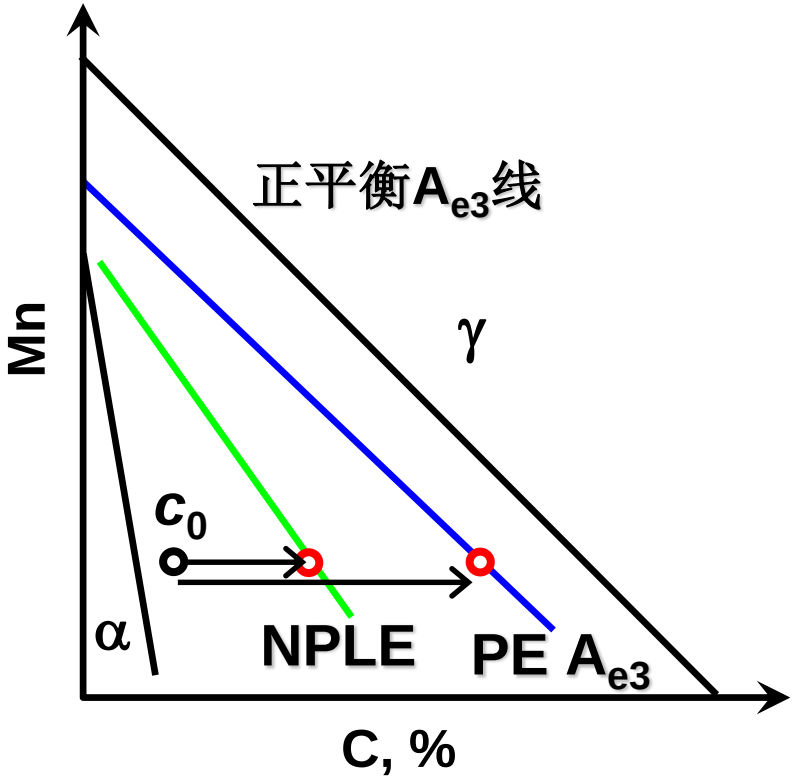
PLE/NPLE~ 700~710℃

Temperature of PLE/NPLE decrease slowly with carbon concentration



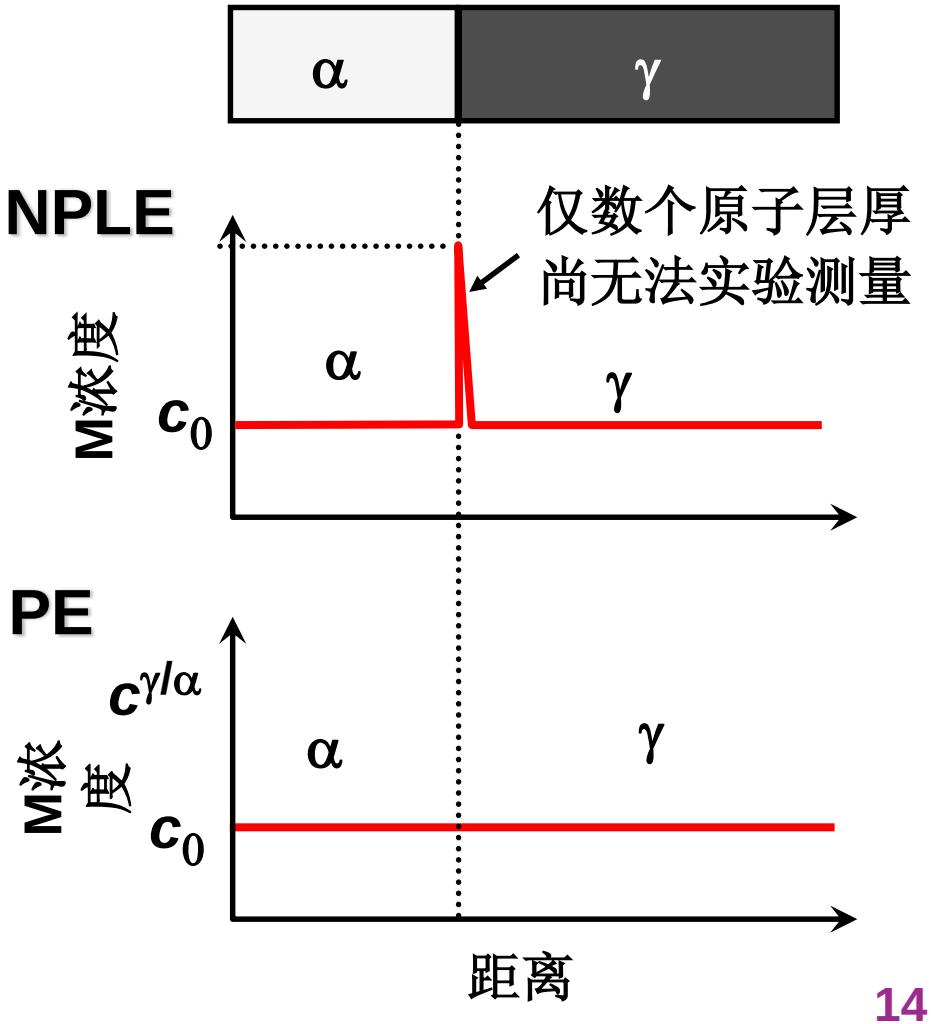
Difference between PE and NPLE

- NPLE：合金元素不配分局部平衡模型
- PE：准平衡模型



NPLE 或 PE?

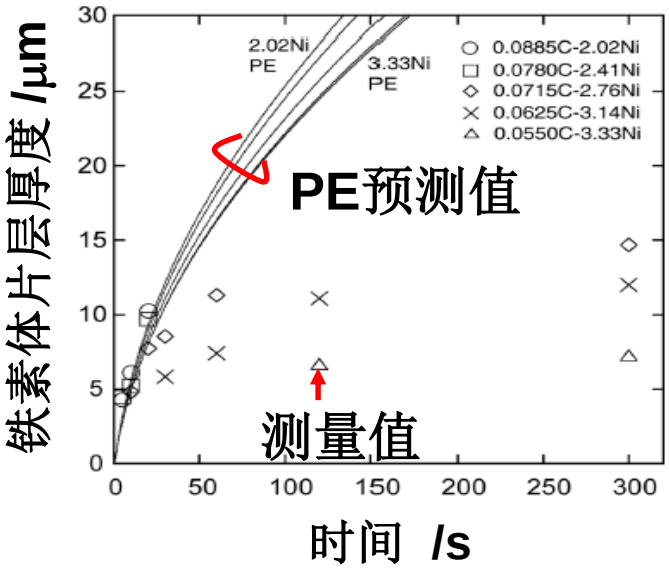
C扩散控制、合金元素不配分



PE at first, NPLE at last

Fe-Ni-C alloys [C.R. Hutchinson et al., Metall Mater Trans A, 2004.]

铁素体生长速率



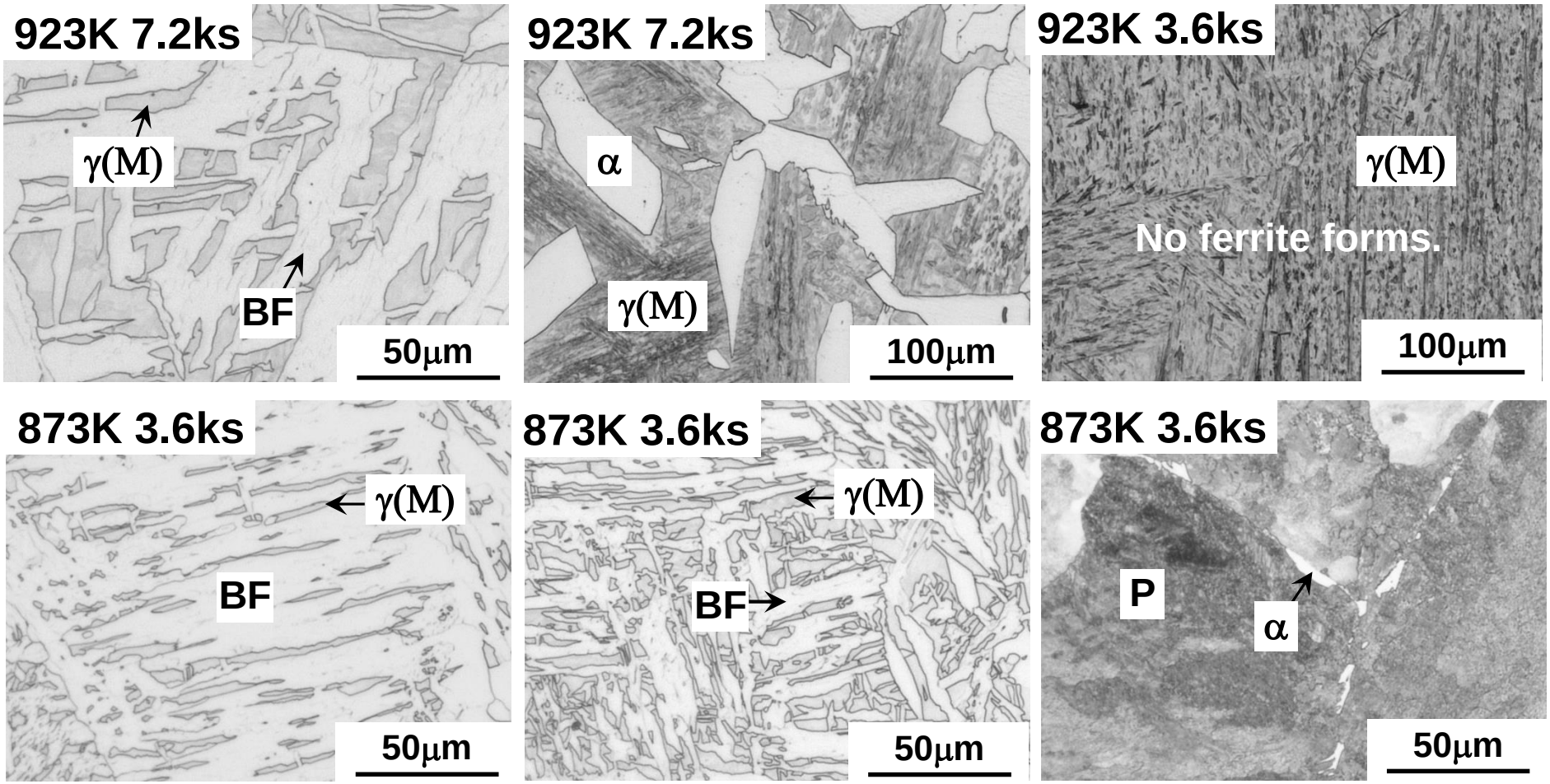
PE模型较好预测铁素体前期长大过程

准稳态铁素体体积分数

合金 /mass%	测量值	PE	NPLE
2.0Ni-0.09C	0.82	0.881	0.817
2.4Ni-0.08C	0.77	0.884	0.761
2.8Ni-0.07C	0.66	0.881	0.574
3.1Ni-0.06C	<0.1	0.881	--
3.3Ni-0.06C	<0.1	0.888	--

