Growth of cementite with alloy partitioning during tempering of martensite

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As-quenched martensite is brittle.
→Improvement of toughness by tempering

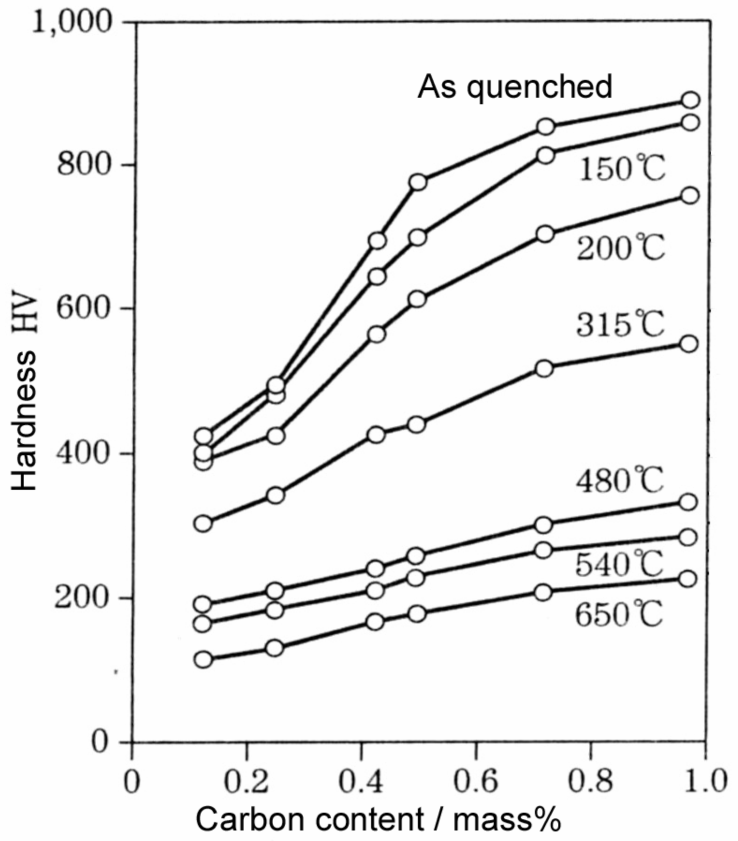
Tempering
Low temperature : 150~250ºC
High temperature : 650ºC

Remarkable softening in Fe-C martensite

Strengthening by precipitation

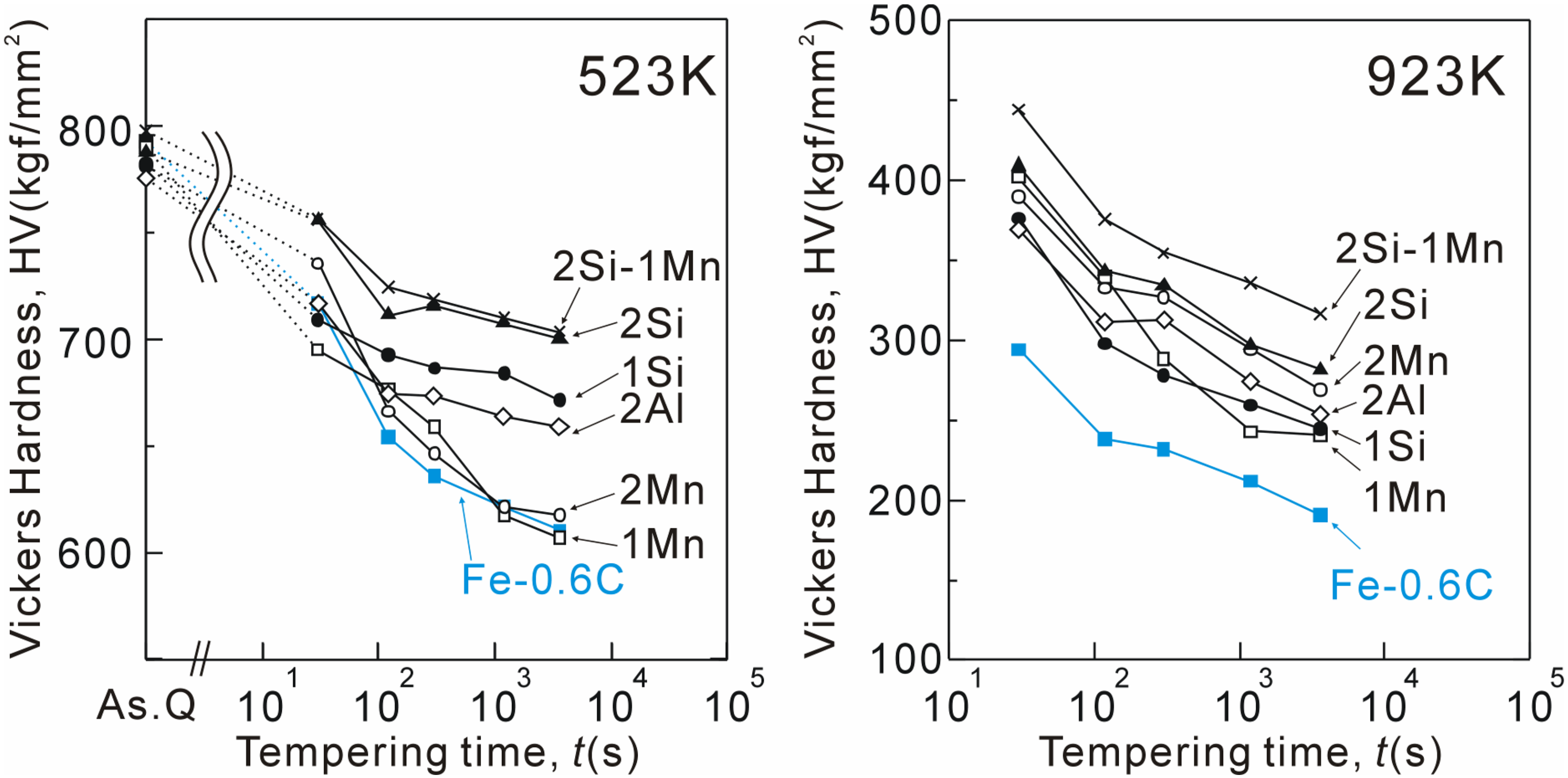
Precipitation	Steels	Alloying element
Alloy carbide (Mo_2C, V_4C_3, Cr_7C_3)	Secondary hardening steel	Mo, Cr, V
Intermetallics etc (Ni_3Ti, Fe_2Mo, ε-Cu)	Maraging steel	Ni, Ti, Cu, Mo
Iron carbide (ε carbide($Fe_{2\sim3}C$), cementite (Fe_3C))	Simple composition steel	Mn, Si

