



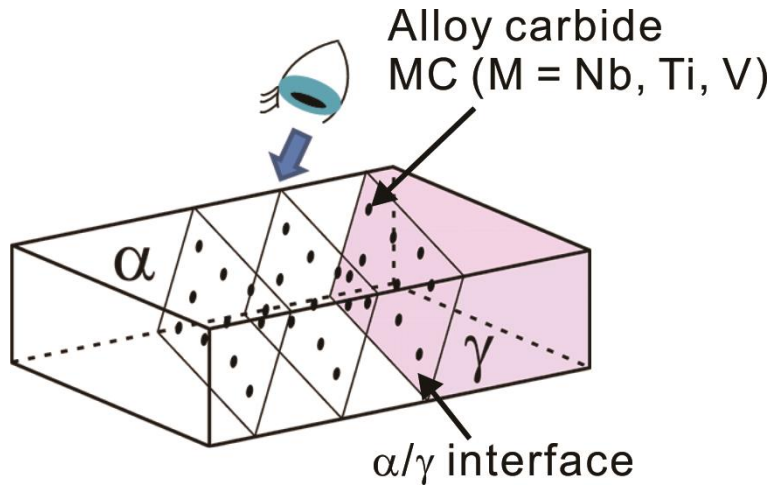
2017.6.26 16th ALEMI Meeting @ Tsinghua University, China

Dominating Factors on Dispersion of MC Interphase Precipitation in Low Carbon Steels

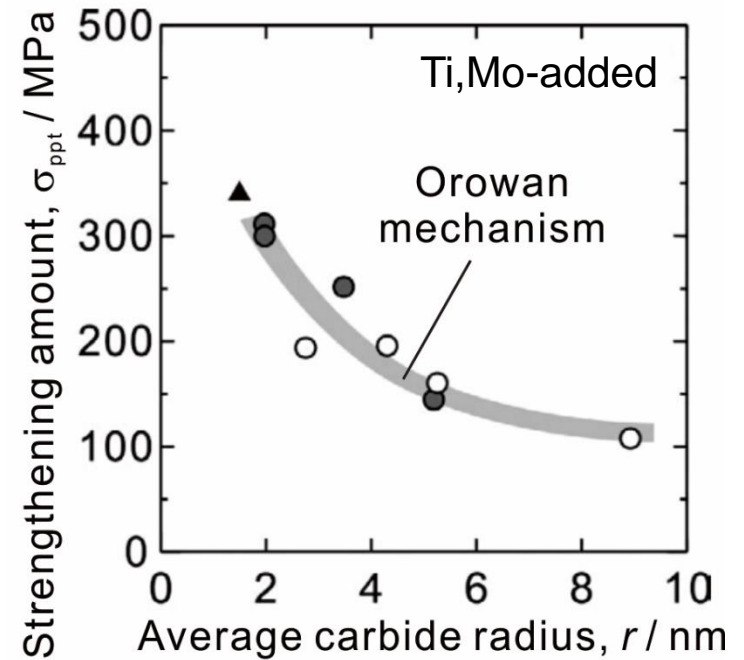
Y.-J. Zhang, G. Miyamoto, T. Furuhashi

Institute for Materials Research, Tohoku University, Japan





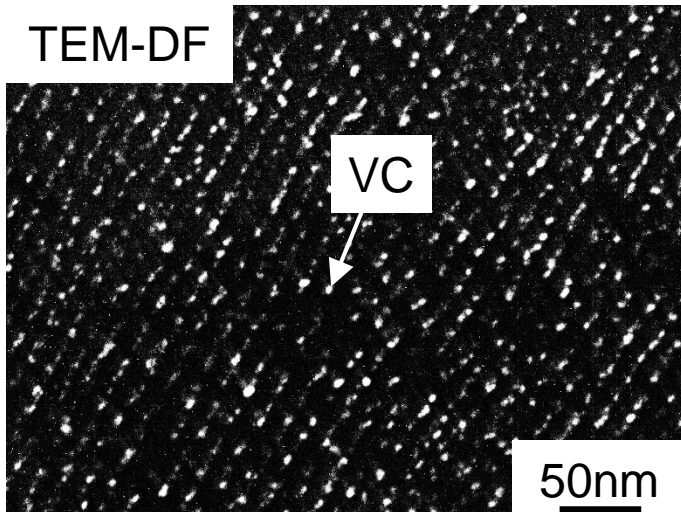
Precipitation strengthening



Periodic nucleation at migrating interface

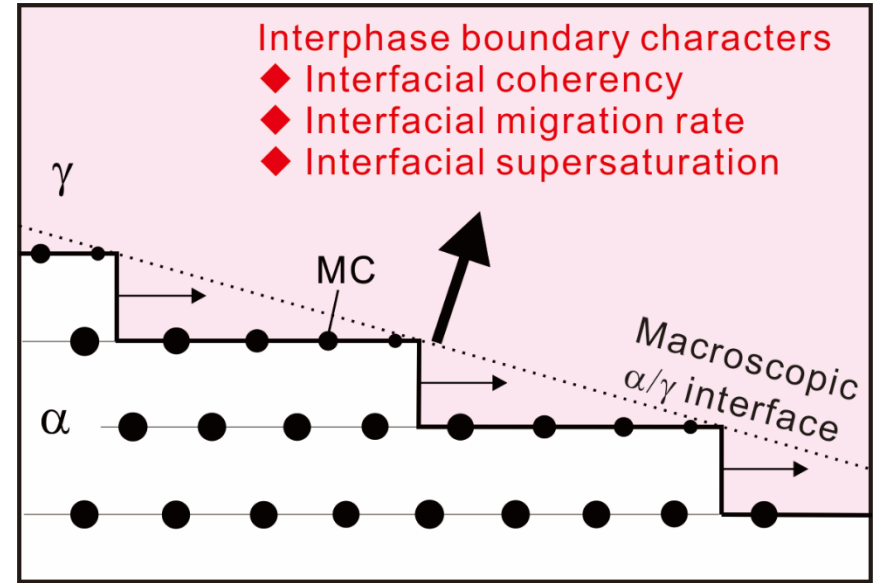
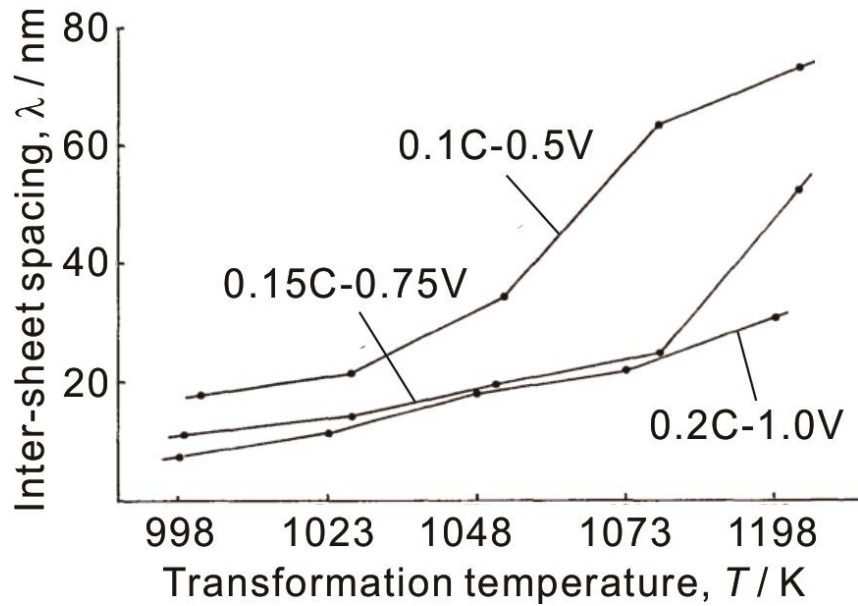
V-added low carbon steel

TEM-DF



N. Kamikawa et al., *ISIJ Int.* 54 (2014) 212.

- Larger precipitation strengthening can be obtained by refining MC until nano size.