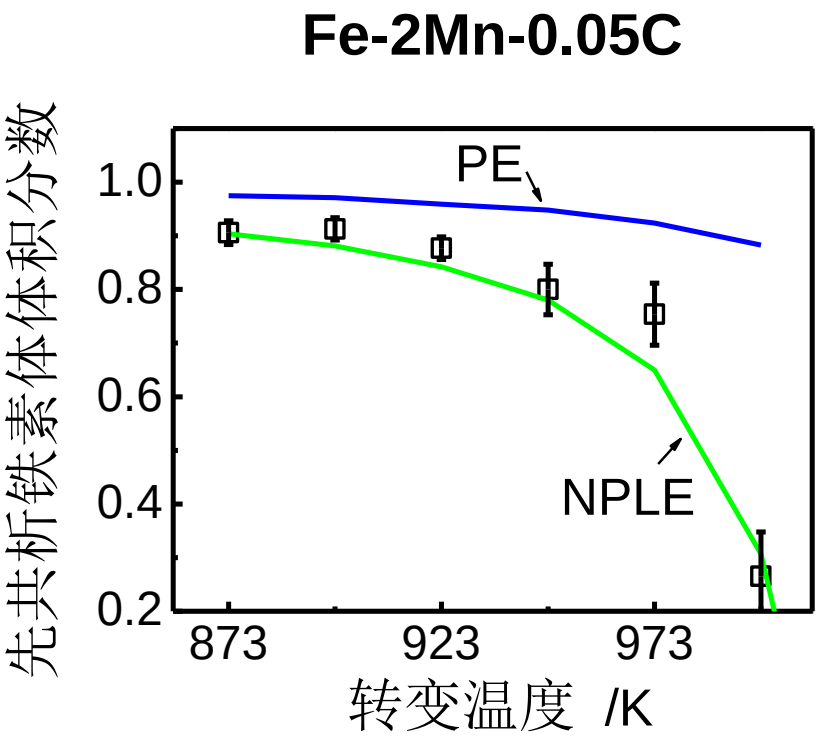
NPLE模型较好预测准稳态铁素体体积分数

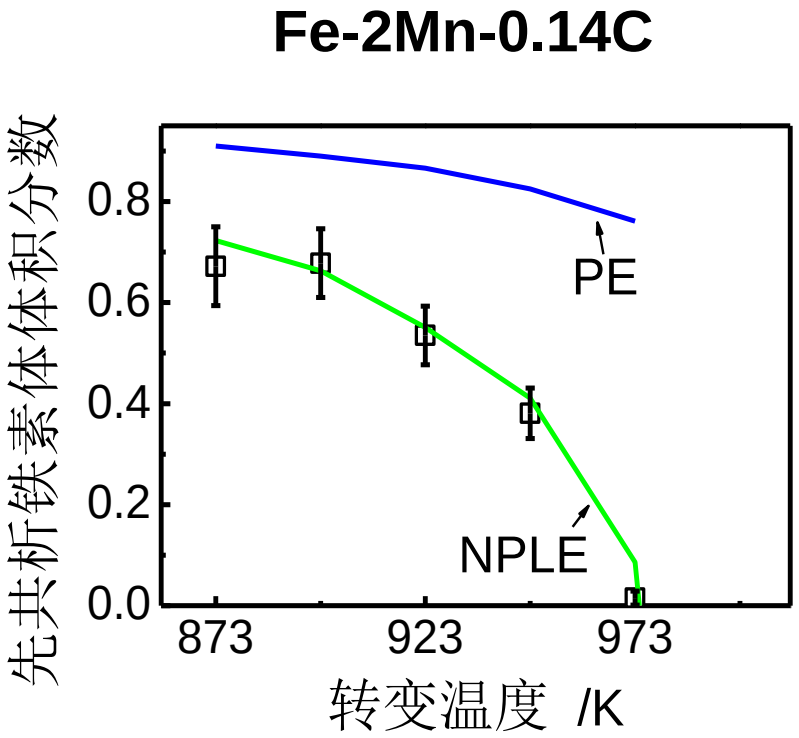
合金碳含量对准稳态组织的影响



随着合金碳含量的增加，准稳态先共析铁素体量不断下降

准稳态阶段先共析铁素体体积分数



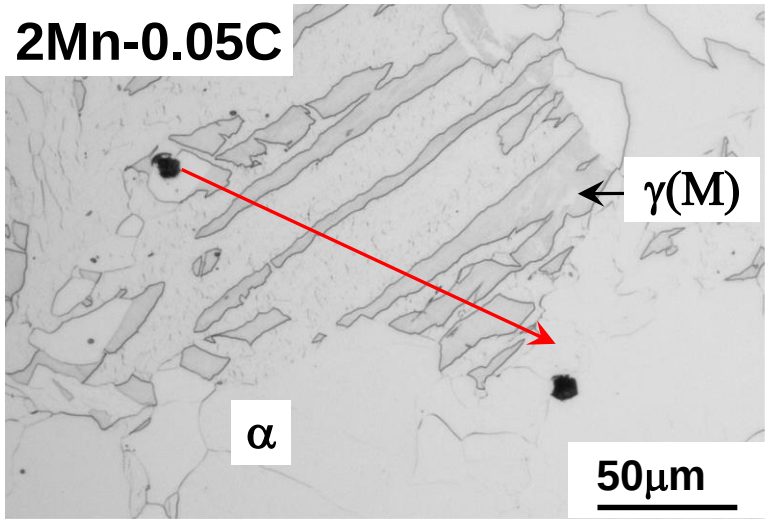


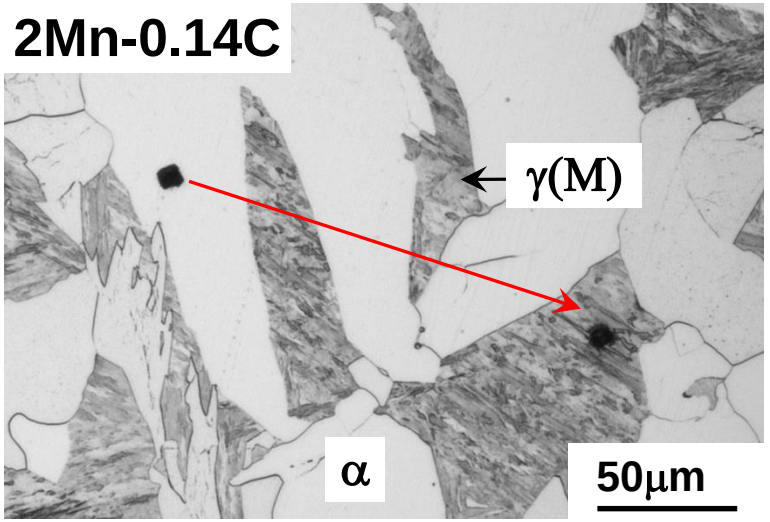
- NPLE模型能更好的预测准稳态组织；
- PE模型预测值远高于实验值

Direct measurement of C in γ and α

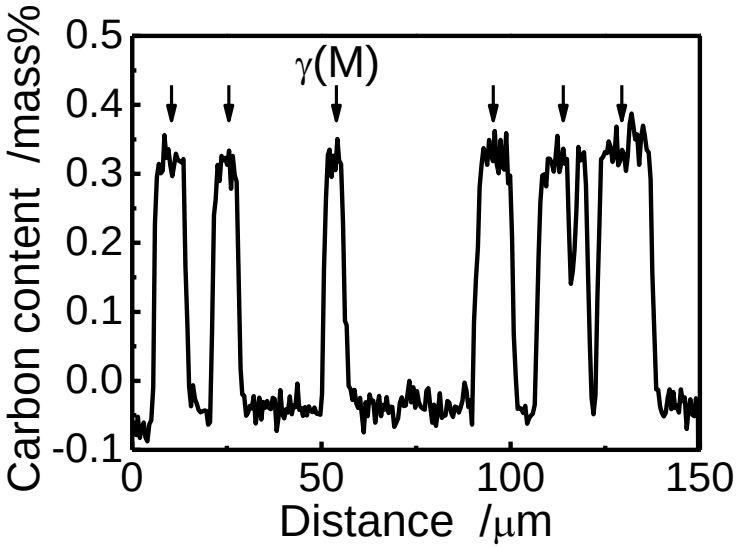
准稳态阶段奥氏体中的碳含量测定(650C, 7.2ks)

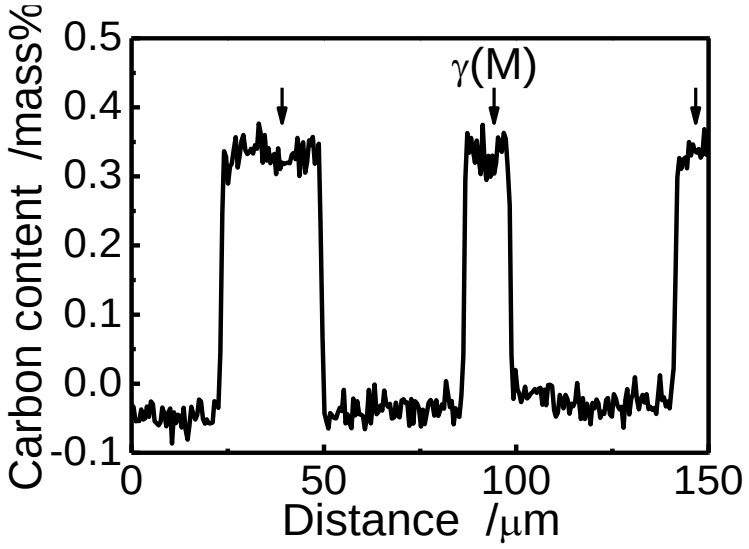
EPMA





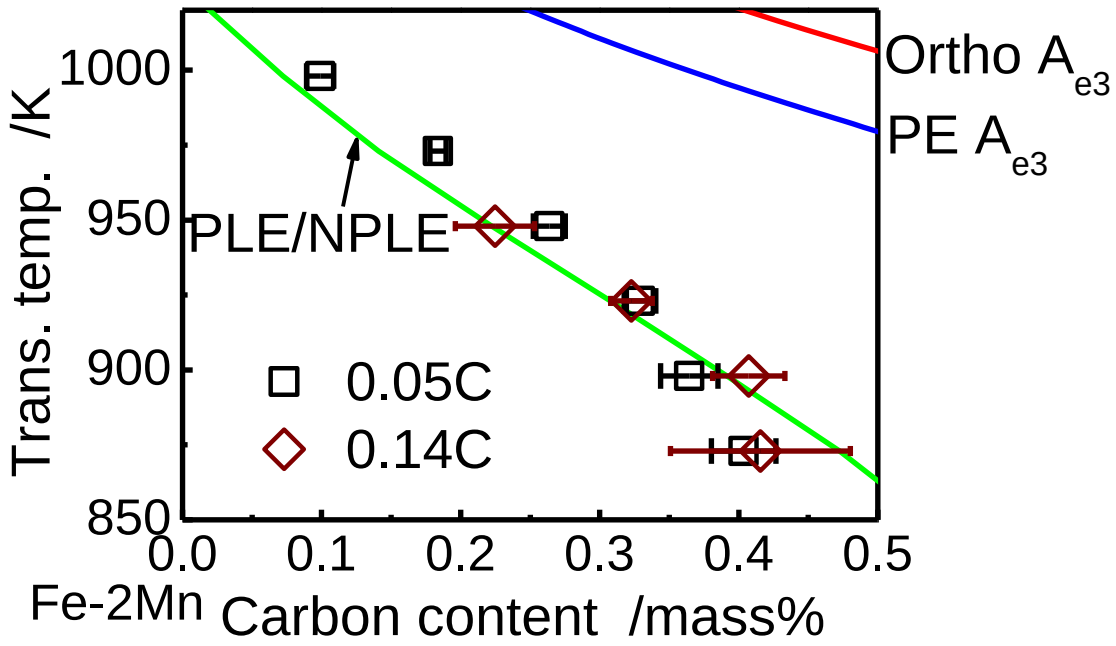
碳浓度





准稳态阶段未转变奥氏体中的碳富集

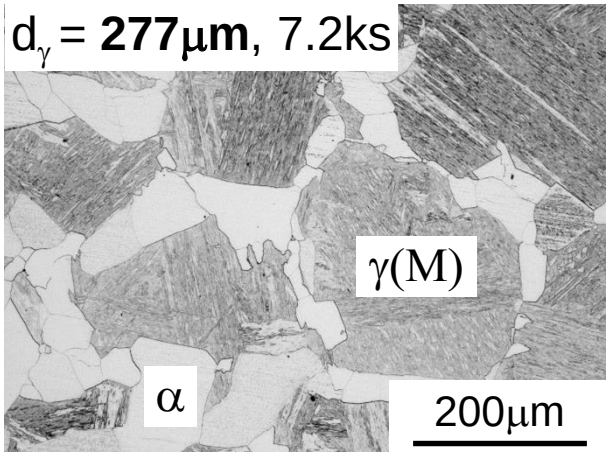
准稳态阶段未转变奥氏体中碳含量

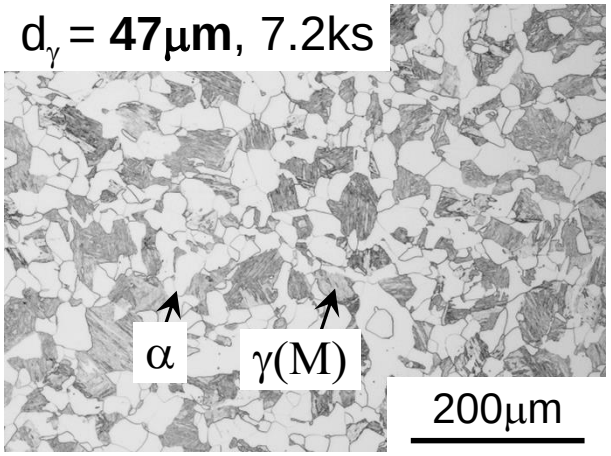


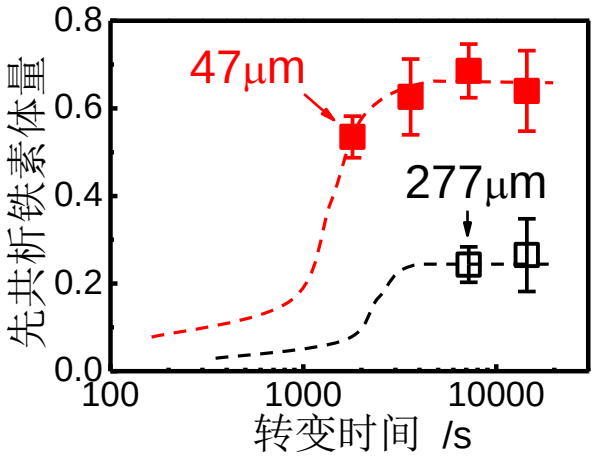
- ✓ 准稳态阶段未转变奥氏体中的碳含量远低于正平衡以及准平衡的**A_{e3}**线，但与**PLE/NPLE**转变线有较好的吻合；
- ✓ 当相变温度降至**898K**以及**873K**时，未转变奥氏体中的碳含量逐渐偏离**PLE/NPLE**转变线，可能与类溶质拖曳效应有关。