Fe-C martensite tempered for 1h



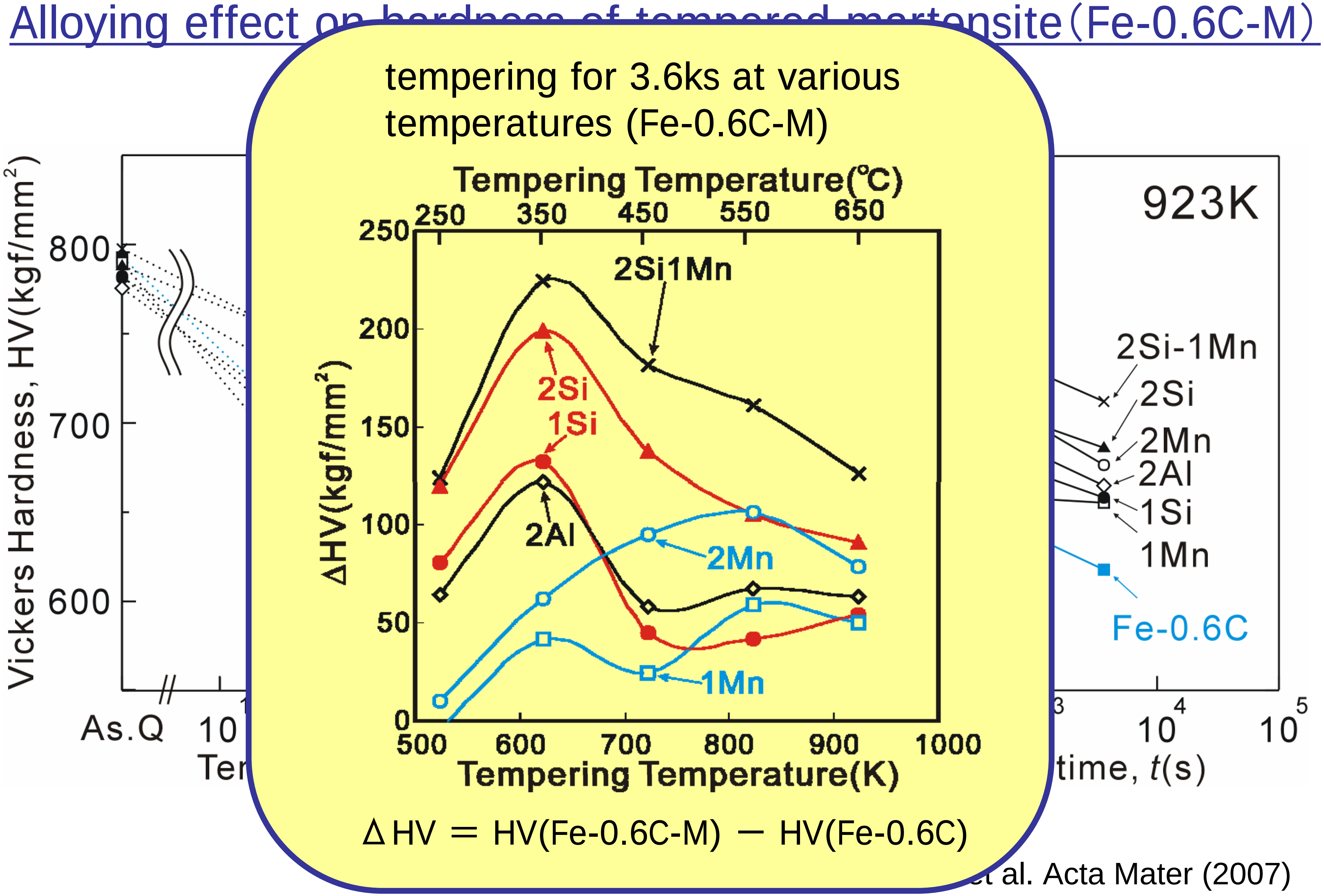
R. A. Grange et al.(1977)

Alloying effect on hardness of tempered martensite（Fe-0.6C-M）



Miyamoto et al. Acta Mater (2007)

Alloying effect on hardness of tempered martensite（Fe-0.6C-M）



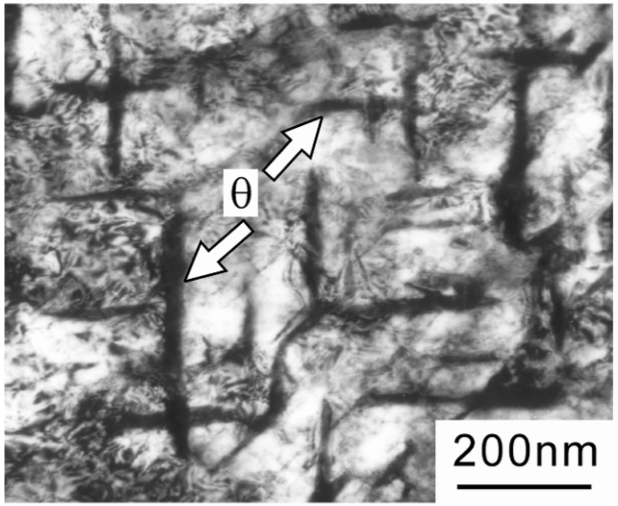
tempering for 3.6ks at various temperatures (Fe-0.6C-M)

ΔHV ＝ HV(Fe-0.6C-M) － HV(Fe-0.6C)

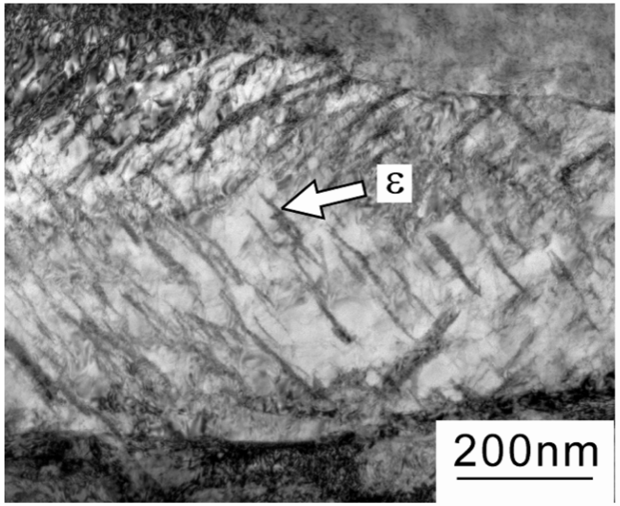
et al. Acta Mater (2007)

ε→θ transition in Fe-0.6C-M alloys

Tempered at 523K for 1.2ks



Fe−0.6C−2Mn



Fe−0.6C−2Si

Temperature & time / Alloy	523K		723K	
	30s	1.2ks	30s	1.2ks
Fe-0.6C	ε	θ	θ	θ
Fe-0.6C-2Mn	ε	θ	θ	θ
Fe-0.6C-2Si	ε	ε	ε	θ

retarding ε → θ transition by Si

⇩

Large softening retardation at low temperature tempering

How do Mn and Si retard softening at higher temperatures?

- Growth of cementite with alloy partitioning

  Theoretical coarsening rate of θ in Fe-C-M ternary system was derived by assuming equilibrium partitioning.

  S. Björklund, et al. : Acta Met., 20(1972), 867

- Alloy partitioning between α / θ
  - Equilibrium state : Mn is enriched in θ while Si is rejected from θ.
  - Tempered martensite :

    para-θ (no macroscopic redistribution of alloying element between α / θ) is frequently observed.