A.D. Batte et al., *Met. Sci. J.*, 7 (1973) 160.

- Interfacial coherency → Density of defects
 - Interfacial migration rate → Time
 - Interfacial supersaturation → Driving force
- } for nucleation



Variations in dispersion of interphase precipitation

The effects of transformation temperature and alloying elements on the dispersion of interphase precipitation and resultant strengthening in low carbon steels were quantitatively studied mainly by using **three-dimensional atom probe**.

Based on this, **the dominating factors** on the dispersion of interphase precipitation will be further discussed.

- Alloys (mass%)

Base: Fe-0.1C-1.5Mn-0.05Si (M-free)

V-added: Fe-0.1C-1.5Mn-0.05Si-**0.1V / 0.2V / 0.4V**

Fe-**0.2C**-1.5Mn-0.05Si-**0.4V (High C)**

Fe-0.1C-**0.7Mn**-0.05Si-**0.4V (Low Mn)**

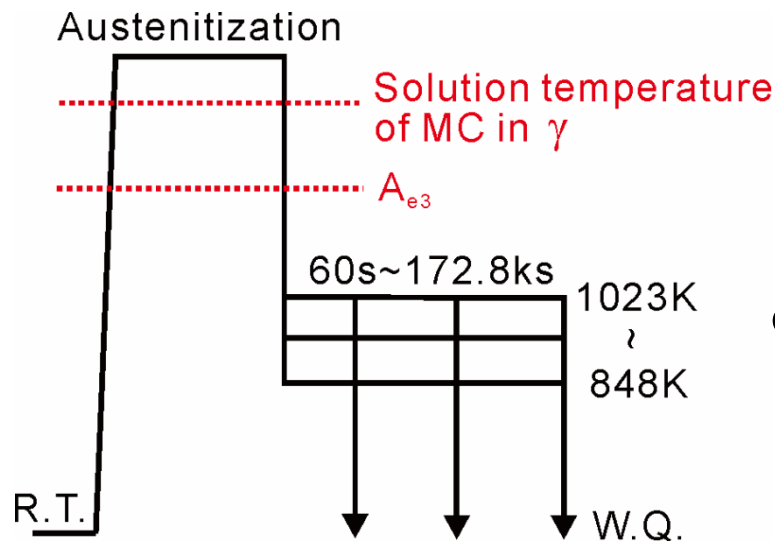
Fe-0.1C-1.5Mn-**0.4Si**-**0.4V (High Si)**

Fe-0.1C-1.5Mn-0.05Si-**0.4V-150ppmN (High N)**

Nb-added: Fe-0.1C-1.5Mn-0.05Si-**0.05Nb / 0.1Nb**

Ti-added: Fe-0.1C-1.5Mn-0.05Si-**0.05Ti / 0.1Ti / 0.2Ti**

- Heat treatment



- Microstructural characterization

- Optical microscopy (OM)
- Scanning electron microscopy (SEM) / Electron backscatter diffraction (EBSD)
- Three-dimensional atom probe (3DAP)

- Property measurement

- Vickers hardness measurement (9.8N / 0.25N)
- Nanoindentation measurement (500 μ N)

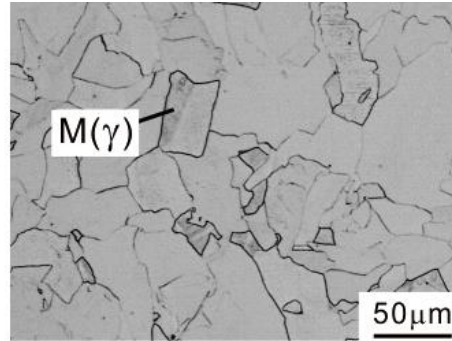
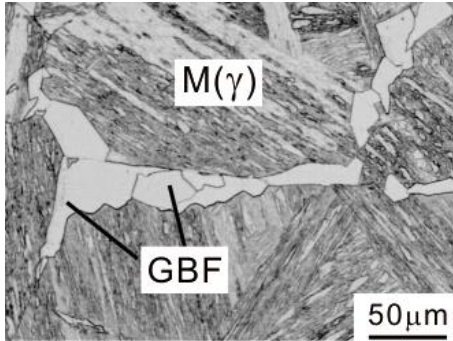
0.1C-0.4V

60s

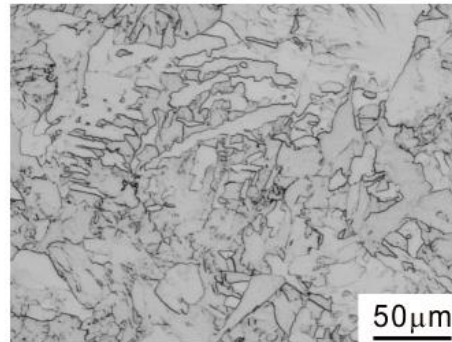
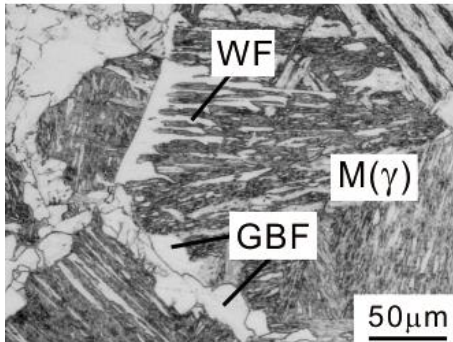
1.8ks

Hardness-1.8ks

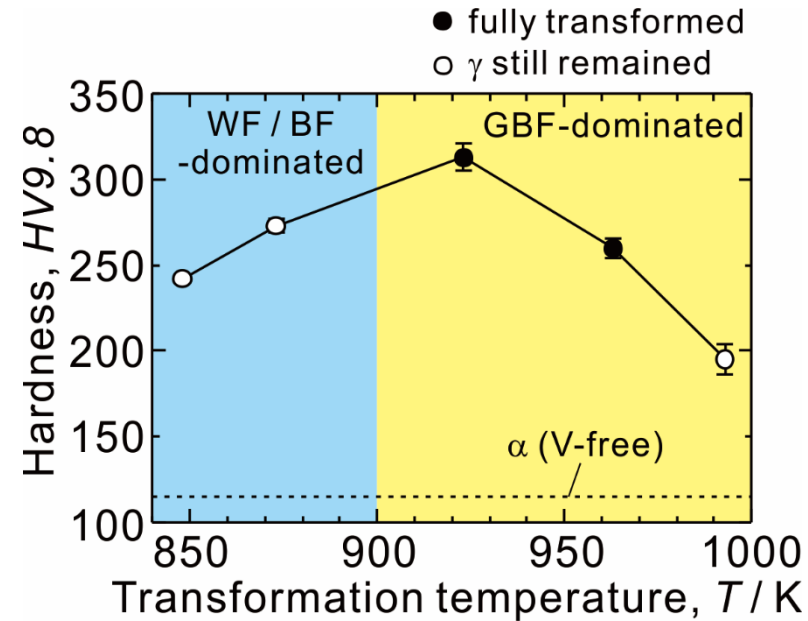
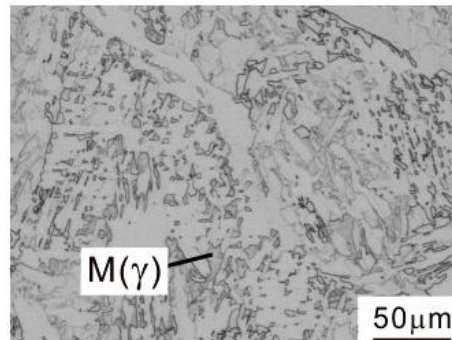
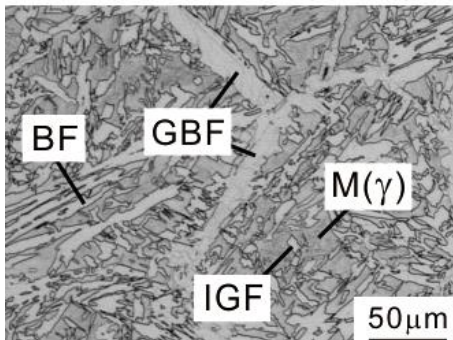
993K



923K



873K



- By lowering transformation temperature, the morphology of α changes from GBF into WF/BF, corresponding to the reduction in hardness.