原奥氏体晶粒尺寸对准稳态组织的影响

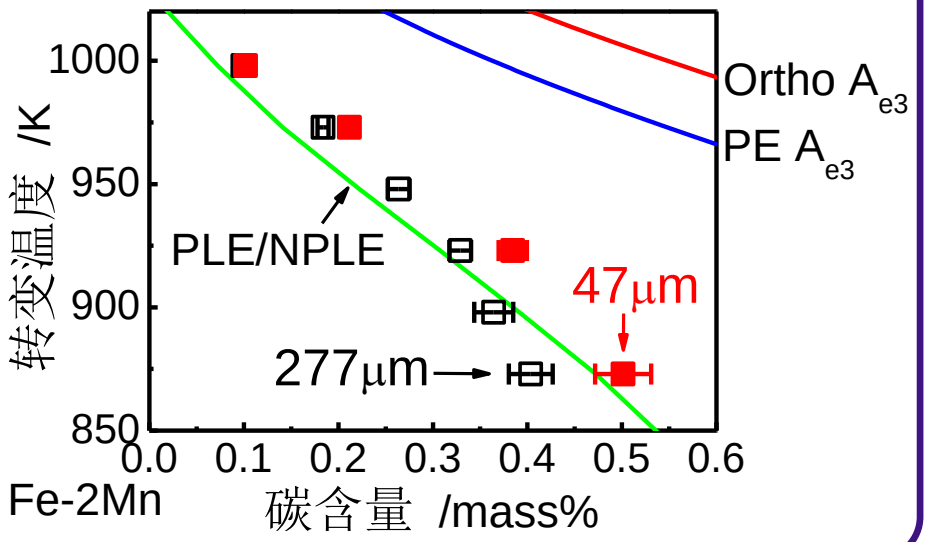
Fe-2Mn-0.05C, 998K







碳含量测量

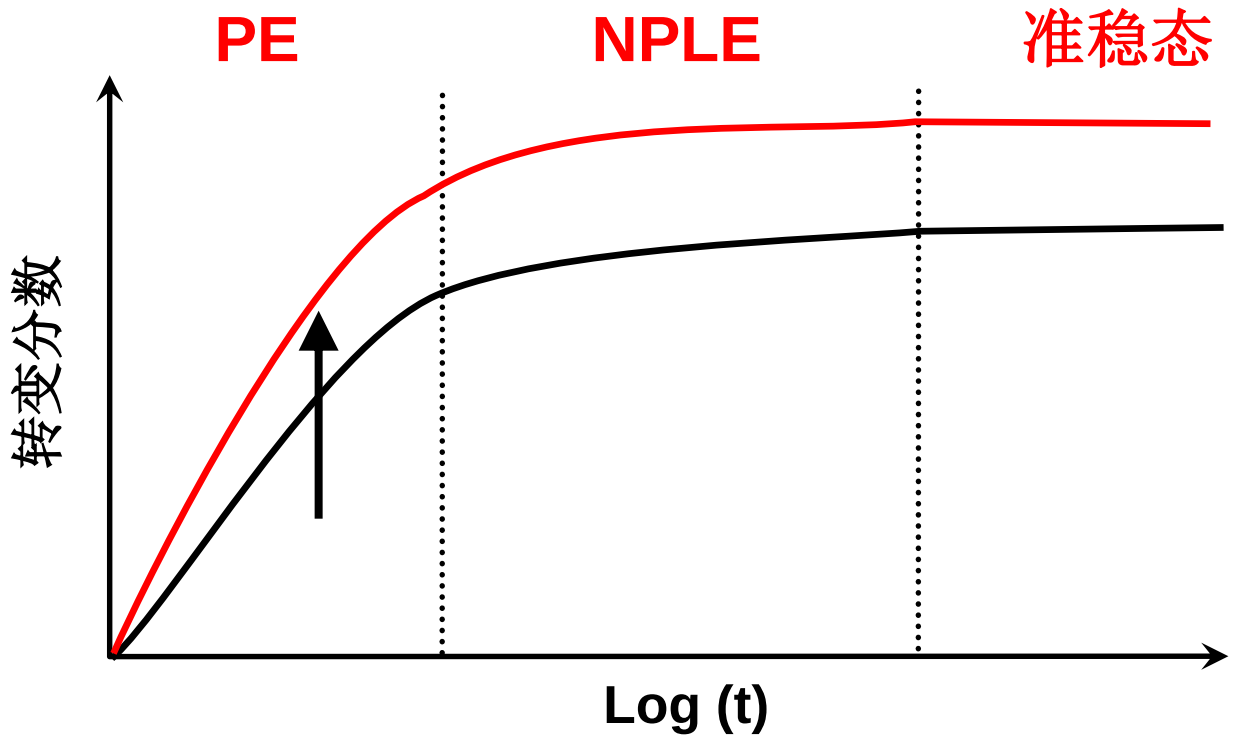


- 准稳态阶段奥氏体碳含量随原奥氏体组织的细化而提高；
- 表明准稳态组织及其成分受动力学因素的影响。

原奥氏体晶粒尺寸对准稳态组织的影响

元素配分模式转换 （前期 PE → 后期 NPLE）

转变动力学曲线

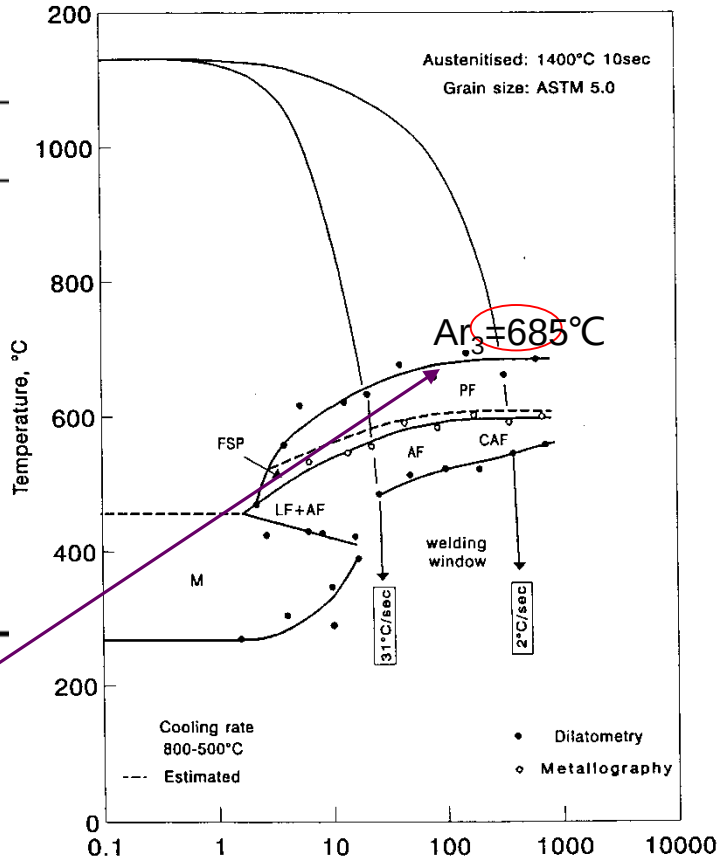


细化奥氏体组织可促进铁素体在晶界的形核，加速铁素体的前期转变过程，使得更多数量的铁素体在PE阶段生成。

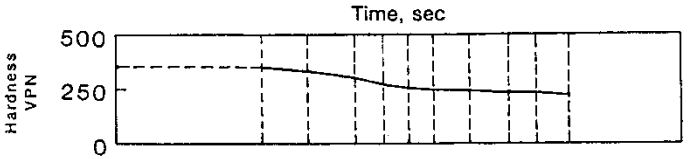
Temp of PLE/NPLE vs Ar_3 within 10C?

C	Mn	Si	Ac_3	Ar_3	OrthoAe_3	PLE/NPLE
0.11	0.46		1132	1101	1118	1101.6
0.11	0.46	0.22	1133	1105	1125	1105
0.11	0.47	0.56	1155	1100	1130.7	1115
0.12	0.43	1.1	1182	1136	1139.4	1123
0.12	0.4	1.64	1222	1127	1147.26	1132
0.12	2.05	0.21	1105	970	1075	978.33

温度单位均为 K



Temp PLE/NPLE＝684℃ for Fe-0.05C-1.18Mn-2.52Ni (wt%)



Chemical composition of the weld metal (wt%)

C	Mn	Si	S	P	Ni	Cr	Mo	Cu	N	O
0.05	1.18	0.38	0.010	0.022	2.52	<0.01	0.08	0.06	0.0178	0.0482

Ar3: 缓慢冷却时铁素体形成温度

- Introduction
- Diffusion control growth by C or M, PLE/NPLE
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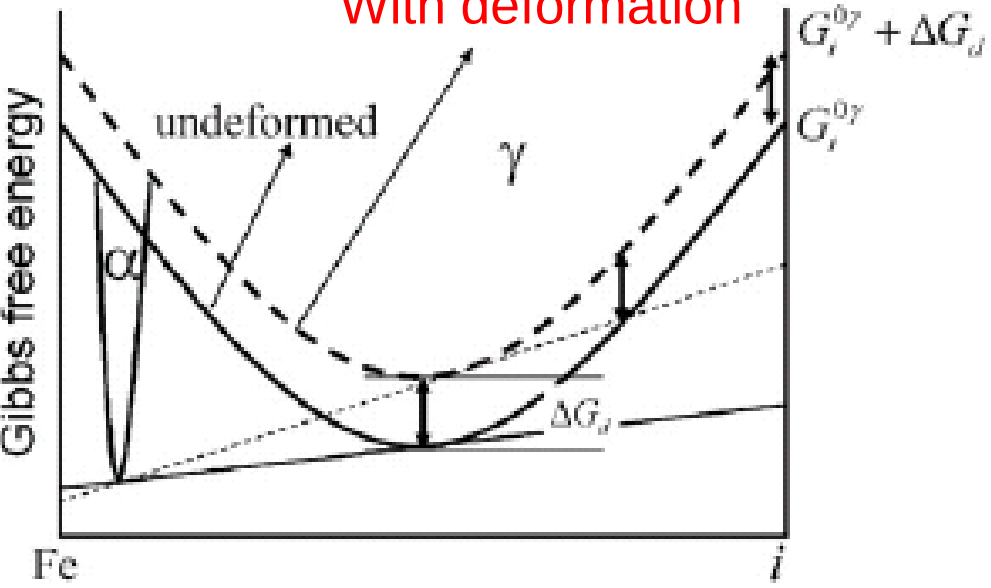
Thermodynamics with deformation

With deformation



Local equilibrium for all elements:

$$\frac{\Delta^0 G_i^{\alpha-\gamma}}{RT} + \ln X_i^{\gamma} + \ln \gamma_i^{\gamma} = \ln X_i^{\alpha} + \ln \gamma_i^{\alpha}$$

With deformation:

$$\frac{\Delta^0 G_i^{\alpha-\gamma} + \Delta G_d}{RT} + \ln X_i^{\gamma} + \ln \gamma_i^{\gamma} = \ln X_i^{\alpha} + \ln \gamma_i^{\alpha}$$

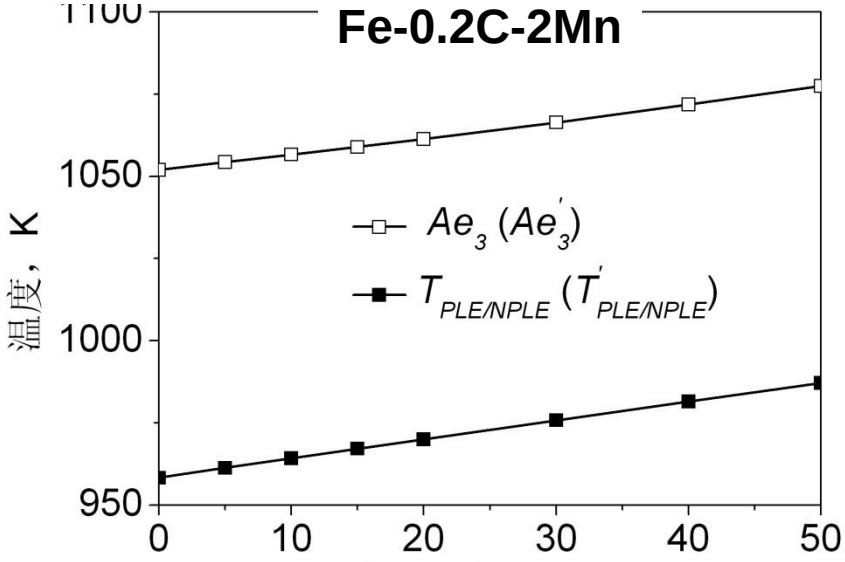
Temp. for PLE/NPLE:

PLE:

$$\frac{(1+\varepsilon_{11}^{\gamma} X_1^{\gamma})}{X_1^{\gamma}}(X_1^{\gamma} - X_1^{0}) + \sum_{i=2}(X_i^{\gamma} - X_i^{0})\varepsilon_{1i}^{\gamma} = 0$$