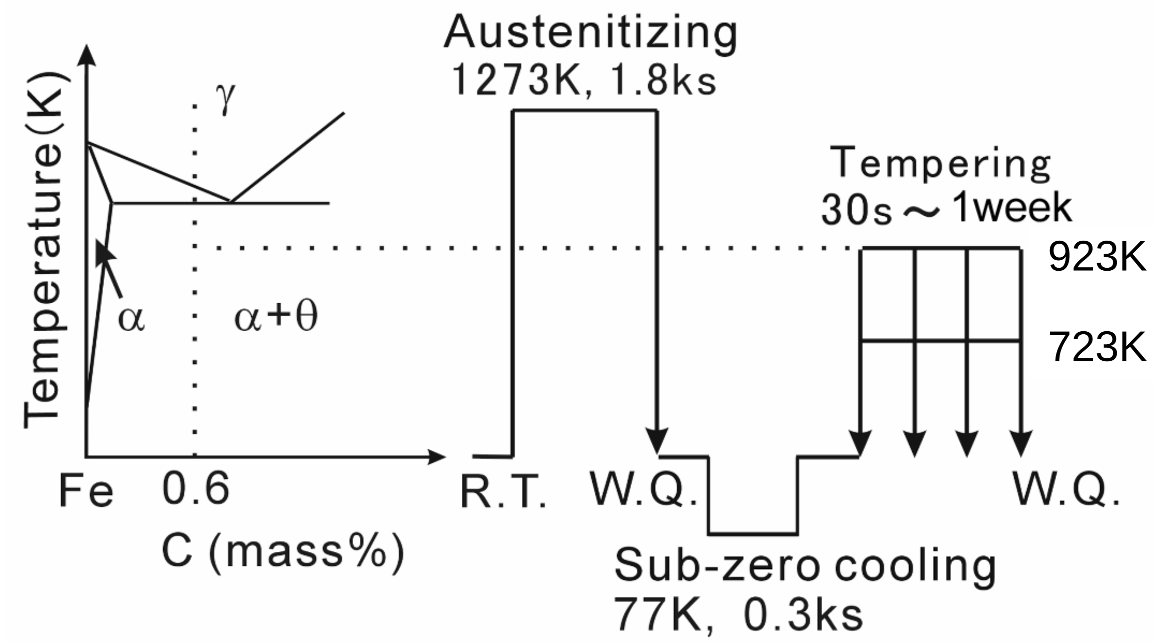
Objective

To clarify the growth kinetics of θ accompanied with solute partitioning in tempered high-carbon martensite

Experimental procedure

◆Alloy(mass%) : Fe-0.6%C, Fe-0.6%C-M(M=1%Mn, 2%Mn, 2%Si)

◆ Heat treatment



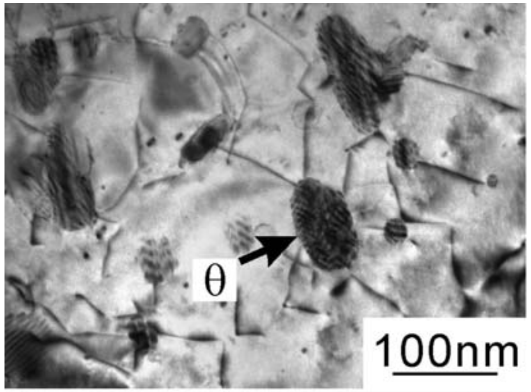
◆ Observation and measurement

SEM, TEM (+EDS), three dimensional atom probe (3DAP)

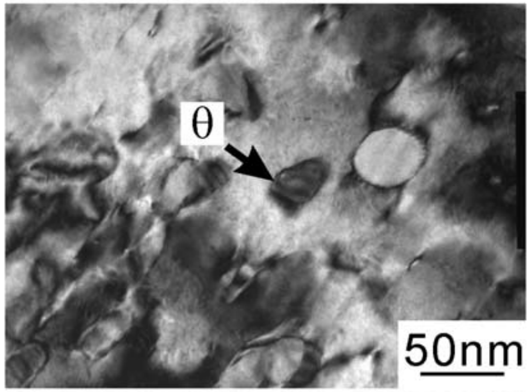
Alloying effect on growth of carbide in tempering at 723K (TEM)