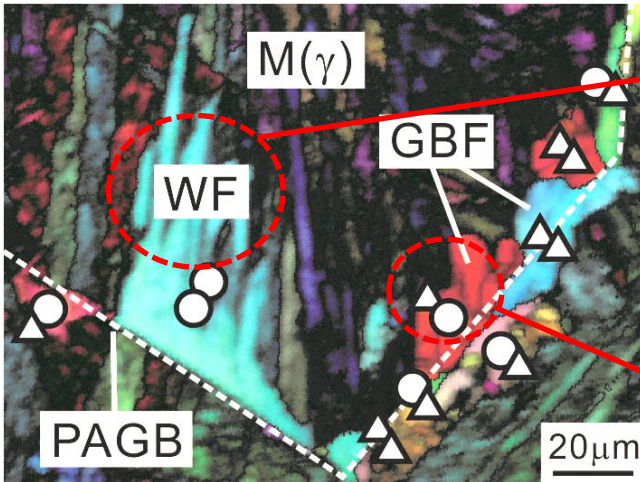
GBF: grain boundary α ; WF: Widmanstätten α ;
 BF: bainite α ; IGF: intragranular α ; M(γ): martensite

923K, 60s

α orientation map

○ : Near K-S ($\Delta\theta \leq 5\text{deg.}$);

△ : Non K-S ($\Delta\theta > 5\text{deg.}$)

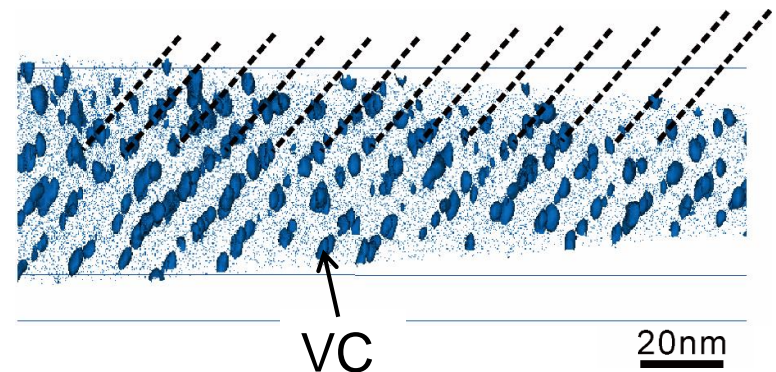


Three-dimensional V atom map

WF ($\Delta\theta = 0.8\text{deg.}$)

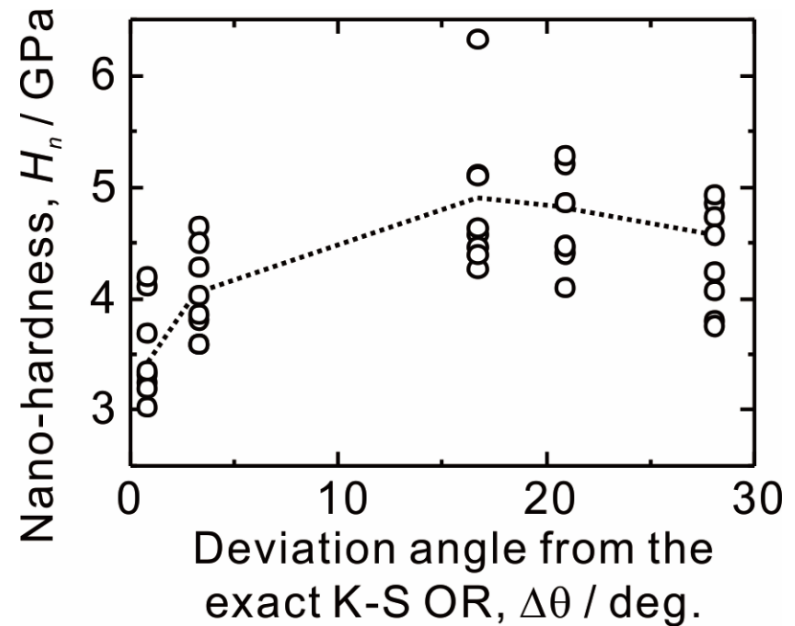
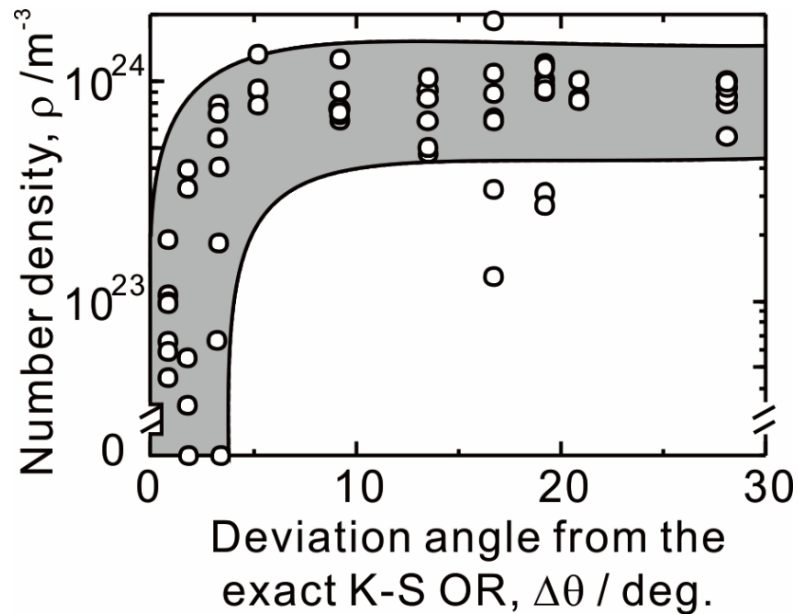


GBF ($\Delta\theta = 19.2\text{deg.}$)



PAGB: prior γ grain boundary; $M(\gamma)$: martensite;
 GBF: grain boundary α ; WF: Widmanstatten α ;
 $\Delta\theta$: deviation angle from the exact Kurdjumov-Sachs orientation relationship (K-S OR)

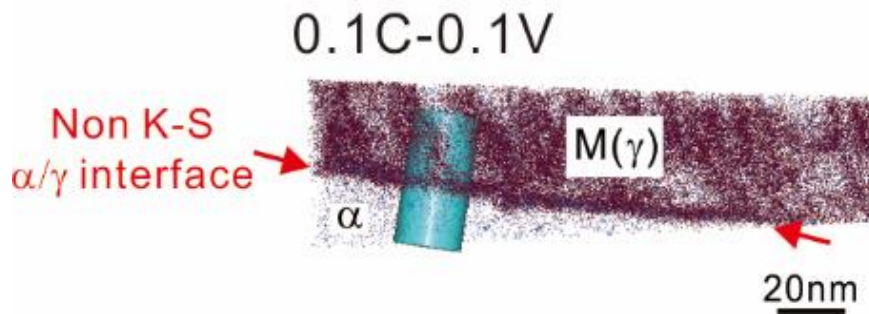
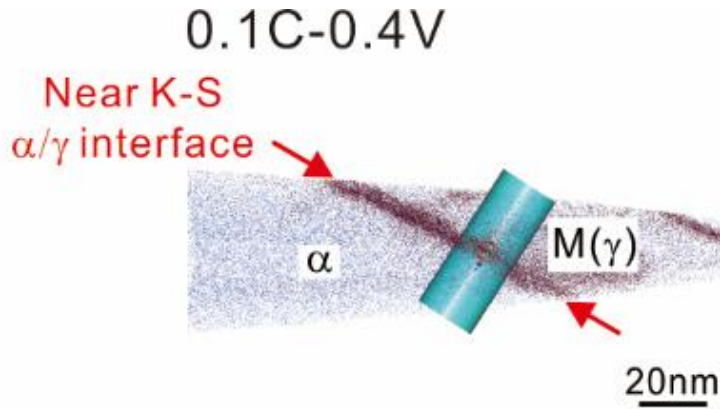
- α transformation is proceeded by the migration of both near K-S and non K-S α/γ interface.
- Almost no VC precipitate exists in WF with near K-S OR, while VC interphase precipitation is observed in GBF with non K-S OR.