NPLE:

$$X_i^{\alpha} \approx X_i^{0} \ (i \geq 2)$$



Deformation energy increases the Temp of Ae_3 and PLE/NPLE

Deformation energy related to dislocation density

$$\Delta G_d = k\mu\left(\rho - \rho_0\right)b^2 V_\gamma$$

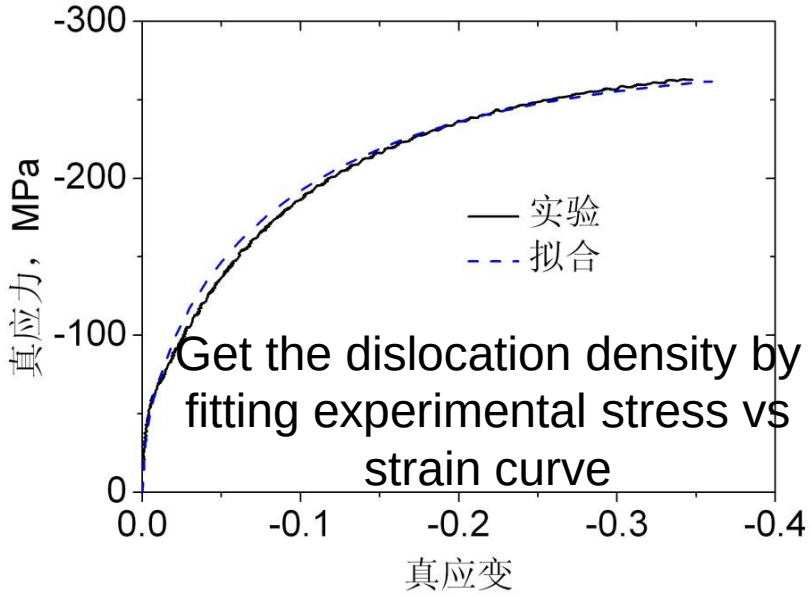
Bergström model：

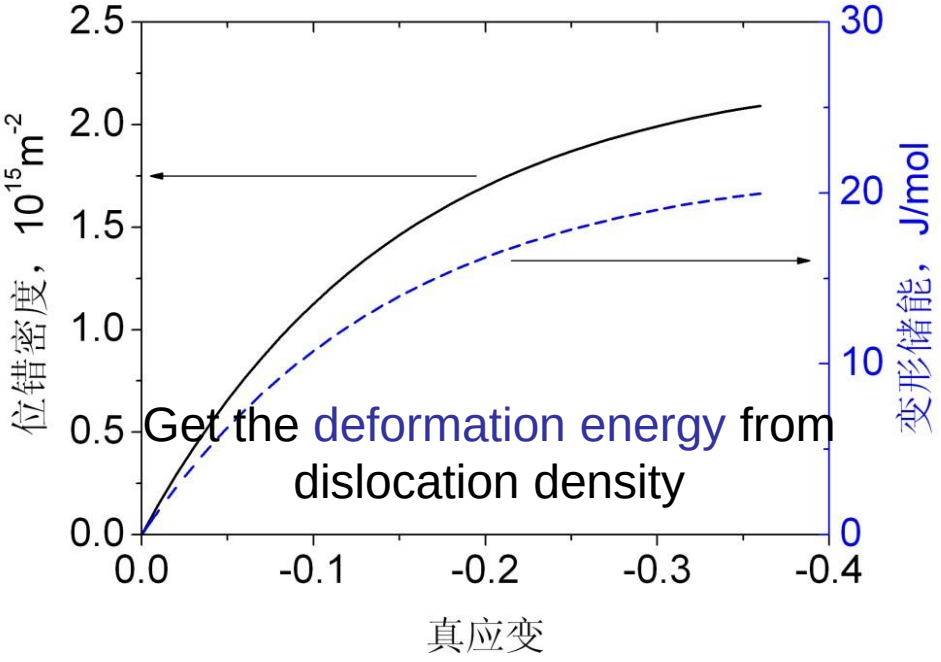
$$\sigma = \alpha M_T \mu b \rho^{1/2}$$

$$= \alpha M_T \mu b \left(U\left(1-\exp\left(-\Omega\varepsilon\right)\right)/\Omega\right)^{1/2}$$

$$\Omega = k'\left(Z\right)^m$$

$$Z = \dot{\varepsilon}\exp\left(Q/RT\right)$$





Fe-0.2C-2Mn, 1023K, maximum strain ε = - 0.36, strain rate 5/s

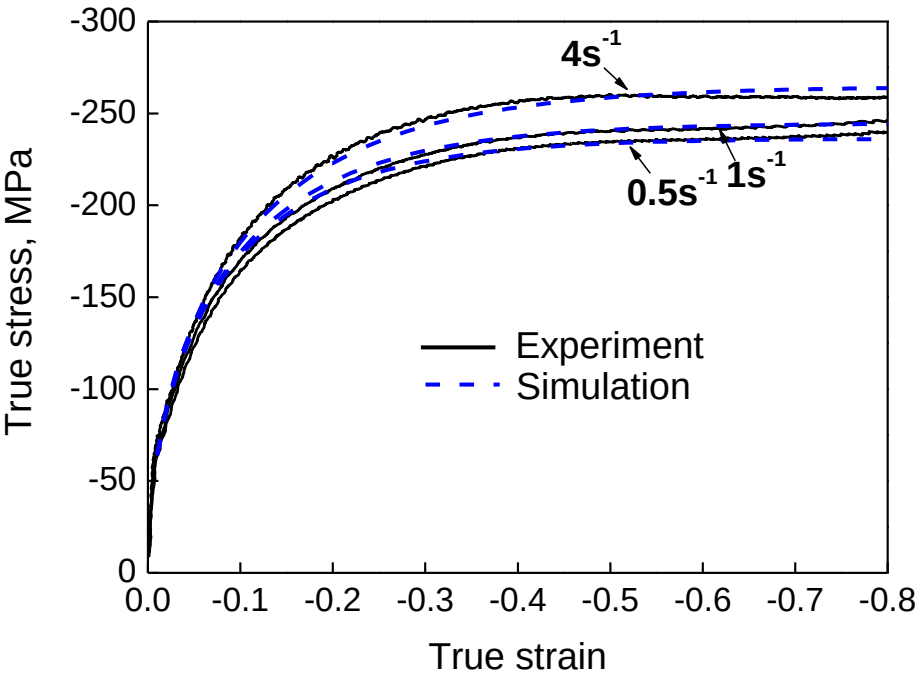
Parameters for the Bergstrom Model

Parameter	Explanation	Value for austenite	Unit
M	Constant	3.11	-
α	Constant, weak dependent of temperature	$\alpha = -0.000628 \times T + 1.0693$ [6]	-
μ	Shear modulus, dependent of temperature	$\mu = 1.45\times10^{5} - 137\times T + 3.48\times10^{-2}\times T^{2}$ [6]	MPa
b	Burgers vector	$b = \frac{\sqrt{2}}{2}\times\left\{0.3620\times\left[1+24.73\times10^{-6}\times(T-1000)\right]\right\}$ [6]	nm
U	immobilization parameter of dislocation density	exact value is not known, 2.6×10^{15} used here	m^{-2}
k	Constant, dependent of grain size	150 used here	s^{m}
m	Exponent for Zener-Hollomon parameter	-0.1[6]	-
Q	Activation energy for deformation	267[11]	kJ/mol
R	Gas constant	8.314	J mol^{-1} K^{-1}
T	Deformation temperature		°C
ε	True strain		-
$\dot{\varepsilon}$	True strain rate		s^{-1}

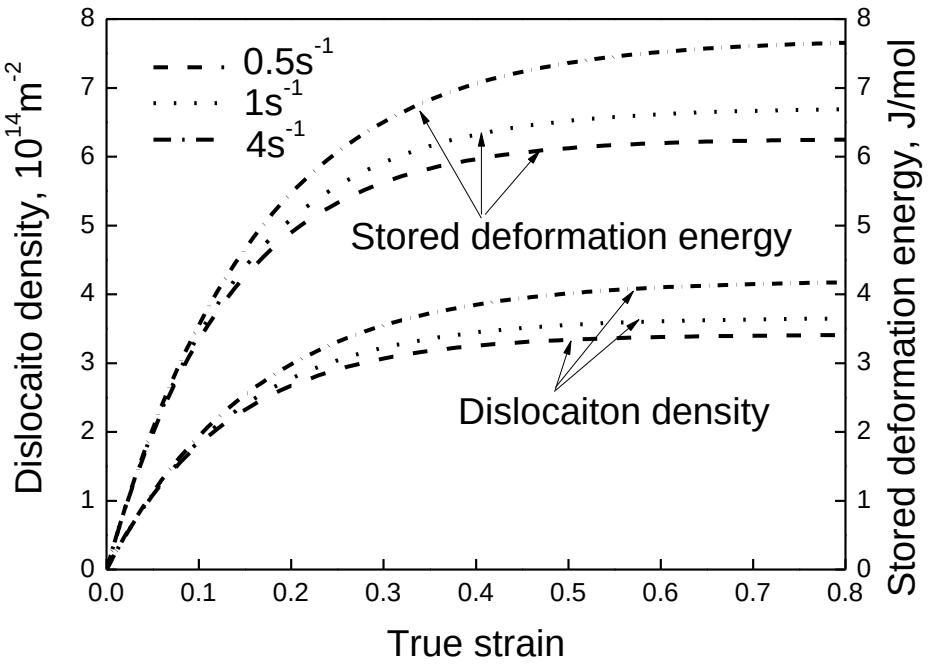
Calculation results of stored deformation energy

Fe-0.073C-2.17Mn-0.88Si-0.80 Cr (wt%)