Tempering for 1.2ks

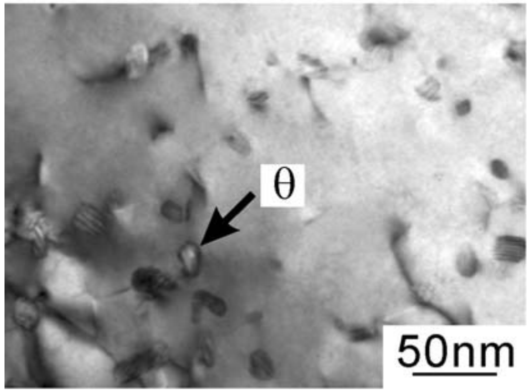
Fe-0.6C

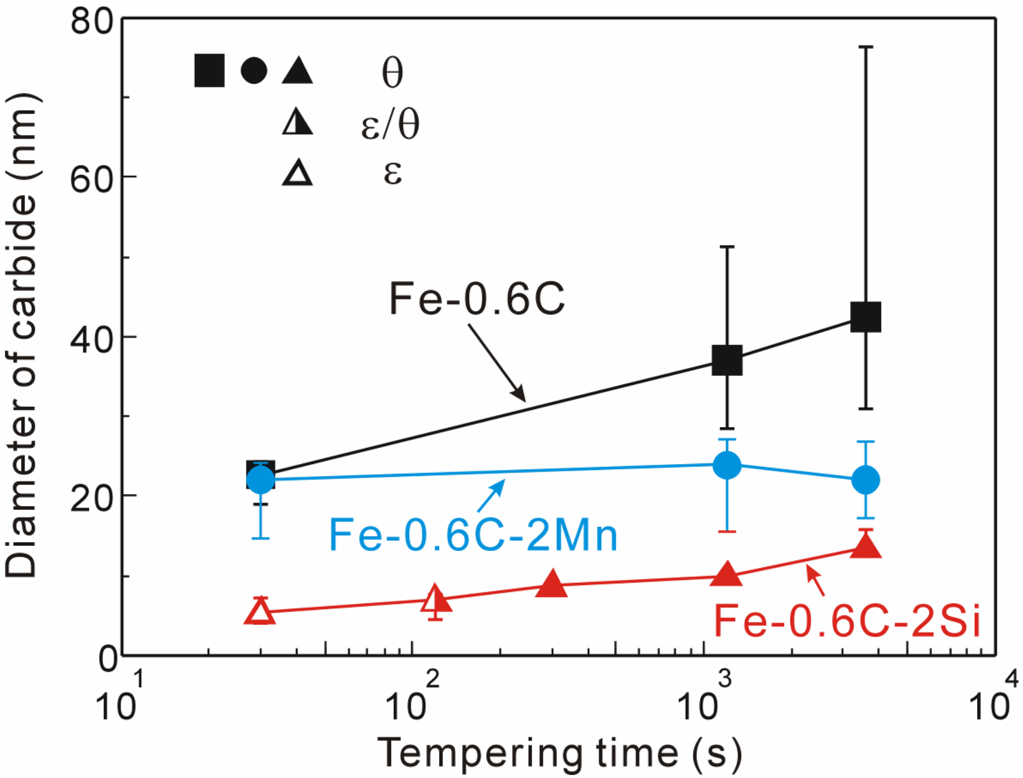


2Mn



2Si

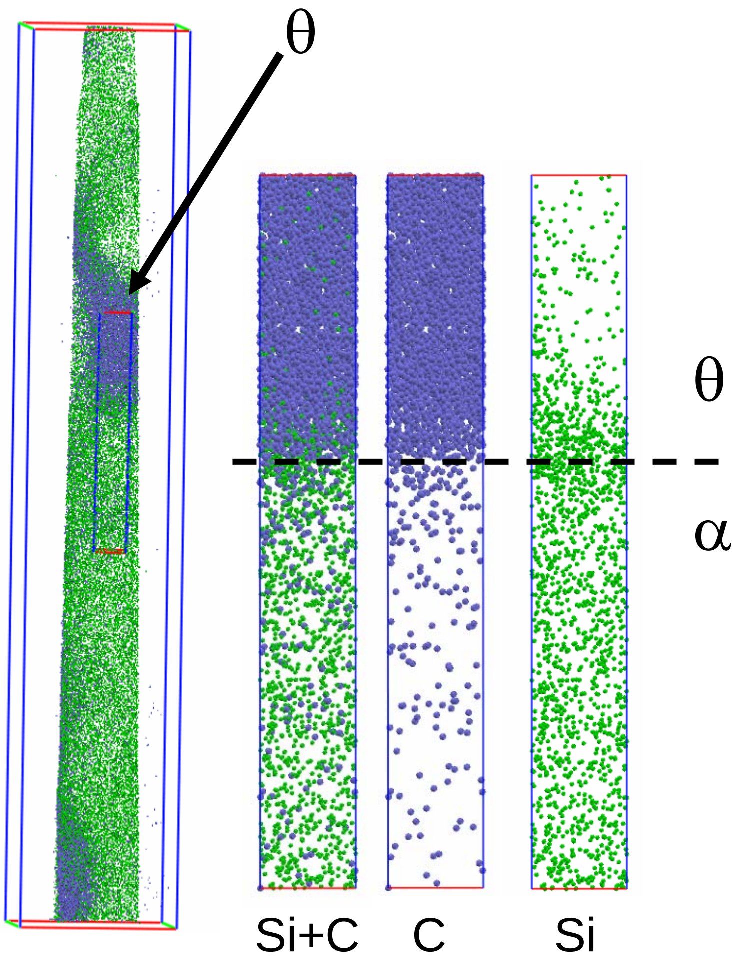




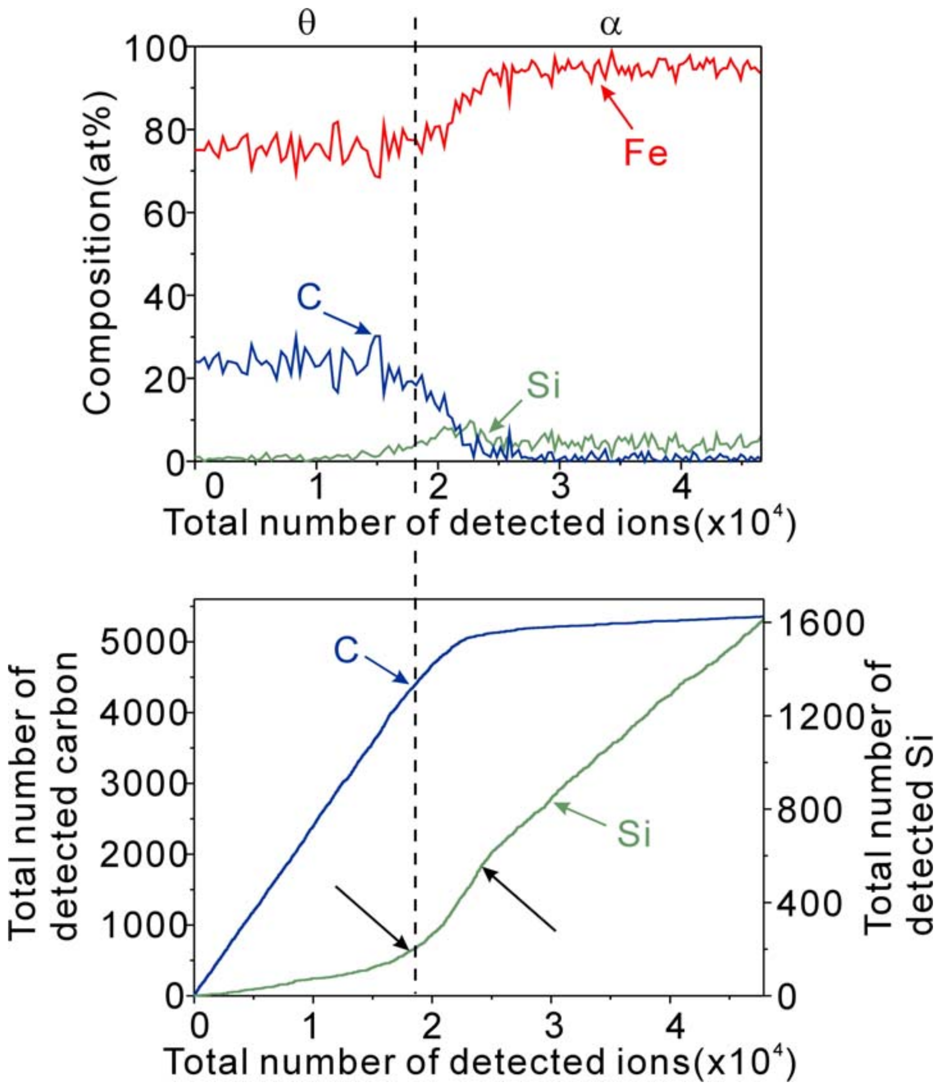
Si ; Retardation of θ(/ε) growth from the initial stage of tempering

Mn ; Retardation of θ only later stage of tempering

Fe-0.6C-2Si tempered at 723K for 1.2ks (3DAP)