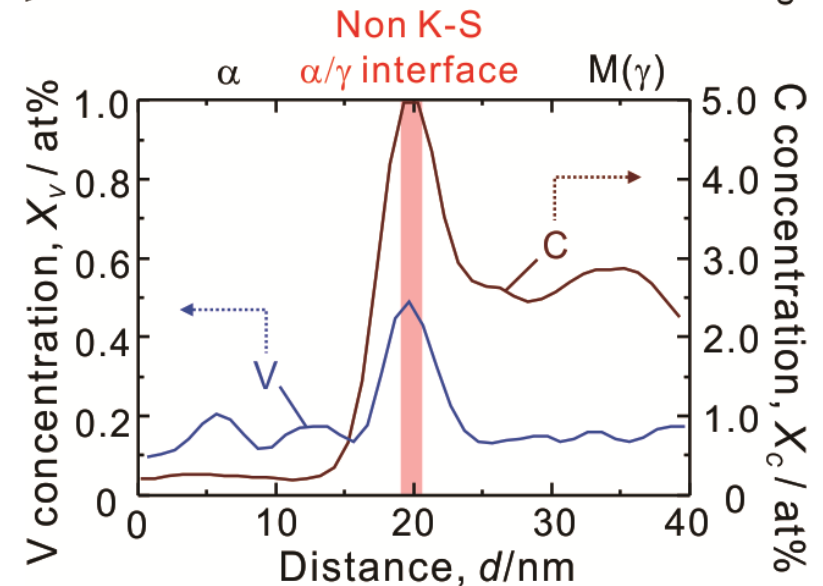
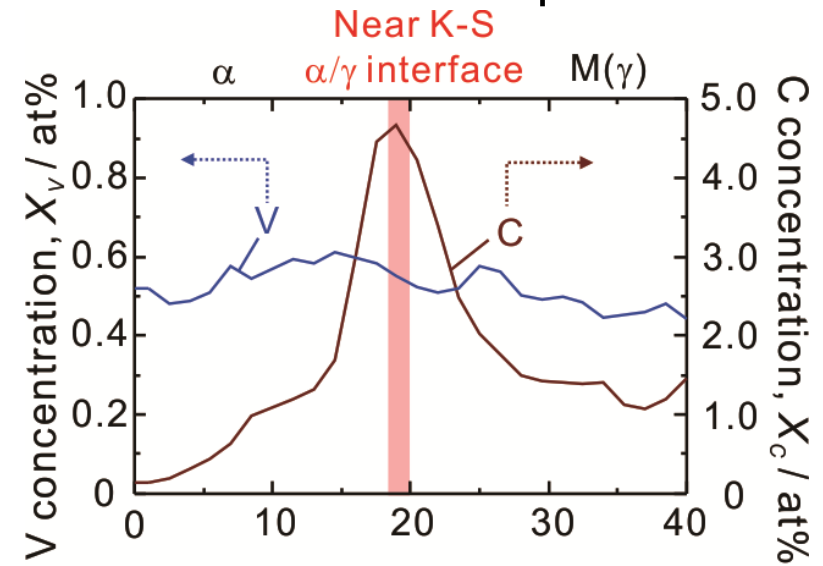
Y.-J. Zhang et al., *Scr. Mater.* 69 (2013) 17.

- As α/γ OR deviates from exact K-S, number density of VC increases significantly at first and remains almost constant later, while the size of VC is only slightly increased.
- Higher number density of VC in α grains with non K-S OR results in higher nanohardness compared with those with near K-S OR.

V + C atom map

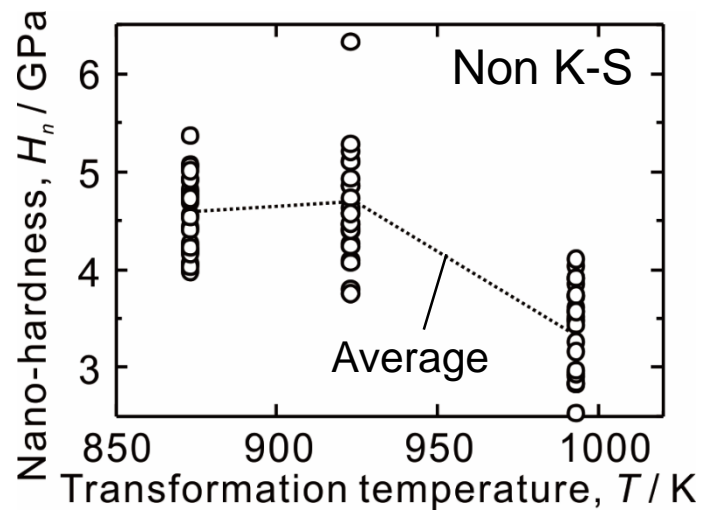
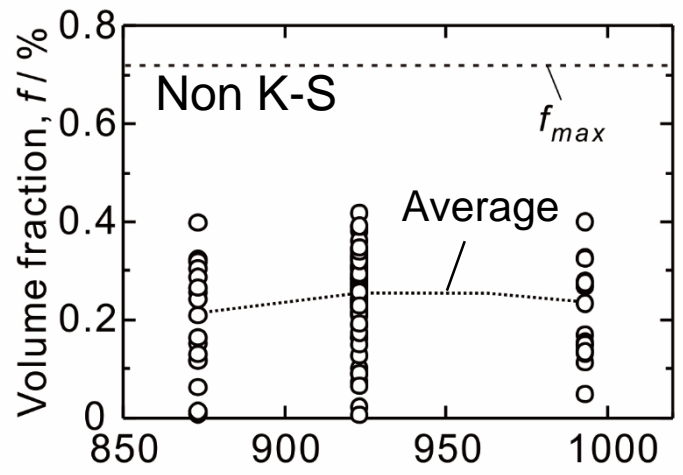
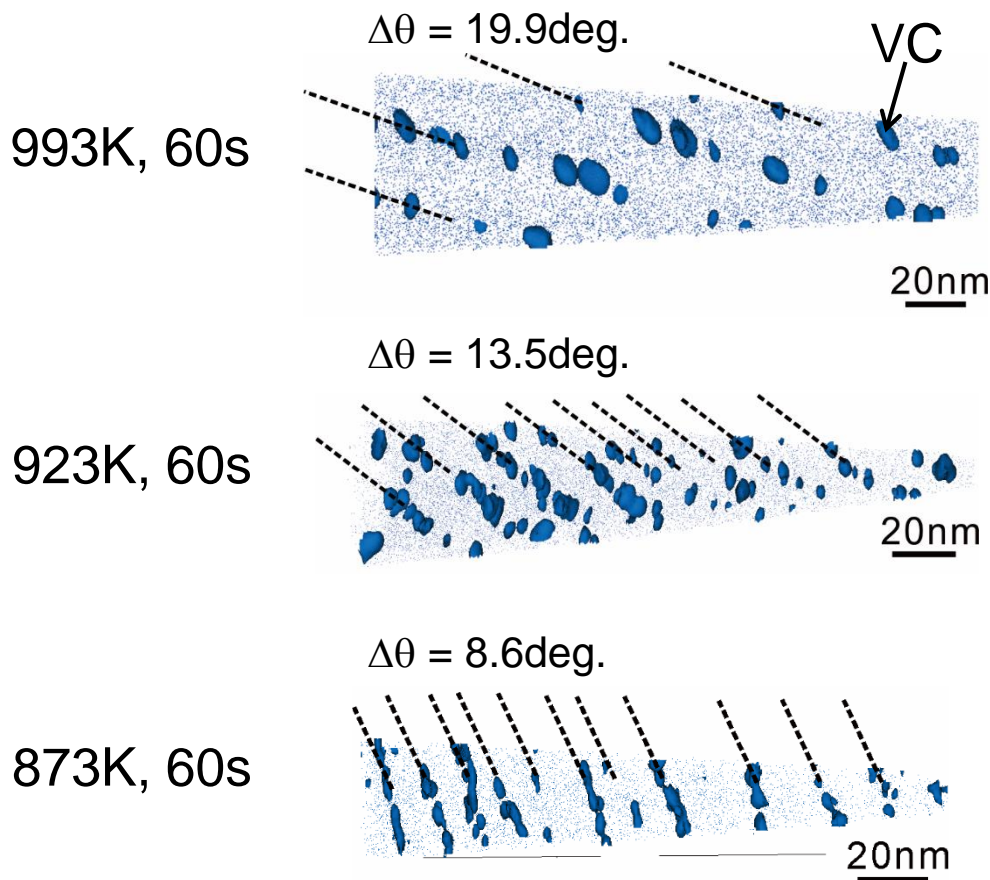