True stress-strain curves at 780 °C for various strain rate



Dislocation density and stored deformation energy at 780 °C

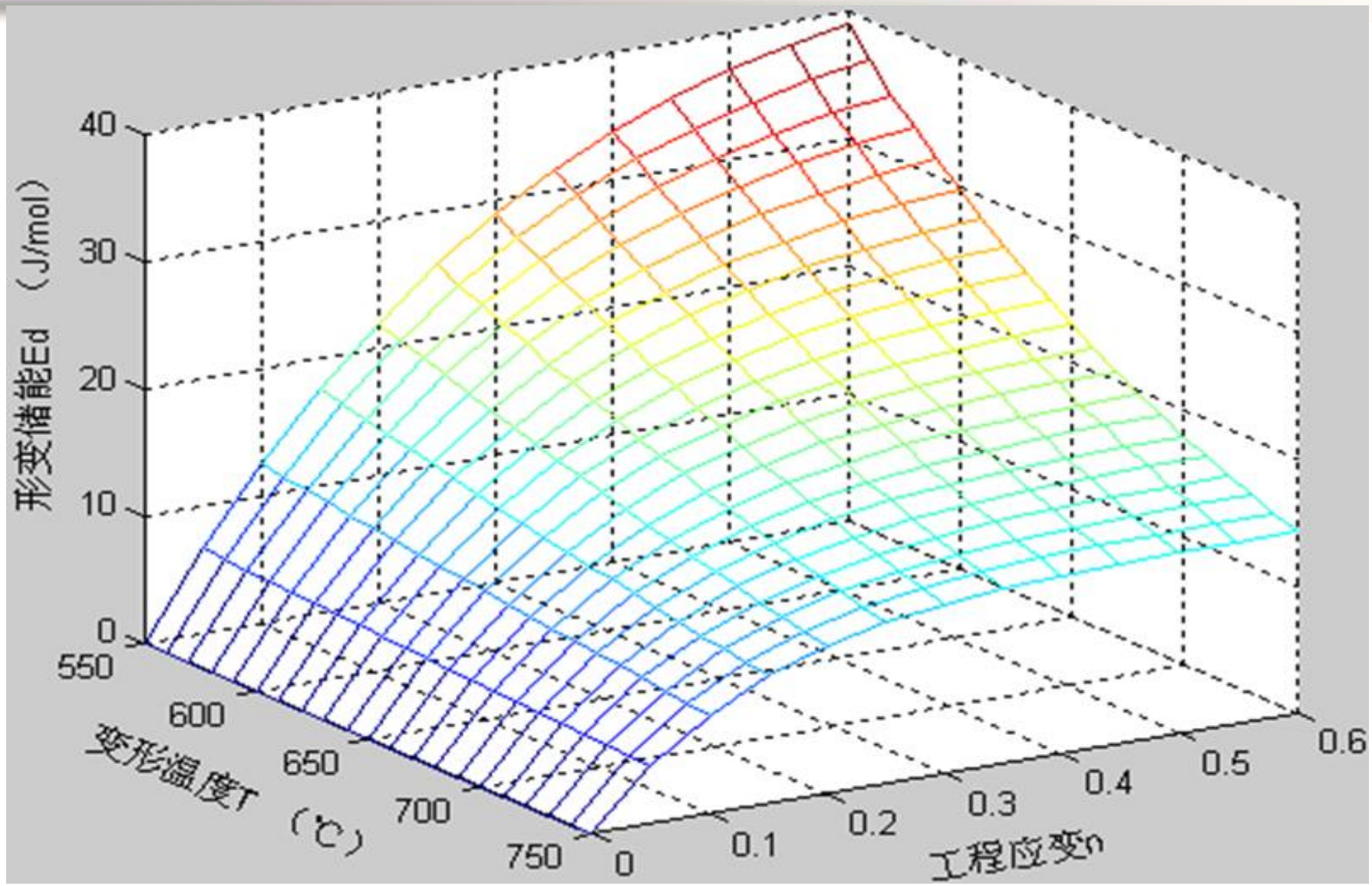


Larger strain yields larger energy but within a limit

Fast strain rate yields a little larger deformation energy

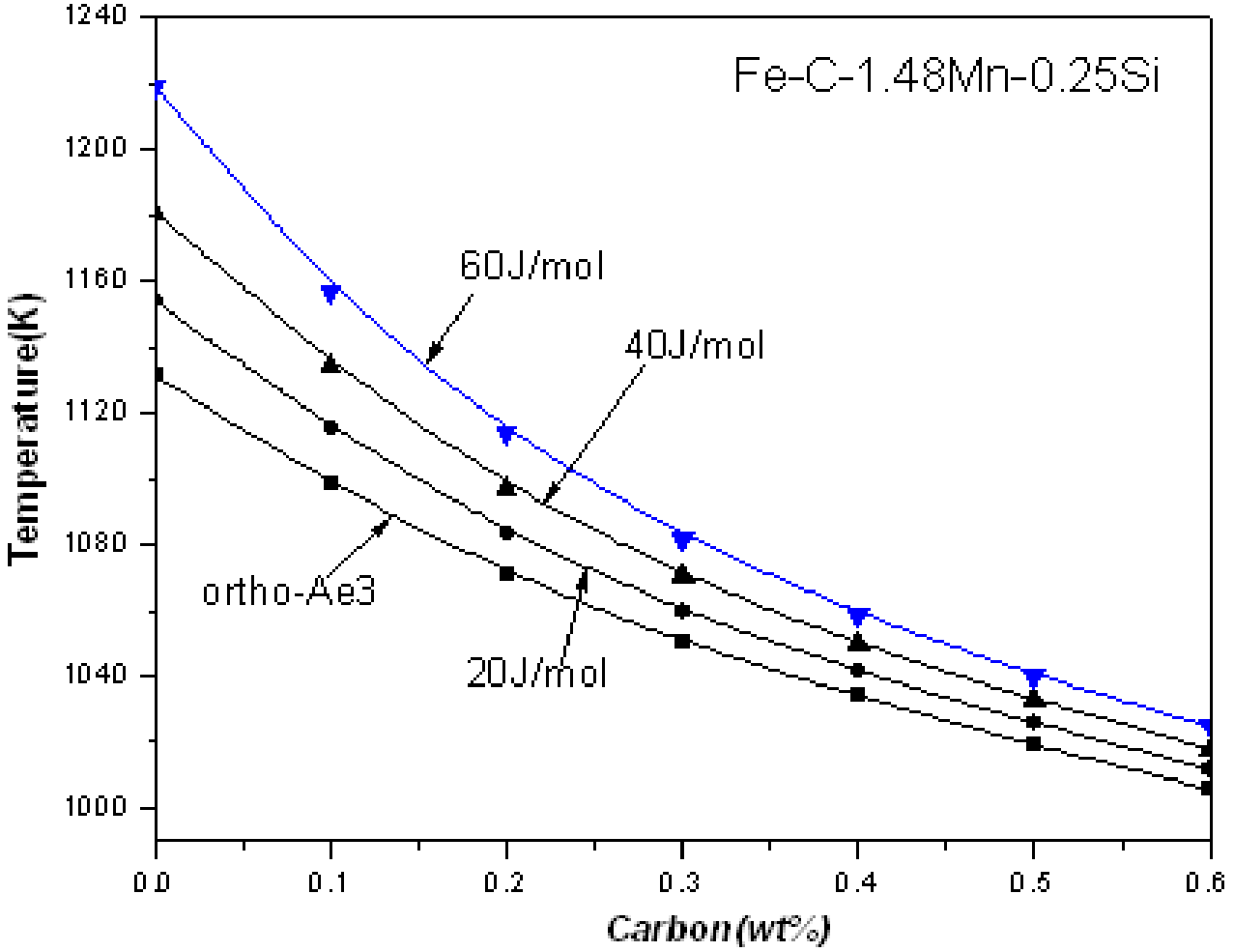
No dynamic recrystallization

Calculated deformation energy vs deformation temperature T and strain n, with a strain rate of $1s^{-1}$



deformation temperature is more important

Increase Ae3 by deformation energy



$$\frac{\Delta^0 G_0^{\alpha-\gamma} + \Delta G_d}{RT} + \ln X_i^{\gamma} + \ln \gamma_i^{\gamma} = \ln X_i^{\alpha} + \ln \gamma_i^{\alpha}$$

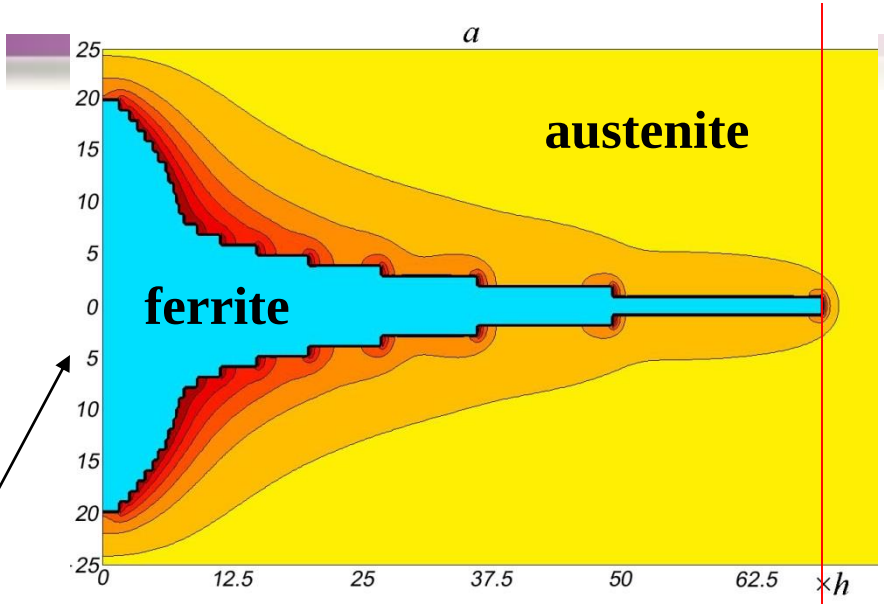
Ledgewise growth of ferrite

Material for modeling:

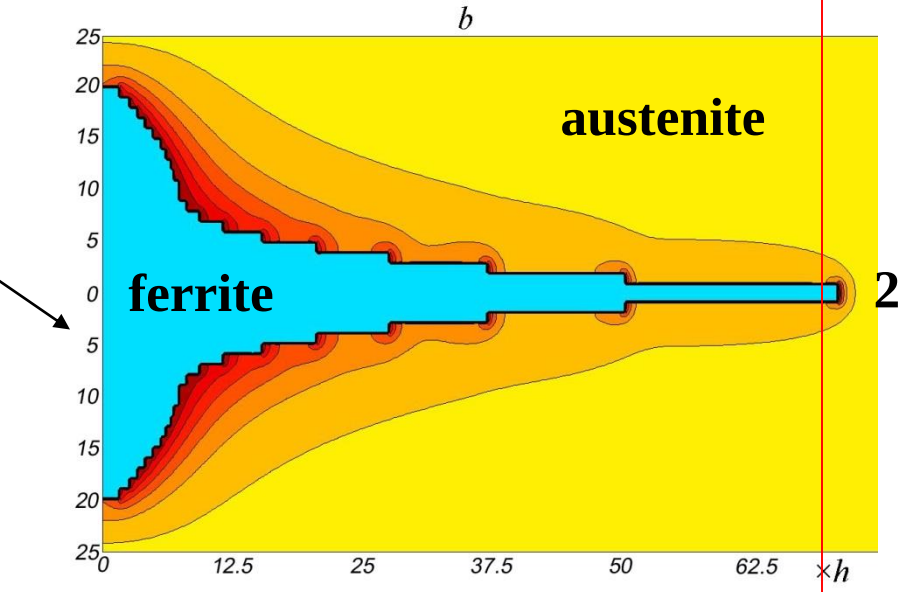
Fe-0.073C (wt%)

Ae_3: 875 °C

undeformed at 780 °C



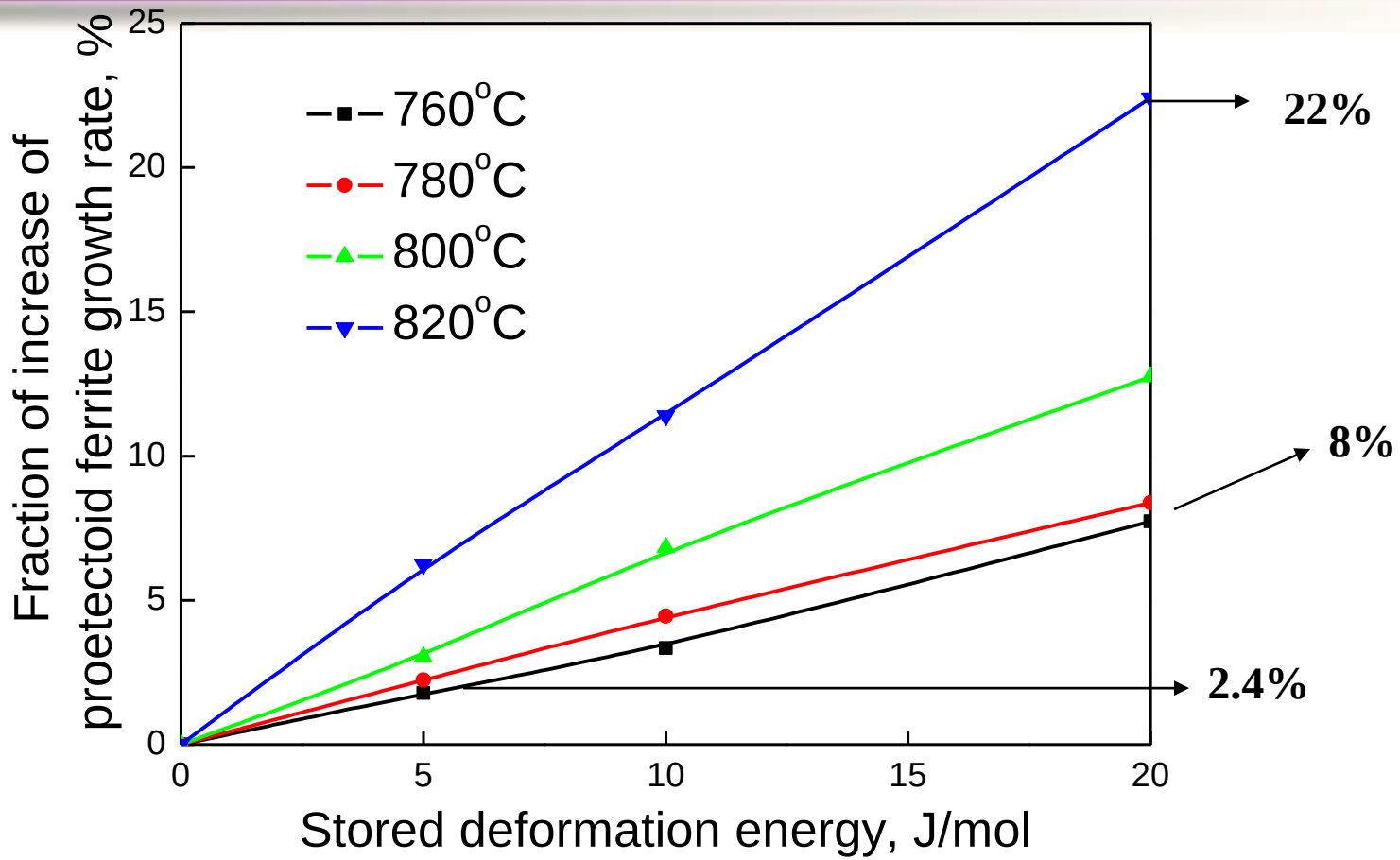
deformed at 780 °C: 5 J/mol energy added



Austenite grain boundary

2.4% longer

Ferrite growth rate vs deformation energy



Fe-0.073wt% C

At high temp. ferrite growth is prompted more significant.