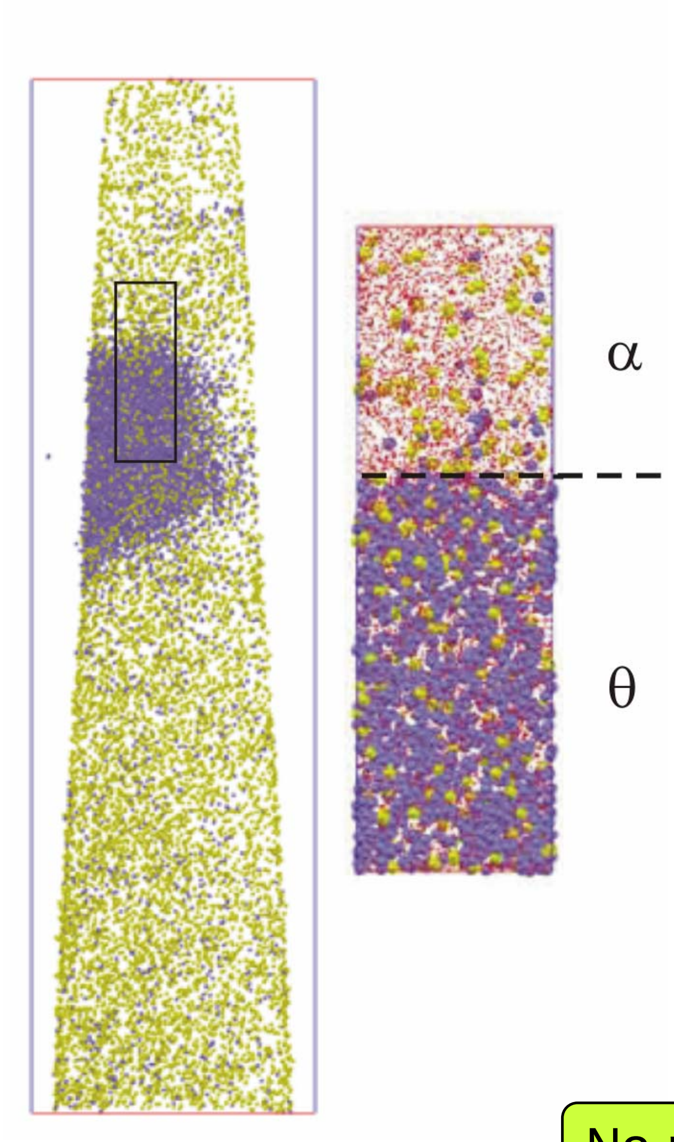


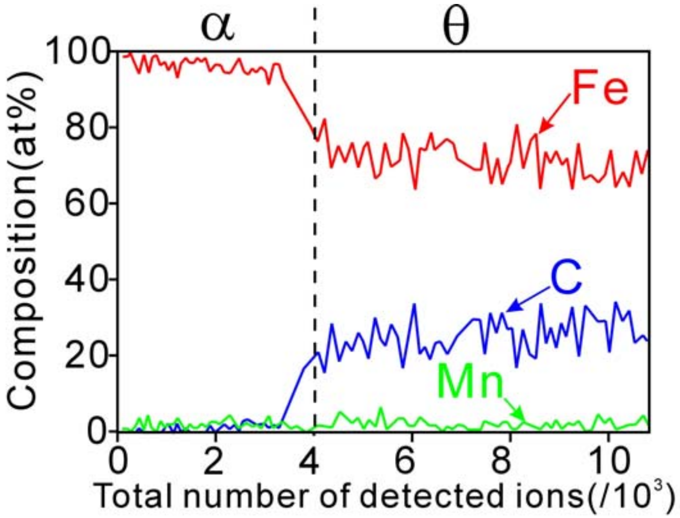
Selected Volume: 4 x 4 x 30 nm

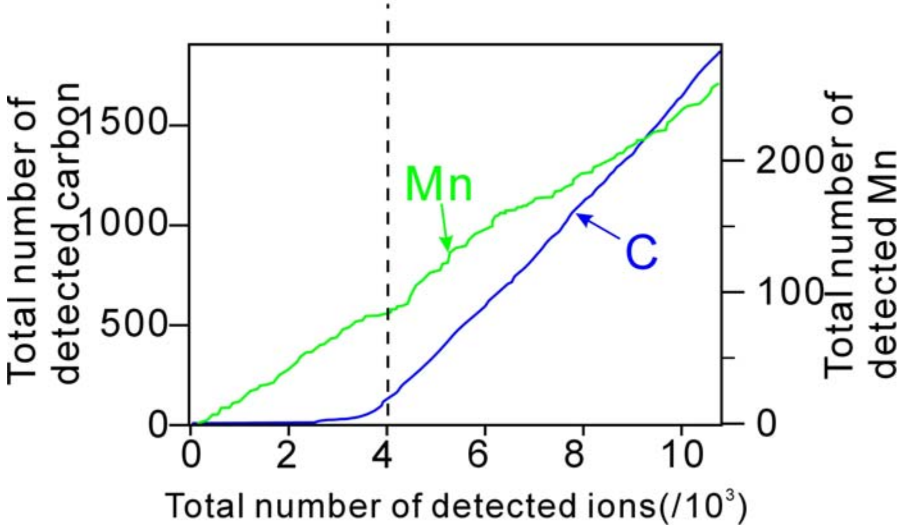


Si is swept out from θ → retarding θ growth

Fe-0.6C-2Mn tempered at 723K for 30s (3DAP)