1D concentration profile



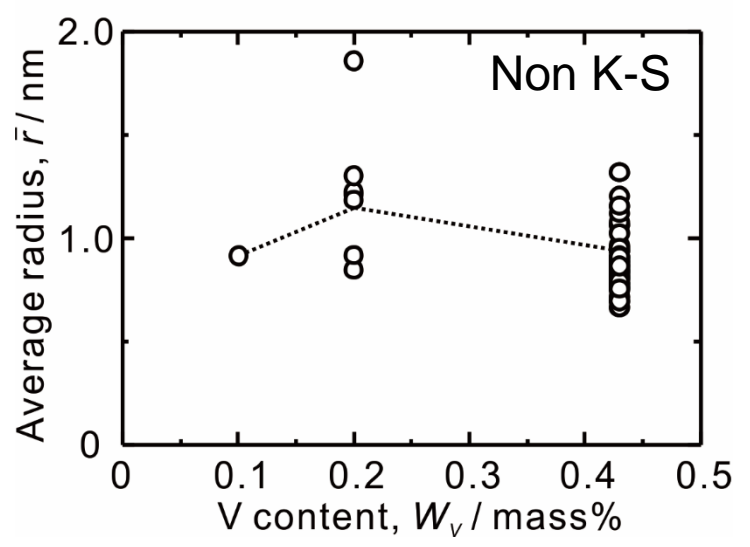
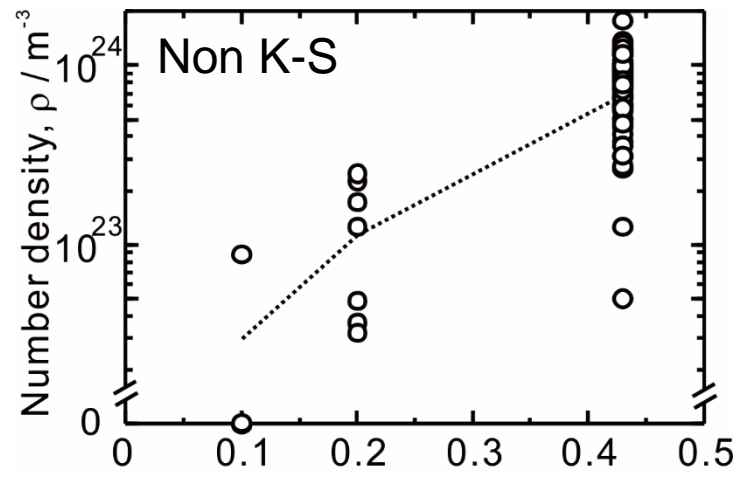
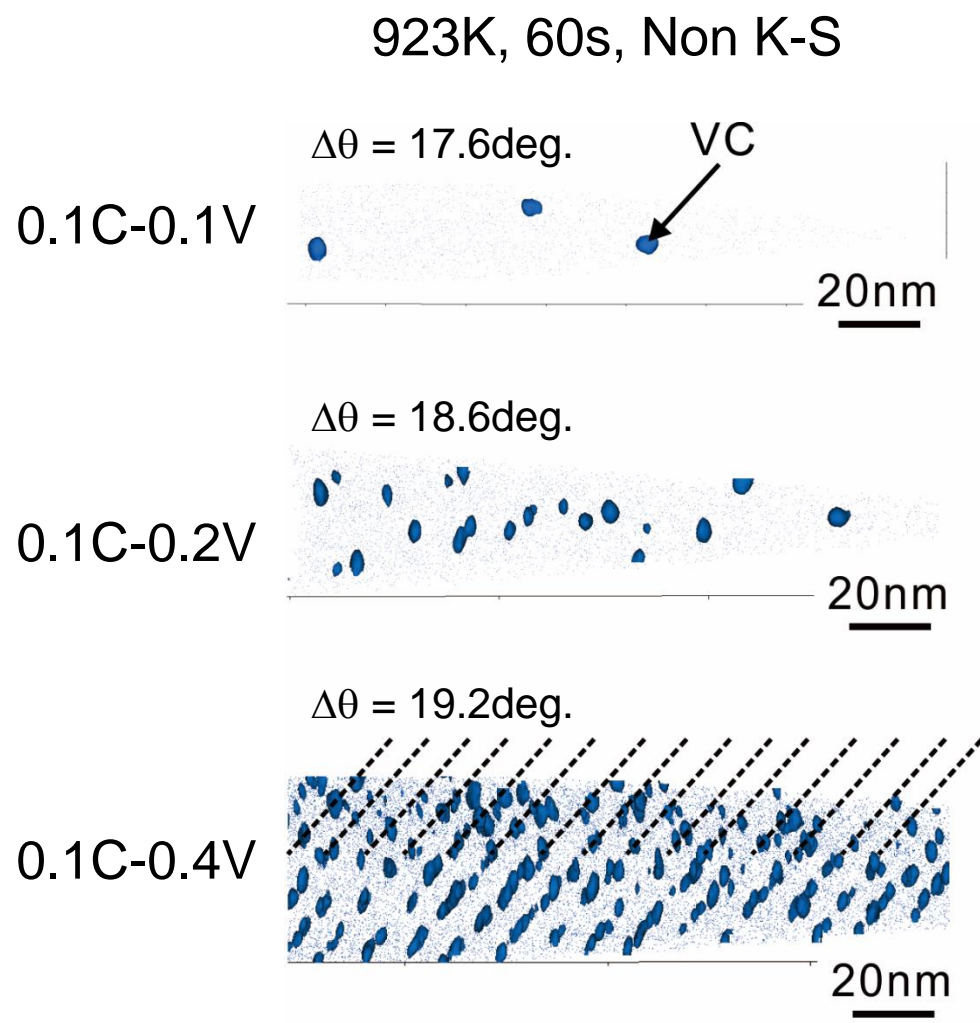
- In addition to C, V is also severely segregated at non K-S α/γ interface.