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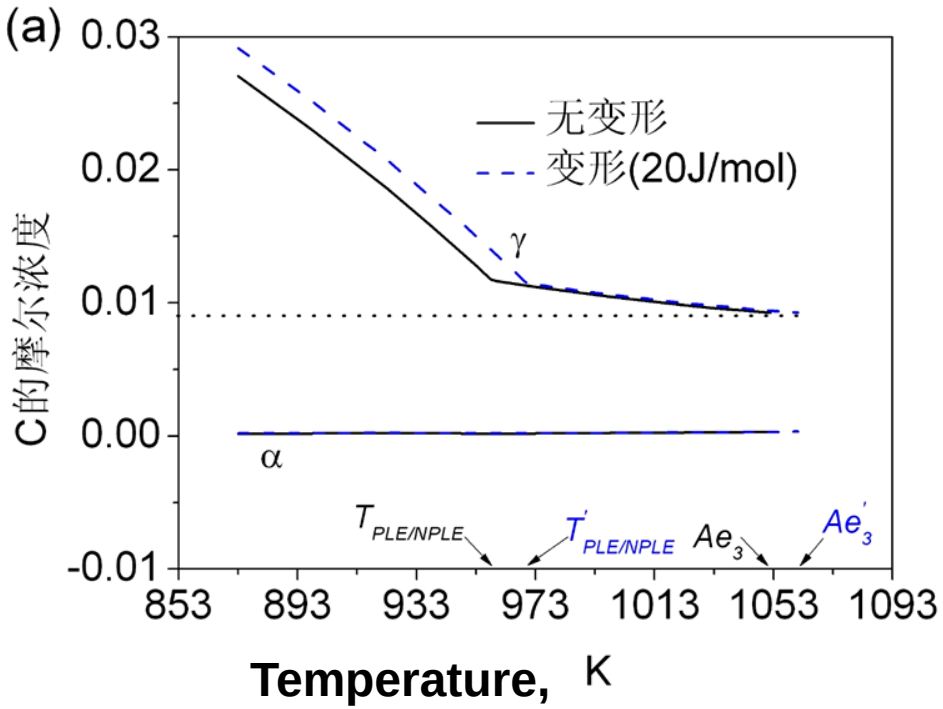
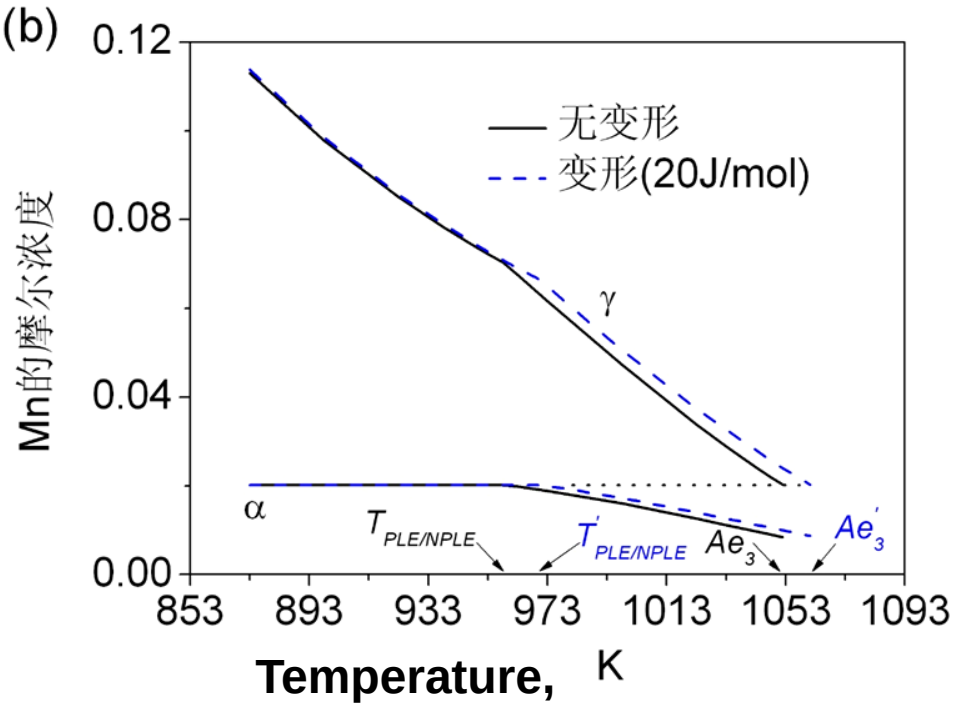
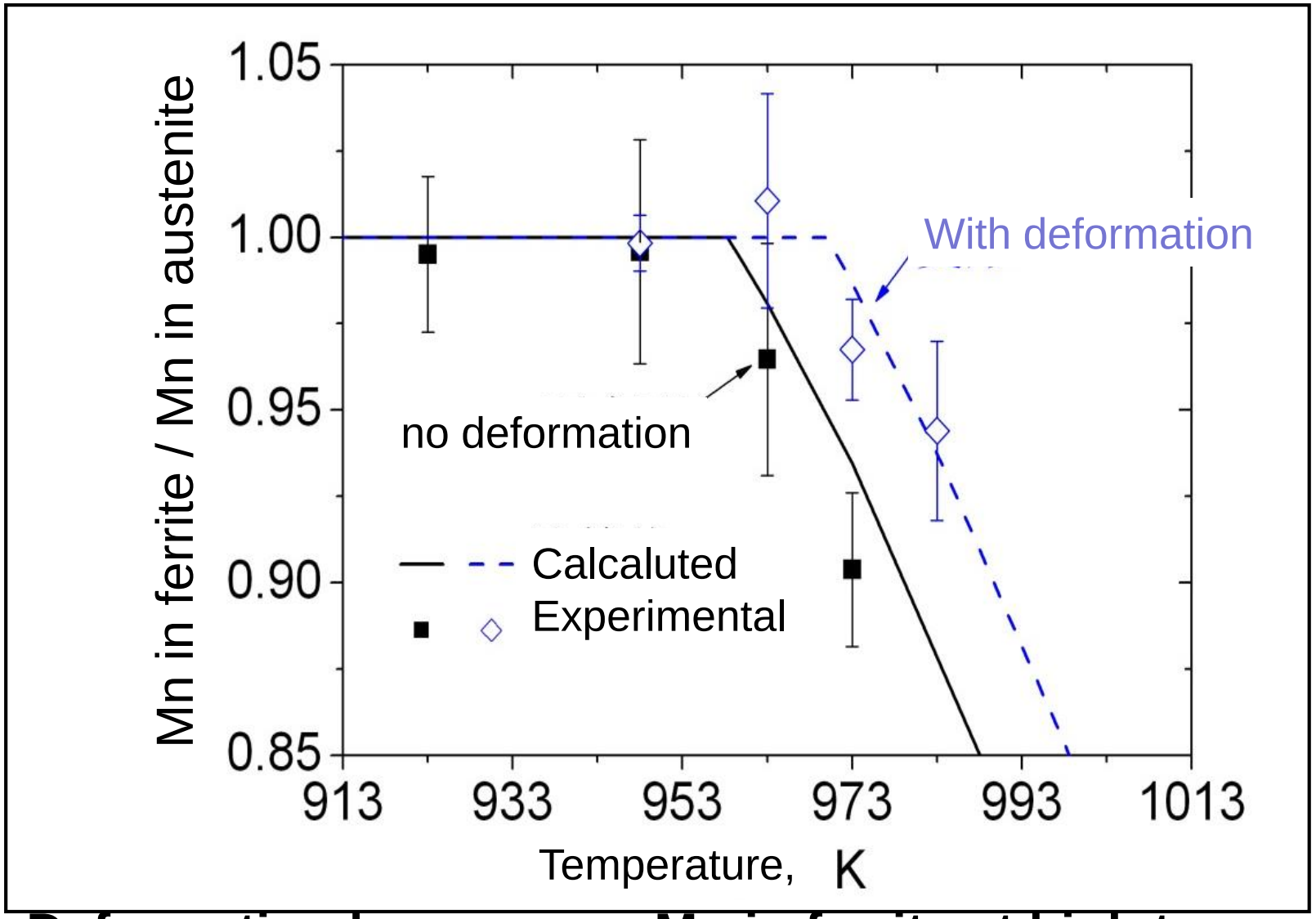
Deformation effect on equilibrium C and Mn



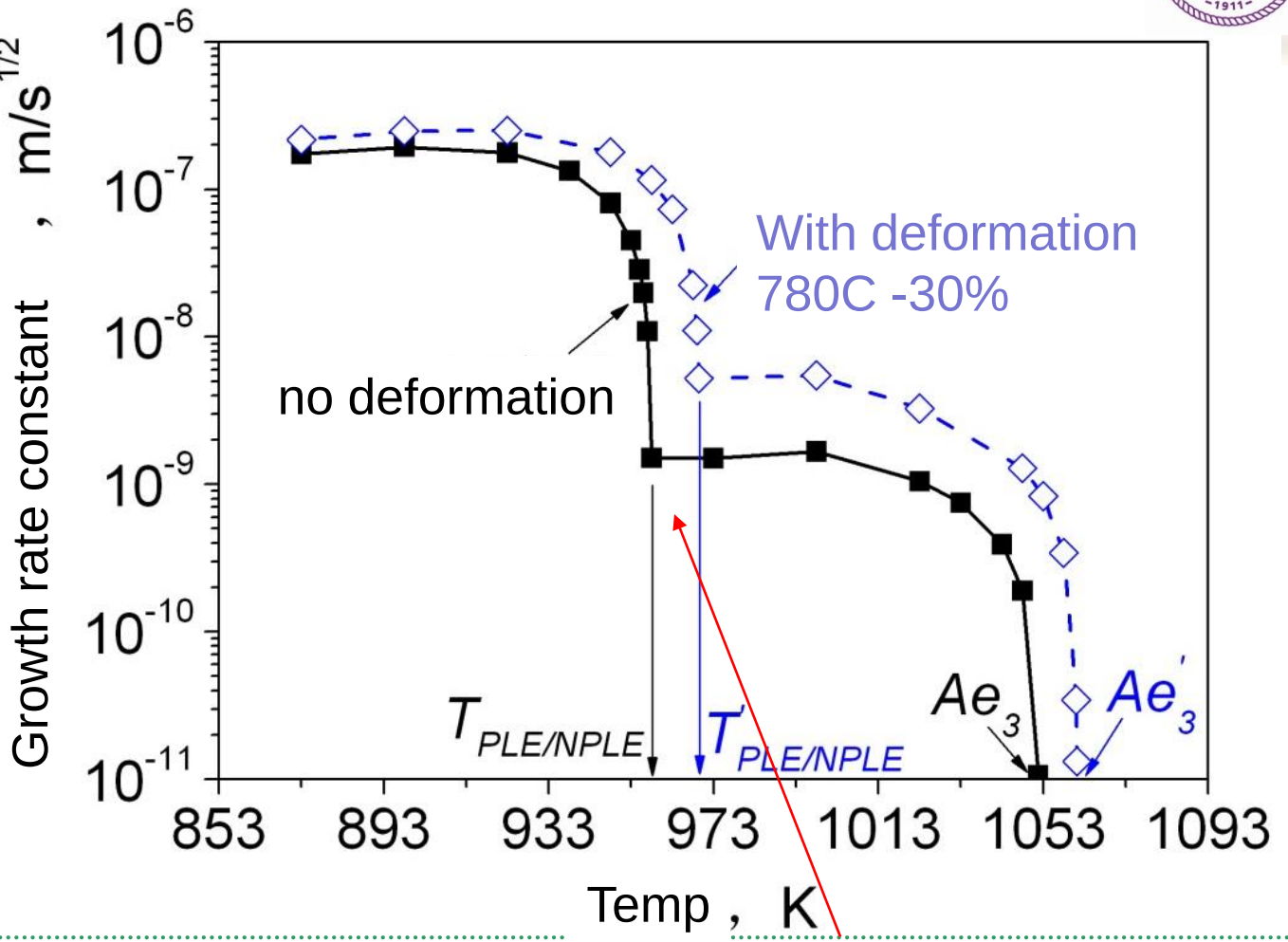


Remarkably increase of (a) C at low temperature and (b) Mn at high temperature by stored energy of 20J/mol in Fe-0.2C-2Mn

Deformation effect on ratio of Mn in ferrite and in austenite in Fe-0.2C-2Mn



Deformation keeps more Mn in ferrite at high temp.

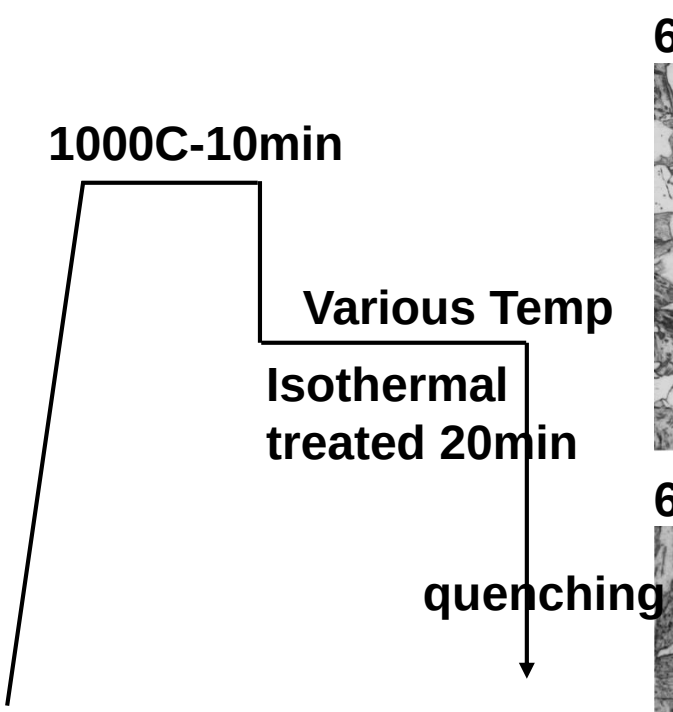


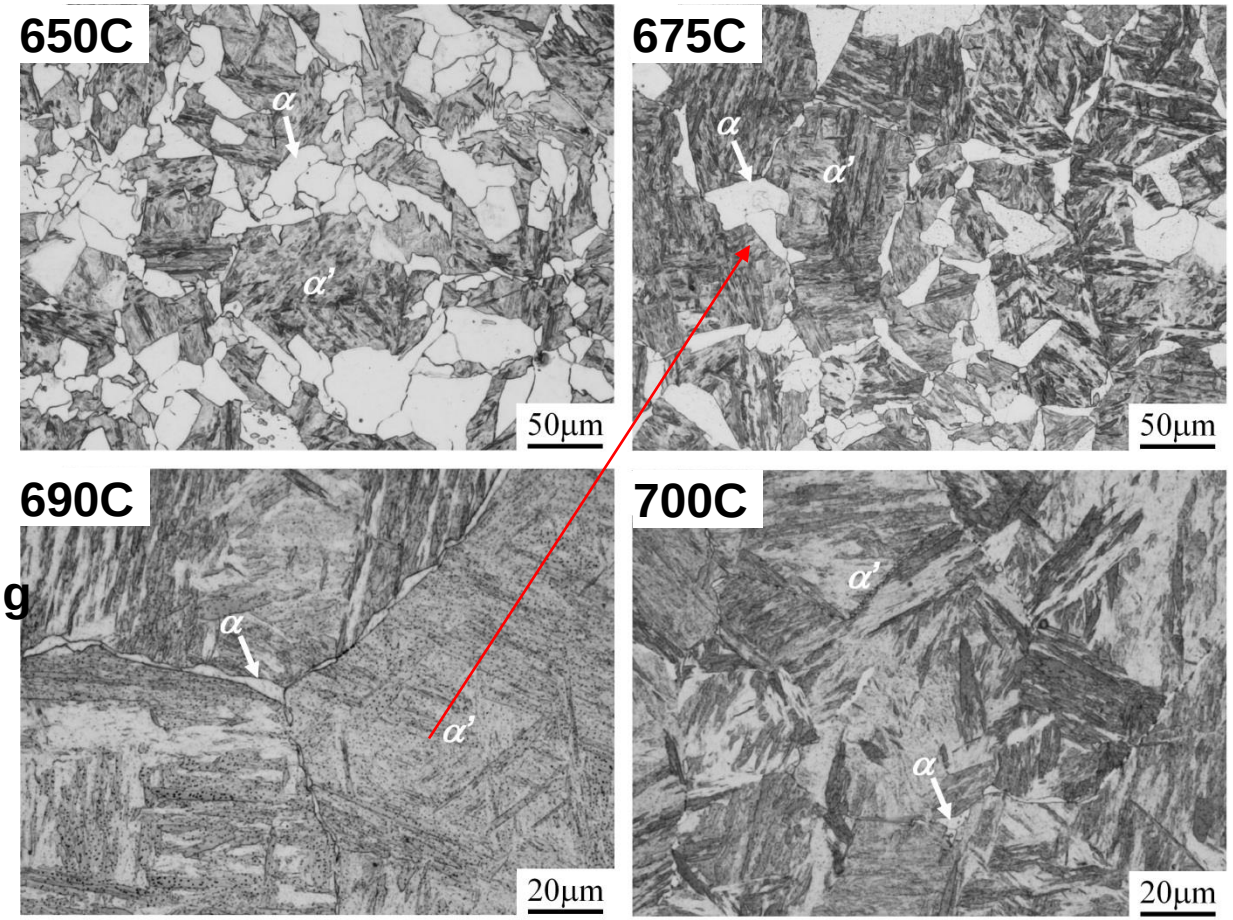
Deformation changes some temperature area of PLE zone to NPLE zone, where the growth rate constant increases by 1 or 2 order. At high temp. ferrite growth is prompted more significant.