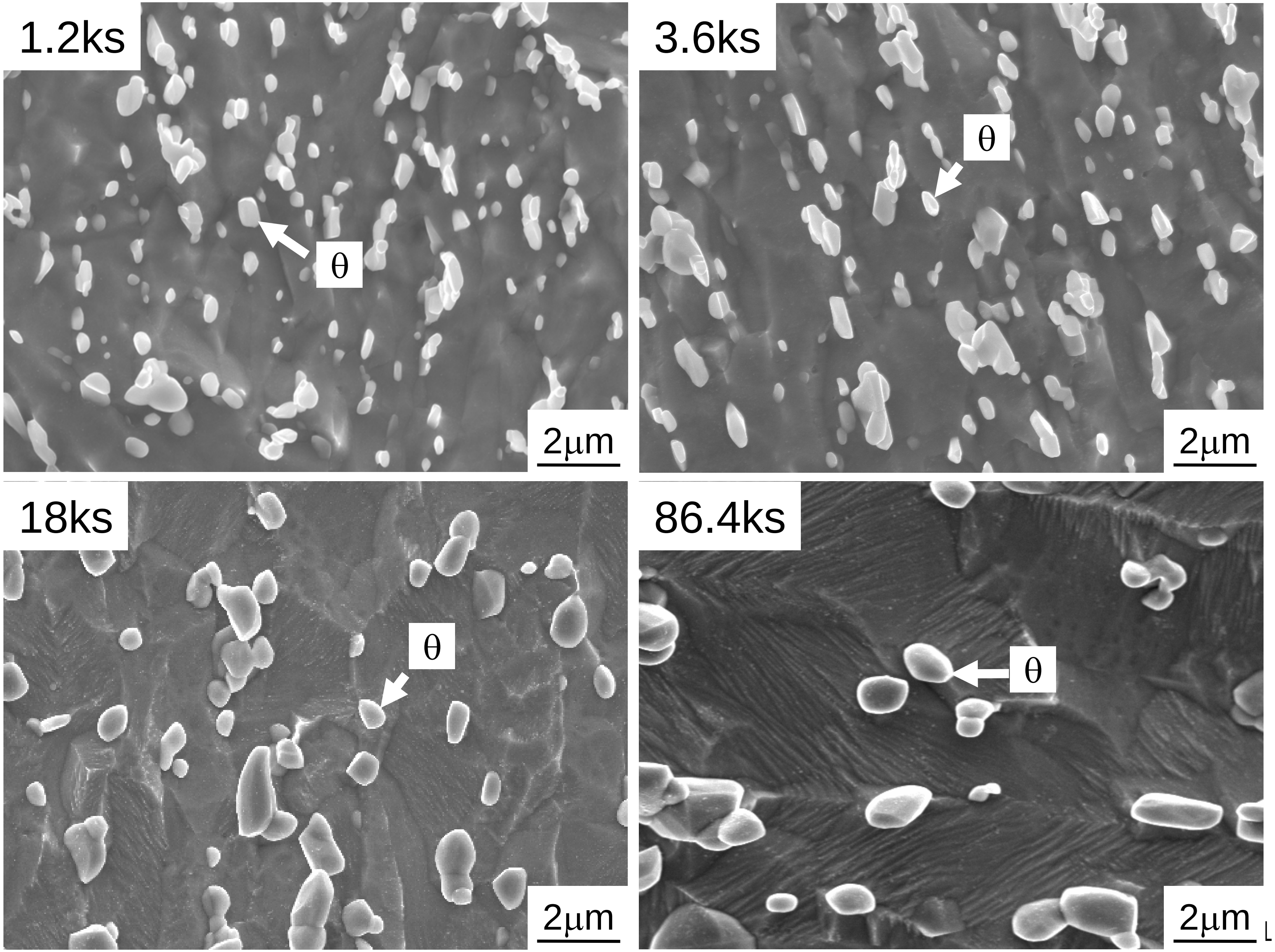






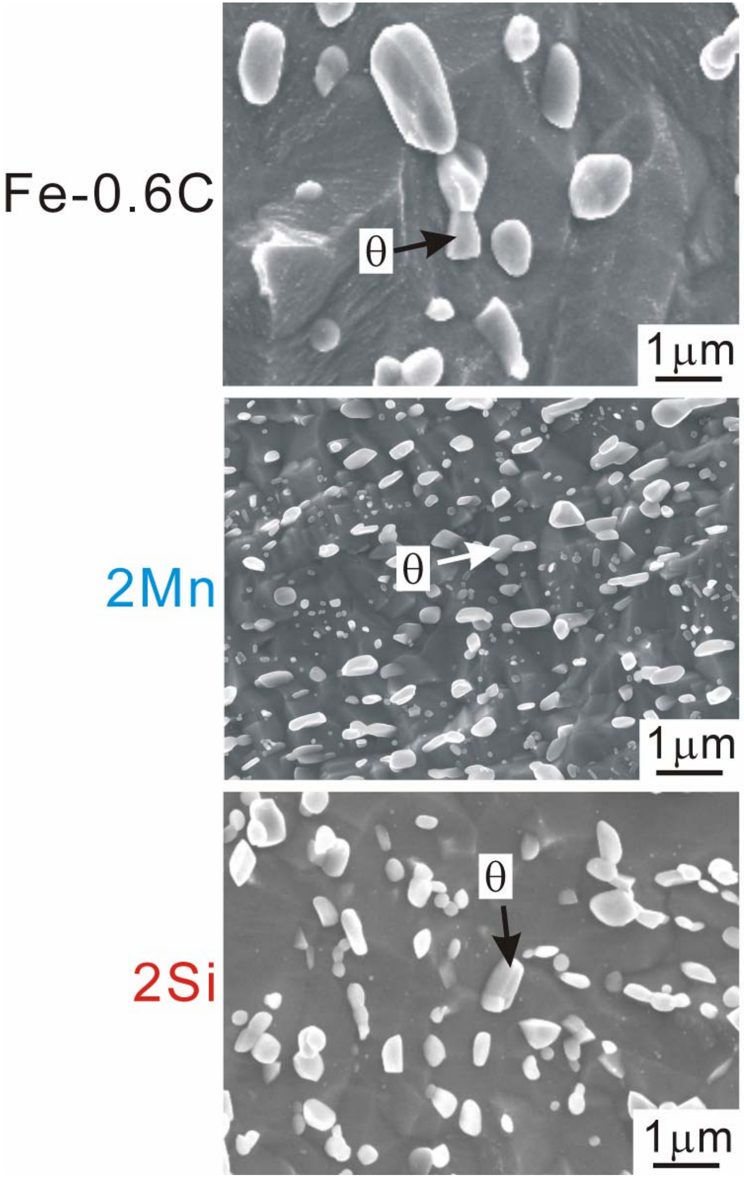
No macroscopic partitioning of Mn between θ / α

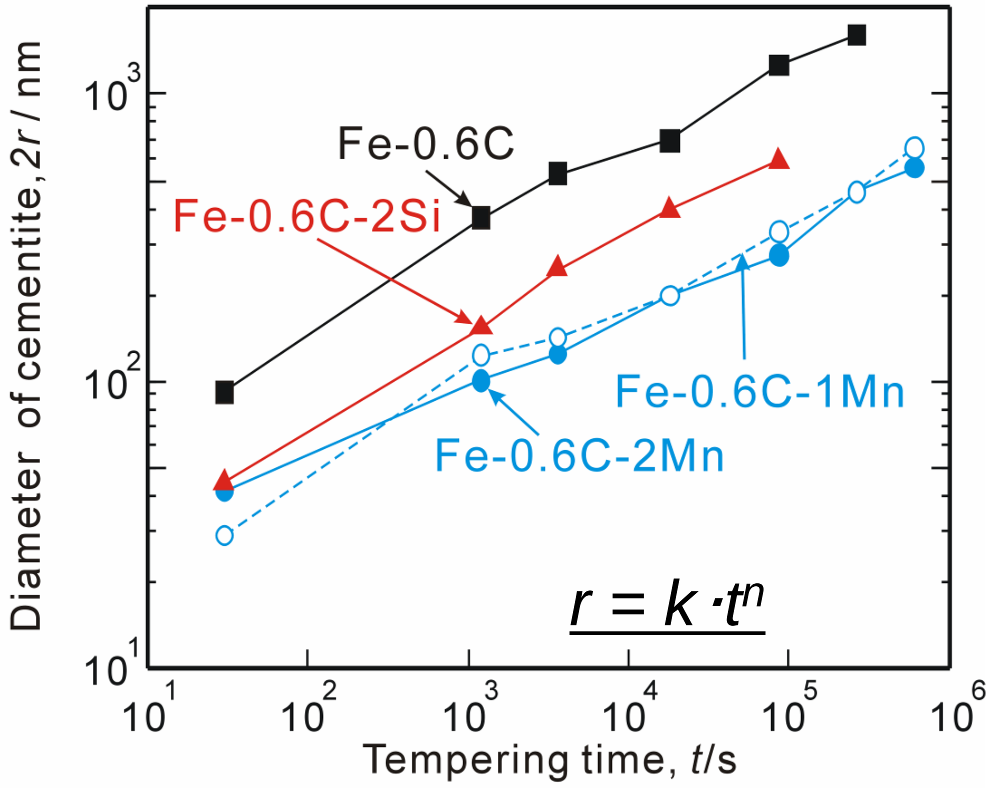
Change in θ distribution during tempering of Fe-0.6C at 923K (SEM)



Effect of Mn and Si on coarsening of θ (923K)

Tempering for 18ks

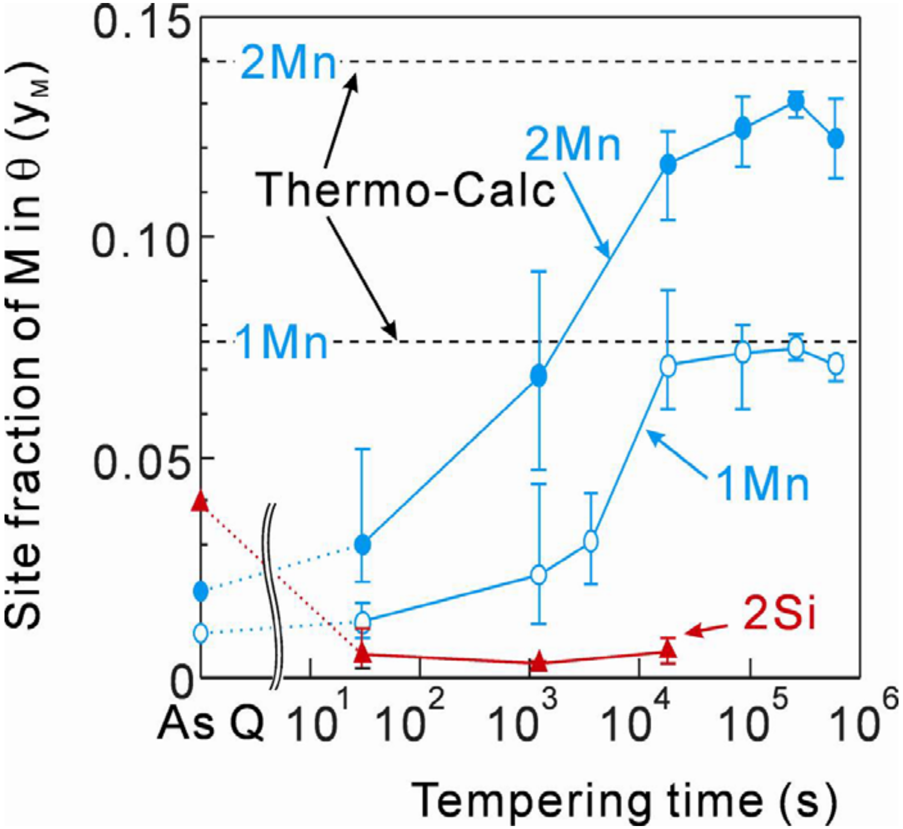




alloy	n	k
Fe-0.6C	0.31	17
Fe-0.6C-2Si	0.33	7.5
Fe-0.6C-1Mn	0.30	5.9
Fe-0.6C-2Mn	0.23	7.8

Variation in composition of θ during tempering at 923K

Fe-0.6C-M tempered at 923K
(TEM / EDS)