0.1C-0.4V, Non K-S



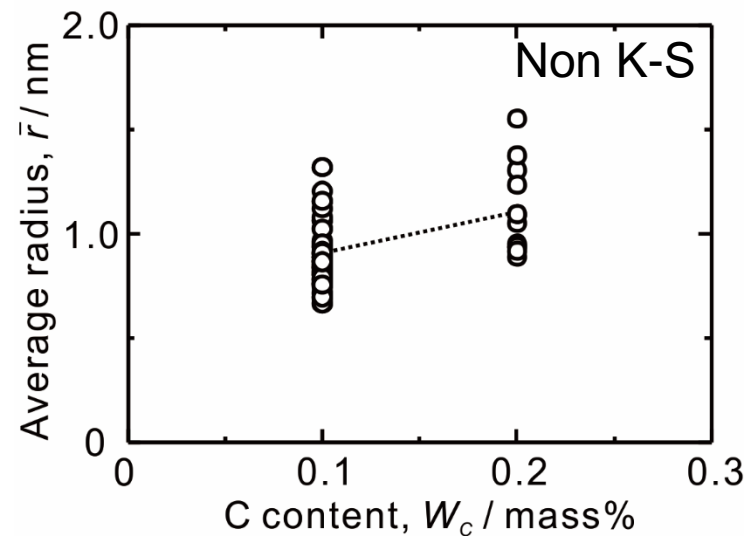
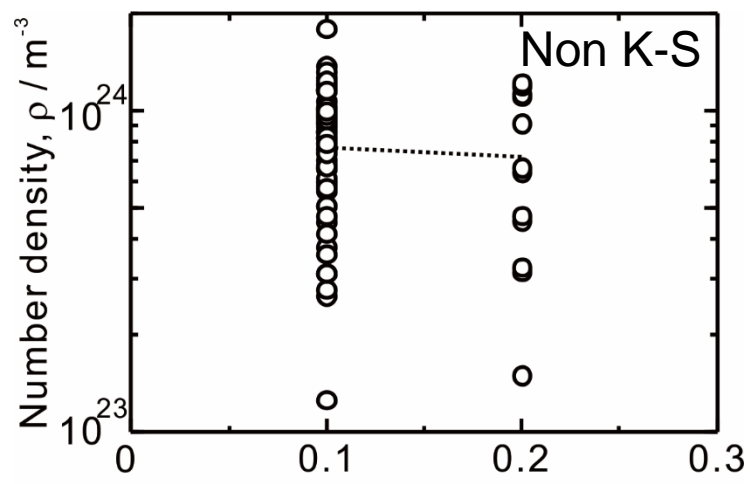
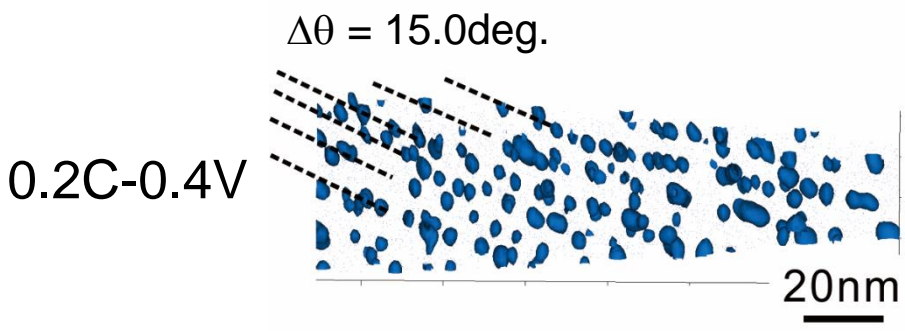
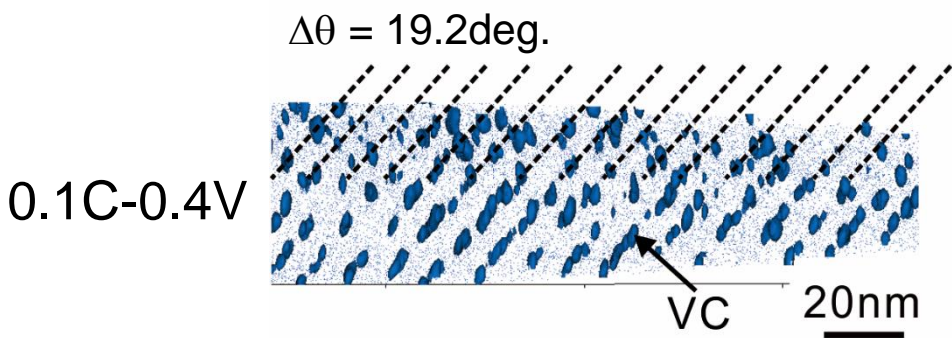
Y.-J. Zhang et al., *Acta Mater.* 84 (2015) 375.

- The dispersion of VC tends to be finer, i.e. higher in number density and smaller in size by lowering the transformation temperature.
- Finer dispersion increases nanohardness with similar volume fraction.



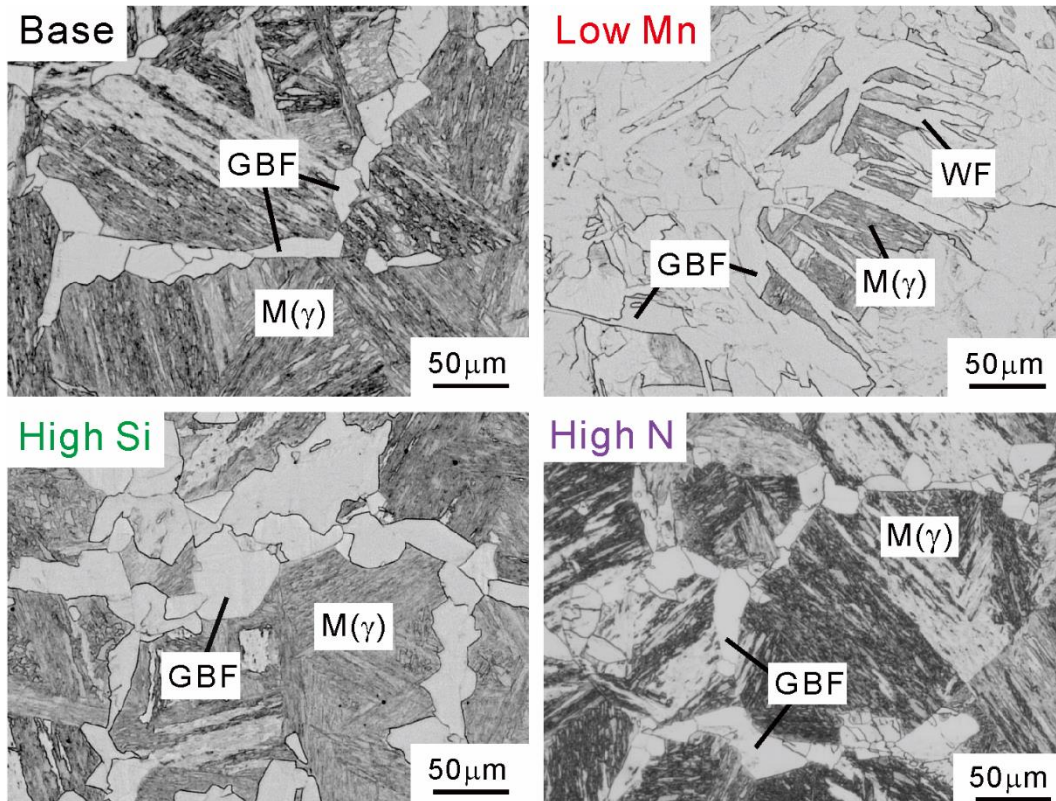
- Number density of VC increases with higher V content, while variations in size of VC is relatively small.