Transformation of ferrite from austenite

Fe-0.2C-2Mn (wt%)

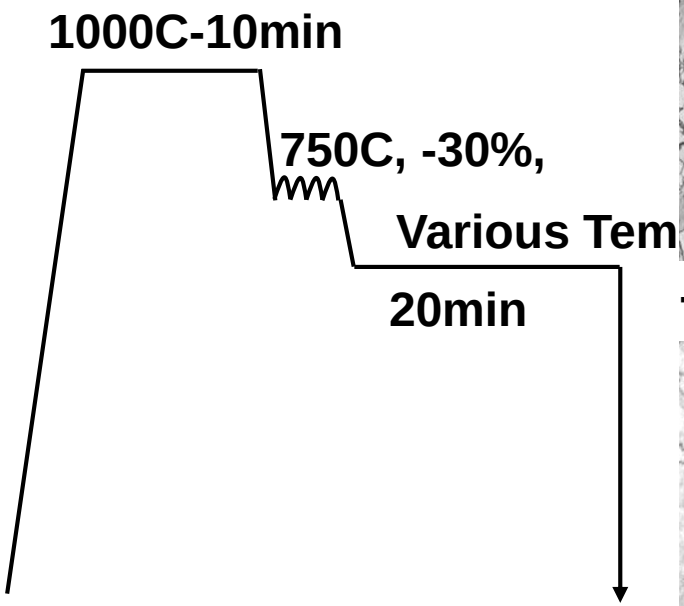
Without deformation of austenite



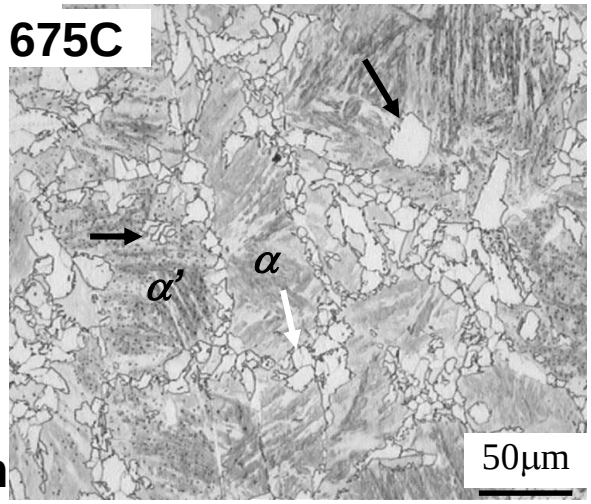


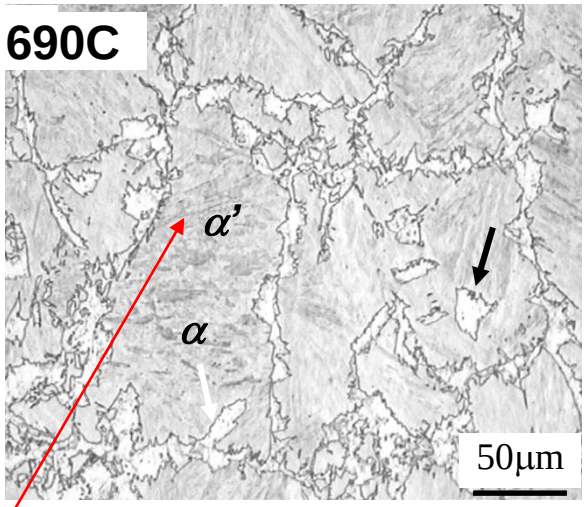
PLE/NPLE temp between 675 and 690C

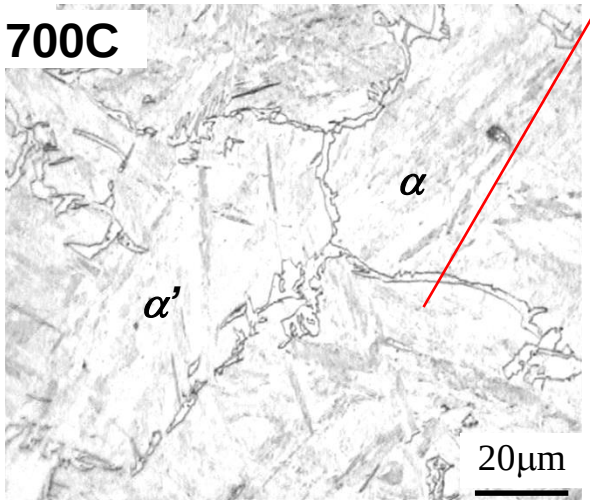
With deformation of austenite

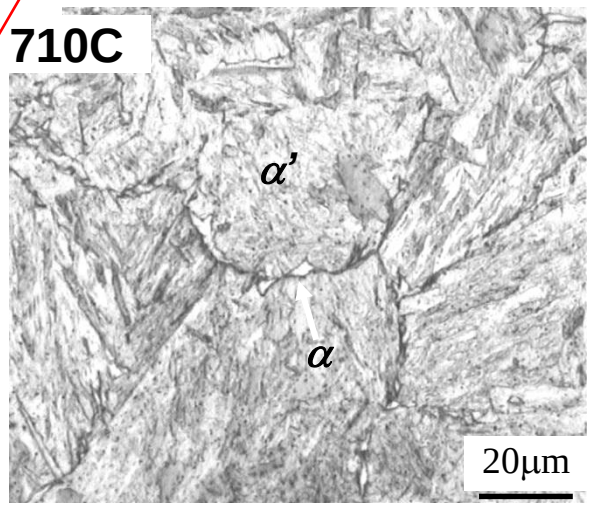


Fe-0.2C-2.Mn (wt)