Si ; Swept out from θ even after short periods of tempering

Mn ; Nearly no partitioning and enriched into θ gradually with increasing time

Partitioning of Mn and Si retards θ coarsening

Coarsening rate of θ in Fe-0.6C alloy

Coarsening rate equation

$$\bar{r}^3 - \bar{r}_0^3 = \frac{8\,\sigma\, V_\theta\, x_C D}{9RT} t$$

$\bar{r}$: average radius of θ at t

$\bar{r}_0$: average radius of θ at t = 0

σ : α / θ interfacial energy

(=0.7 J/m^2)

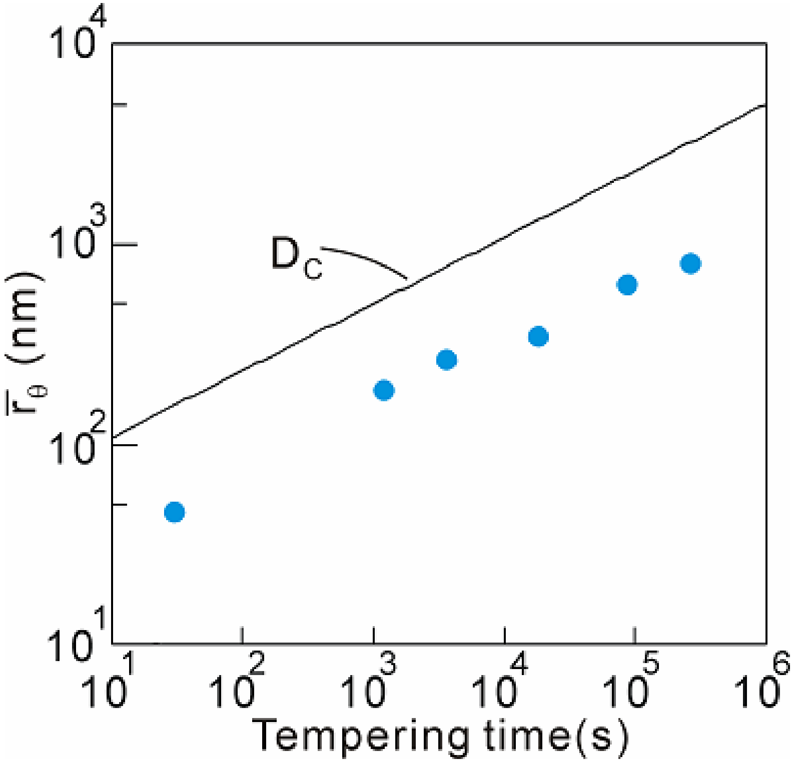
x_c : carbon content in ferrite

equilibrated with cementite

V_θ : molar volume of θ

D : diffusion coefficient of C in α

Fe-0.6C alloy tempered at 923K



Coarsening rate of θ in Fe-0.6C alloy

$$\bar{r}^3 - \bar{r}_0^3 = \frac{8\,\sigma\,V_\theta\,x_C D_{eff}}{9RT}t$$

coupled diffusion :

Volumetric mismatch between α and θ is relaxed by Diffusion of Fe (vacancy)

→ θ coarsening is controlled by Fe and C

Effective diffusion coefficient

$$D_C^{eff} = \frac{n_{Fe} D_c D_{Fe} V_{Fe}}{n_{Fe} D_{Fe} (V_{Fe})^2 + n_c D_c (V_c)^2}\{V_{Fe} + (\frac{n_c}{n_{Fe}})V_c\}$$

V_{Fe} : molar volume of Fe

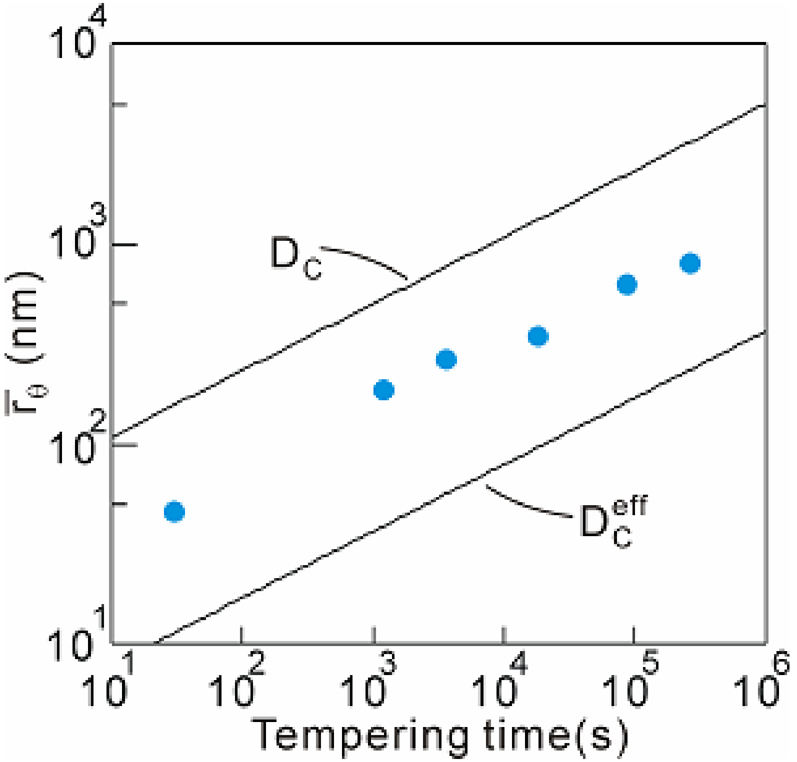
V_C : difference in molar volume of Fe between α and θ

D_C : diffusion coefficient of C

D_{Fe} : diffusion coefficient of Fe

Oriani, (1964), Acta Metall,
Li et al. (1966), Acta Metall

Fe-0.6C alloy tempered at 923K



Coarsening rate of θ in Fe-0.6C-M alloy

$$\bar{r}^3 - \bar{r}_0^3 = \frac{8\,\sigma\,V_\theta}{27RT}\,\frac{D_M^\alpha}{(1-K^{\theta/\alpha})^2\,u_M^\alpha}\,t$$

$K^{\theta/\alpha}$: partitioning coefficient (X_M^θ / X_M^α) → （$K_{Si}\approx 0$, $K_{Mn}\approx 15$）