923K, 60s, Non K-S

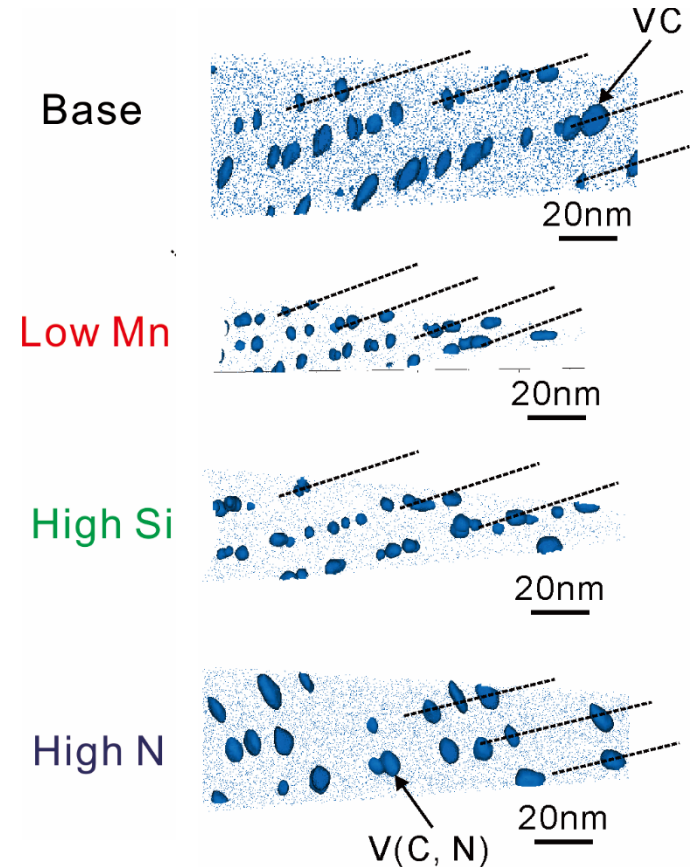


- Although growth rate of α becomes significantly lower by increasing C content, dispersion of VC is almost unchanged.

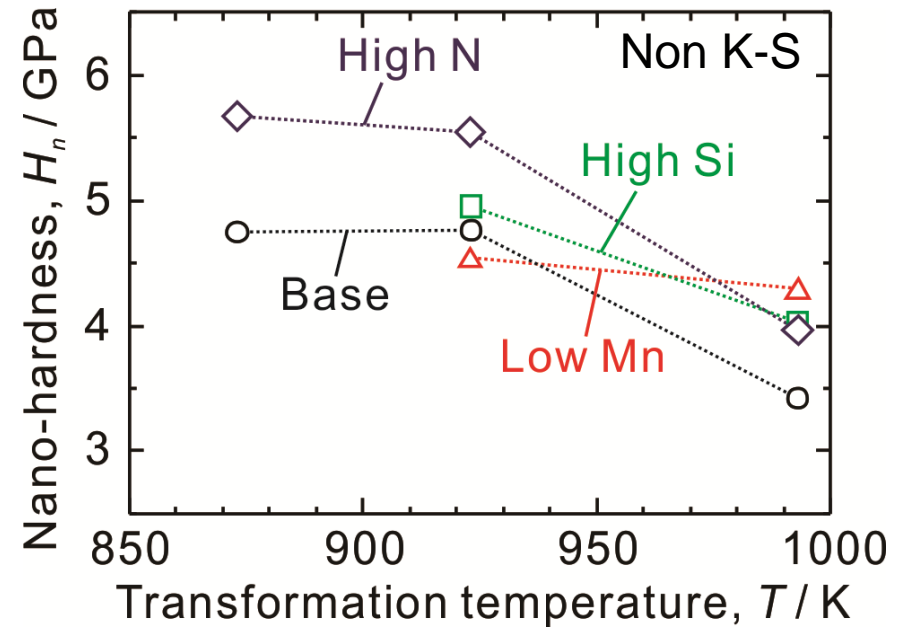
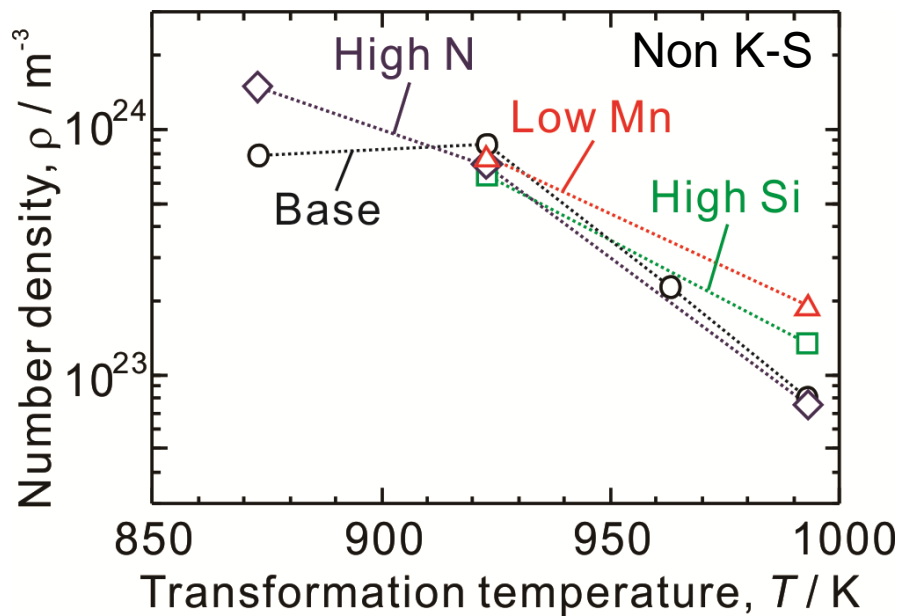
0.1C-0.4V-based, 993K, 60s



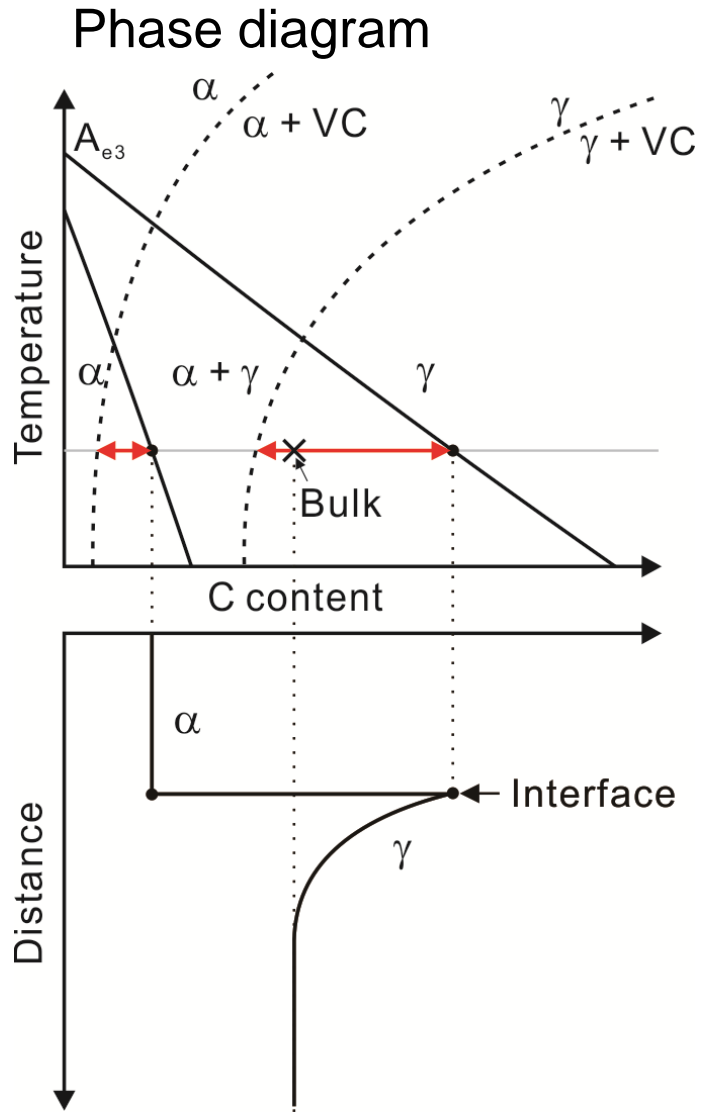
Non K-S



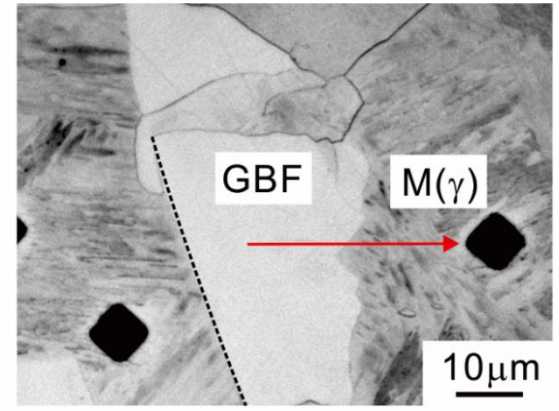
- WF formation is promoted by lower Mn content, but almost unchanged with higher Si or higher N content.
- Dispersion of interphase precipitation is not largely changed by lower Mn, higher Si and N contents, although α growth rate is quite different.