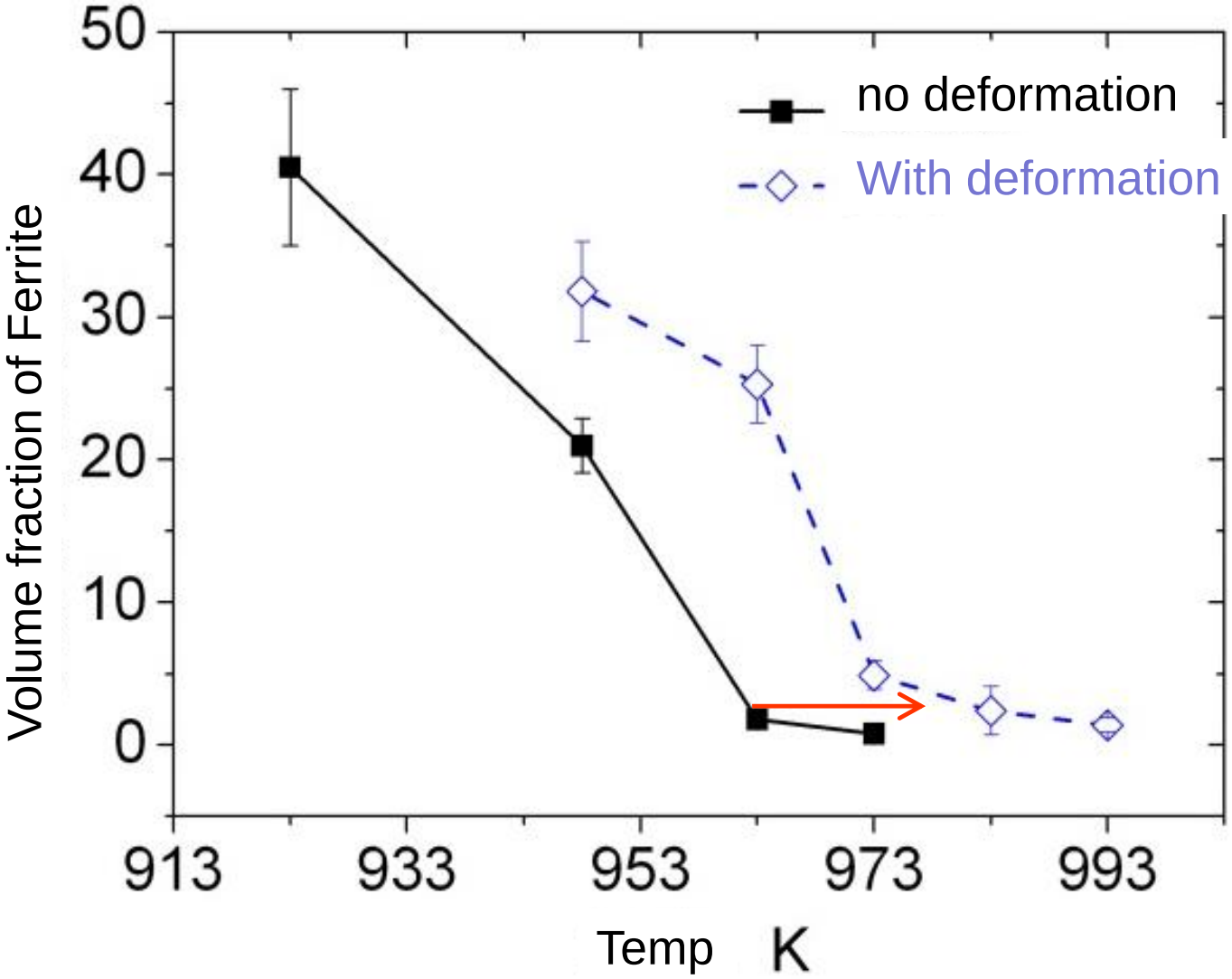






PLE/NPLE Temperature is raised to 690-700C

PLE/NPLE Temperature is raised by ~ 10 degree



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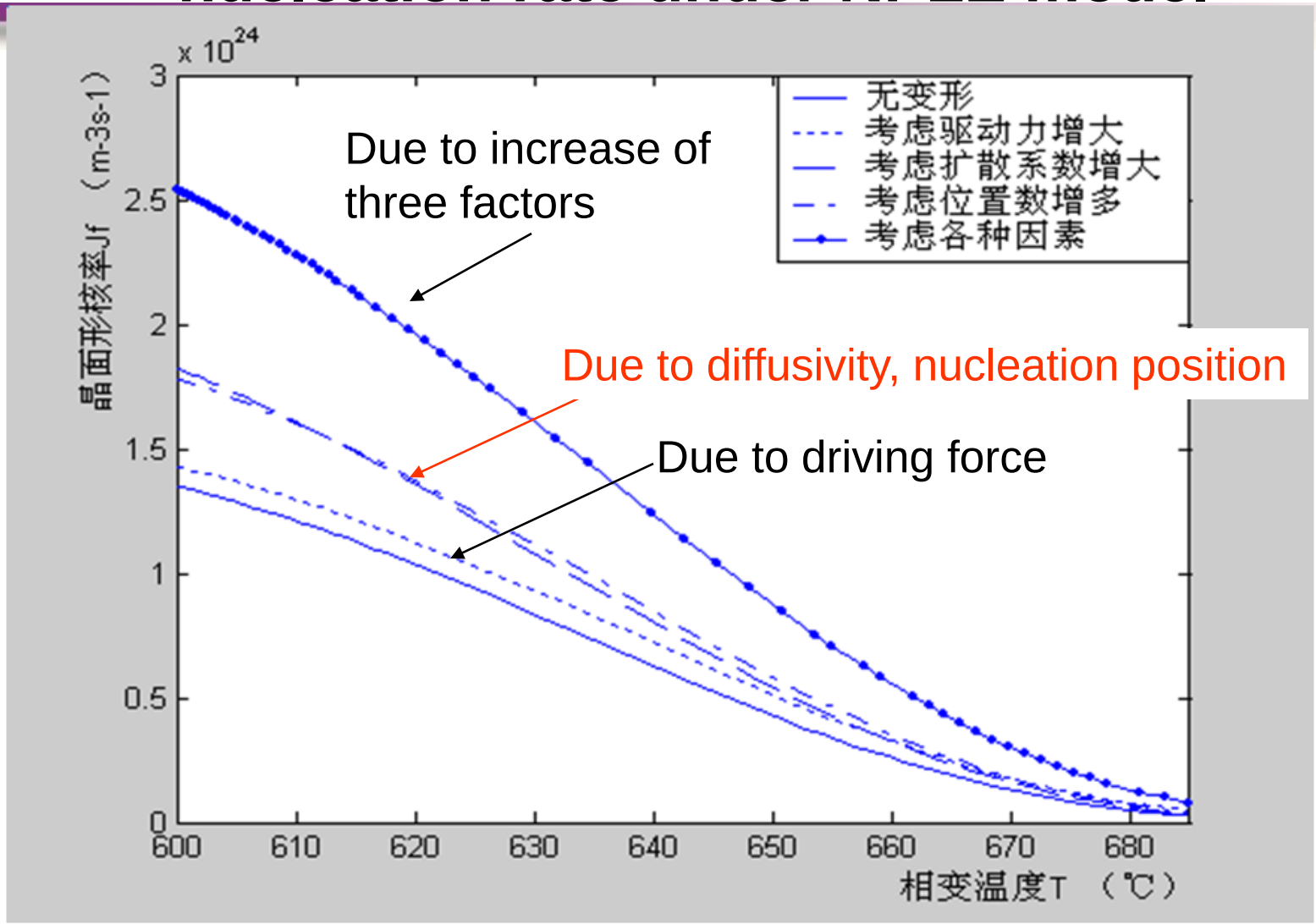
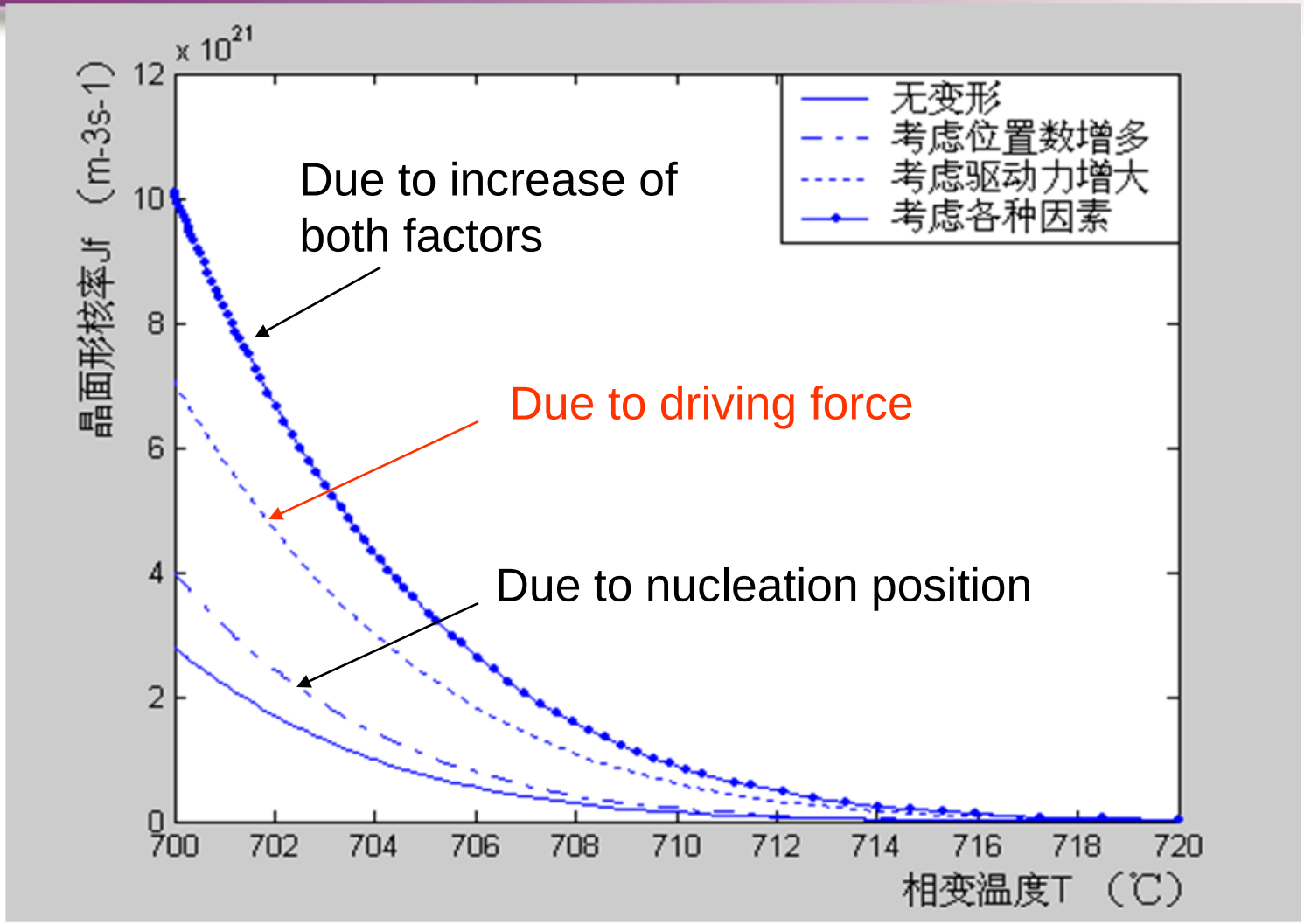
Deformation effect on grain boundary nucleation rate under NPLE model



Increased nucleation rate J_f by deformation

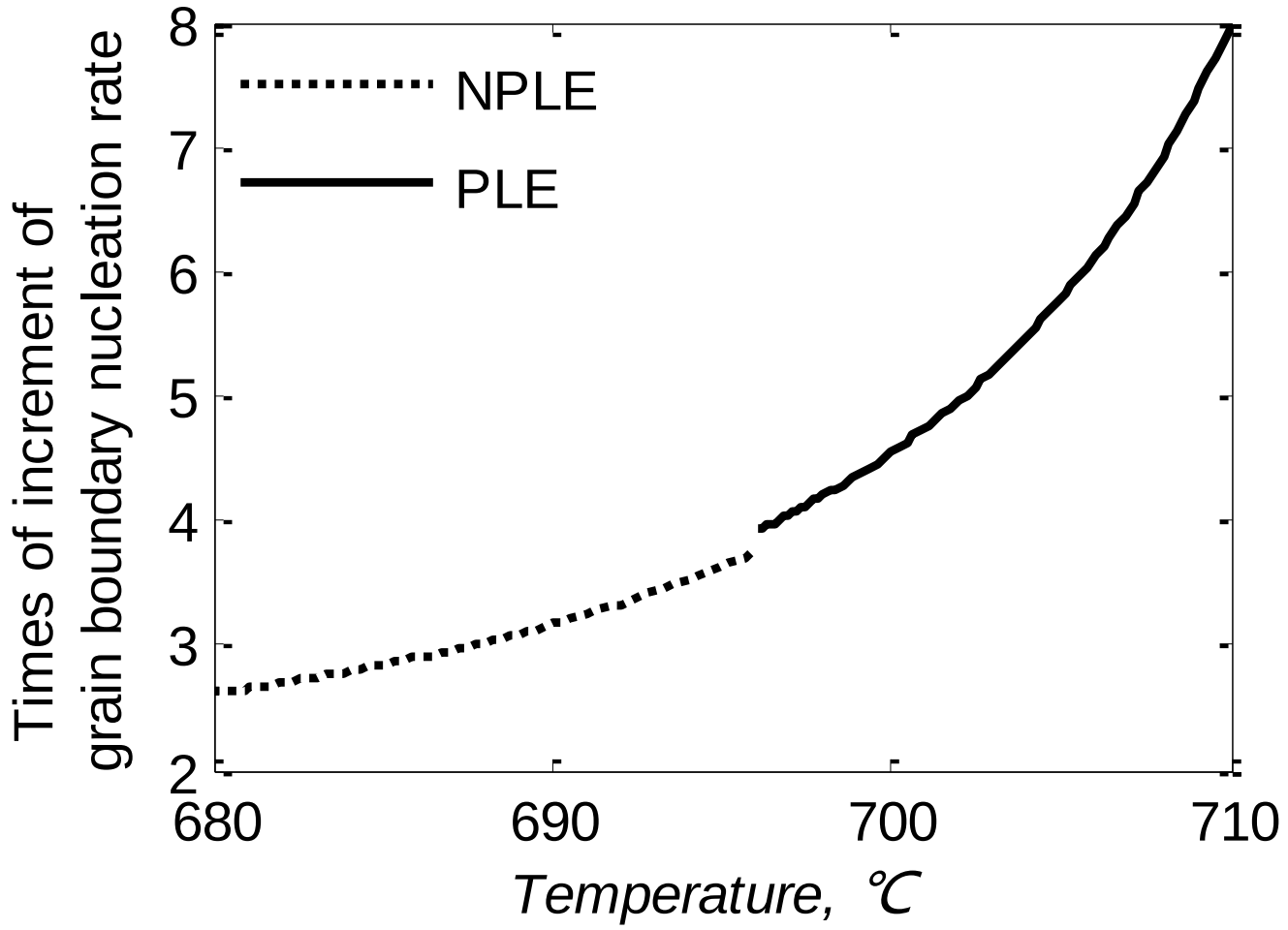
Fe-0.2C-2.0Mn, deformed at 700 ℃ by -50%

Deformation effect on nucleation under PLE model

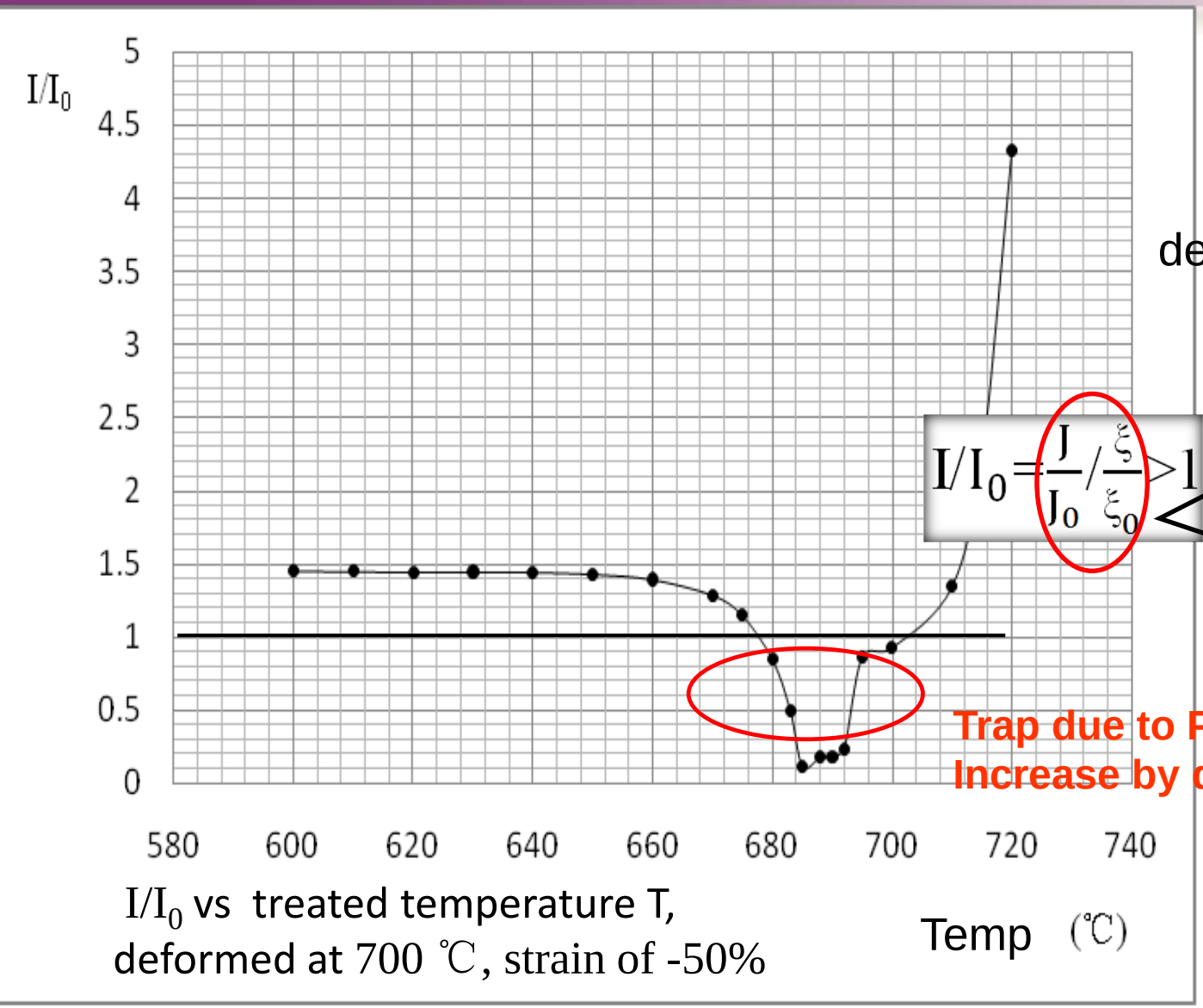


Increased nucleation rate J_f by deformation
Fe-0.2C-2.0Mn, deformed at 700 ℃ by -50%

Increase of nucleation rate several times by deformation



Effect of deformation on nucleation J vs growth constant, ξ



I/I_0 vs treated temperature T, deformed at 700 ℃, strain of -50%

$$I = \frac{J}{\xi}$$

I/I_0: deformed/non-deformed

$$I/I_0 = \frac{J}{J_0} / \frac{\xi}{\xi_0} > 1$$

Deformation promotes more nucleation than growth

Trap due to PLE/NPLE temp Increase by deformation

Summary

- **The transition from PLE to NPLE results rapid growth rate of ferrite by several orders, due to M diffusion or not**
- **Deformation of austenite introduces additional stored energy, increases PLE/NPLE temperature by about 10^{o}C for deformation of 30-50% at 700-800C.**
- **Deformation of austenite increases slightly growth rate of ferrite but nucleation rate efficiently**
- **Deformation changes some area of original PLE zone to NPLE zone, yields rapid increase of ferrite growth**