u_M^α : M content in a at the α / θ interface

$\bar{r}$: average θ radius at tempering time of t

$\bar{r}_0$: average θ radius at tempering time of t=0

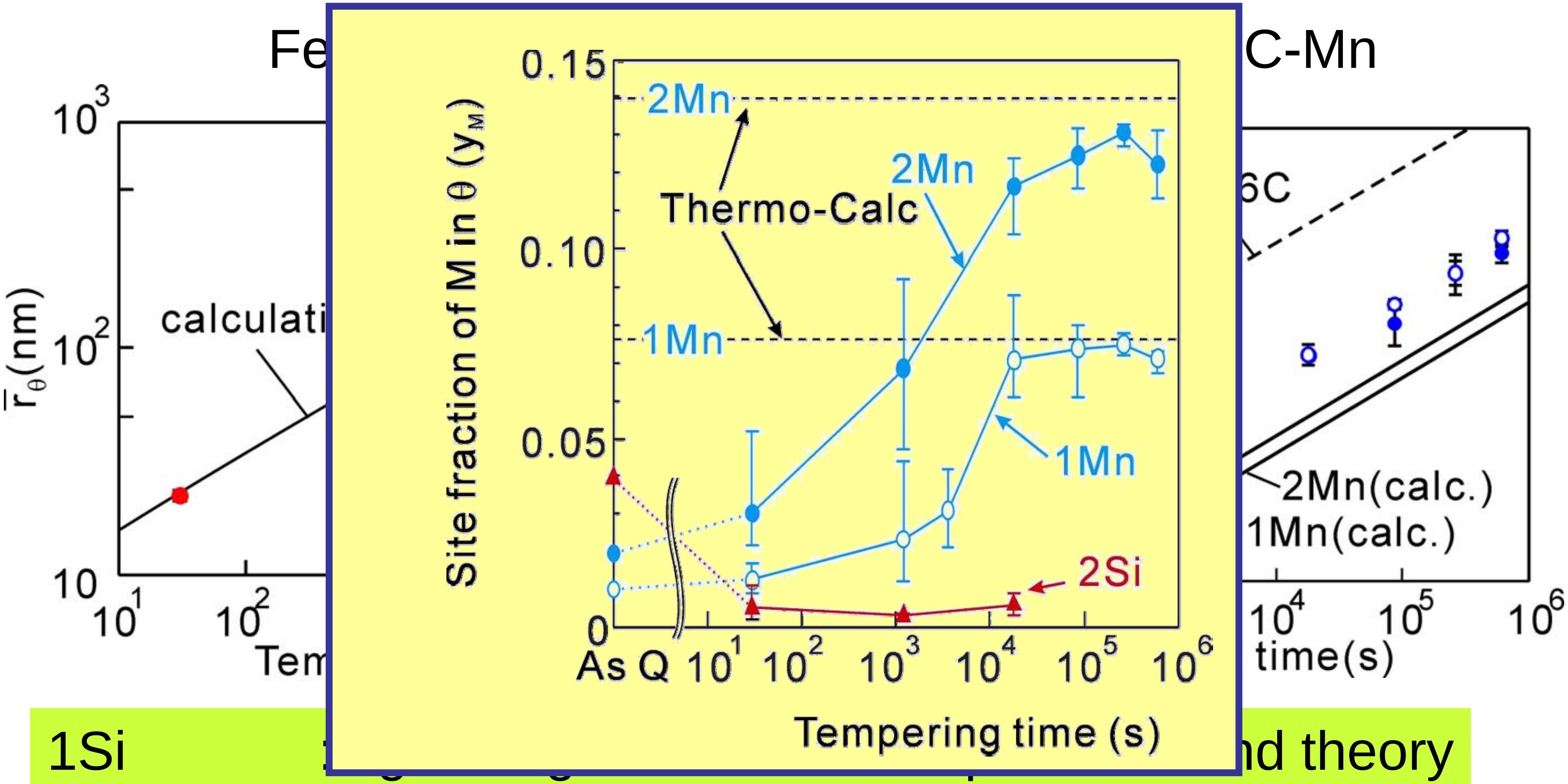
σ : interfacial energy of α / θ (=0.7J / m^2)

D_M^α : lattice diffusion coefficient of M (→Oikawa(1965))

V_θ : molar volume of θ

S. Björklund, et al. : Acta Met., 20(1972), 867

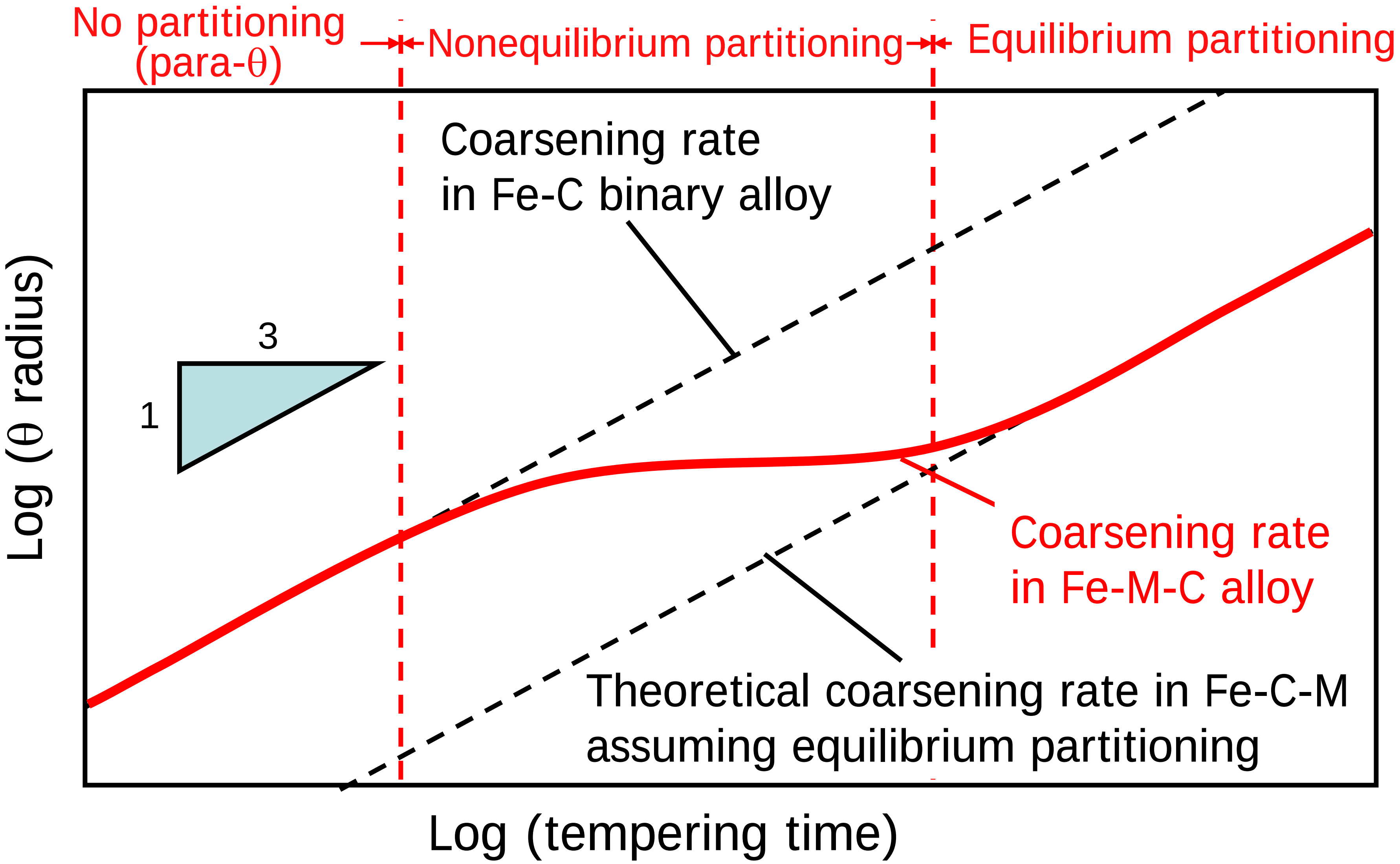
Coarsening rate of θ in Fe-0.6C-M alloy



1Si : nd theory

1Mn, 2Mn : faster coarsening rate than theory
but the difference becomes smaller
after prolonged tempering

Coarsening in Fe-C-M alloy



Conclusion

Effect of Mn and Si addition on growth of θ during tempering of Fe-0.6%C martensite was investigated.

Growth of carbide

- Si and Mn retards θ growth in tempering at 723K(Si>Mn) and 923K(Si<Mn)
- Coarsening rate of θ at 923K in 1Si alloy is in good agreement with theoretical one assuming equilibrium partitioning. While coarsening rate in 1Mn and 2Mn alloys is faster than the theory.

Partitioning of alloying element between α / θ

- Si is rejected from θ from the initial stage of precipitation of θ.
- Mn does not macroscopically redistribute in tempering at 723K, and is gradually enriched in θ after long tempering at 923K.