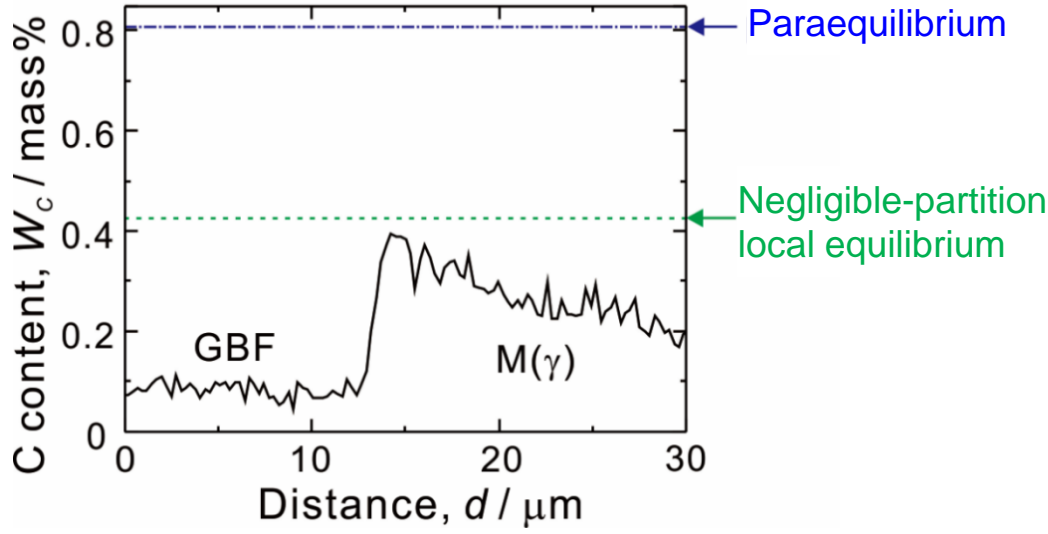
- Lower Mn, higher Si and higher N contents only slightly refine the dispersion of interphase precipitation.
- Finer dispersion of interphase precipitation gives higher nanohardness.



0.2C-0.4V, 963K, 0.3ks

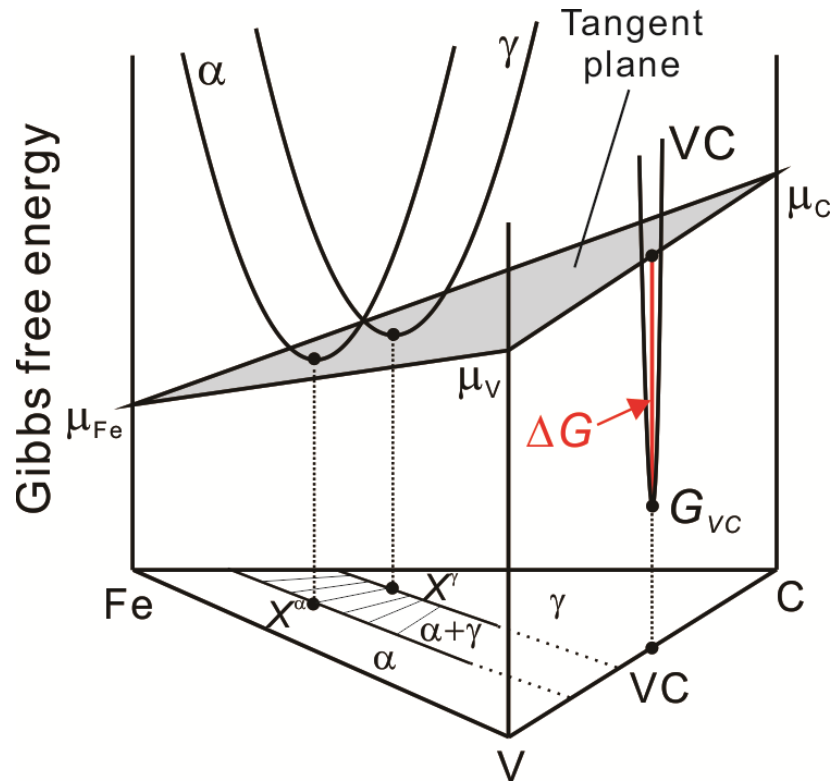


By electron probe microanalysis (EPMA)



Y.-J. Zhang et al., *Acta Mater.* 128 (2017) 166.

- Compared with PE model, NPLE model gives better prediction of α/γ phase equilibria in V-added low carbon steels.



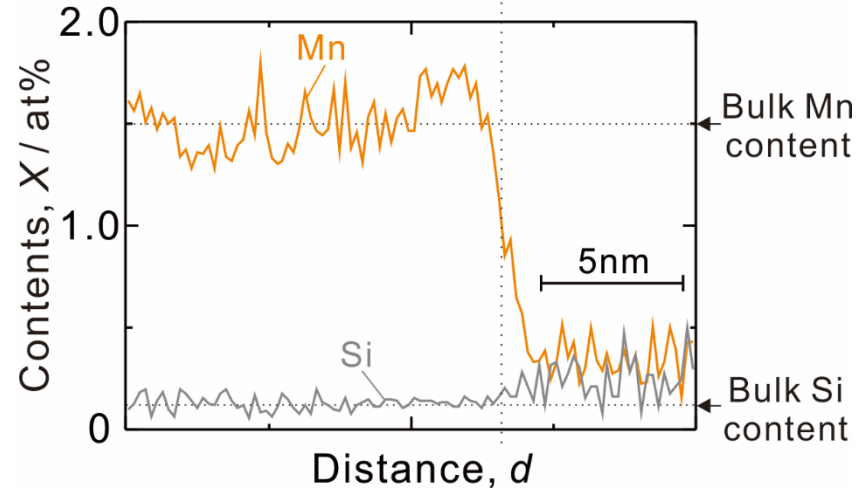
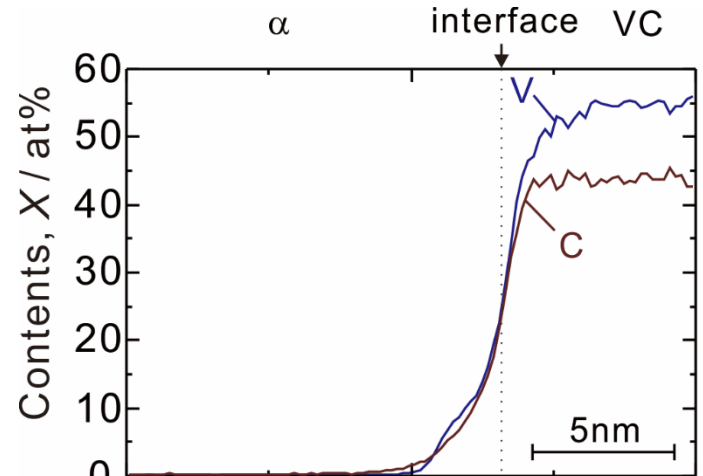
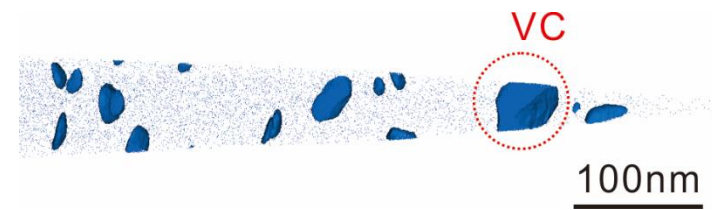
By assuming 50at% V and 50at% C:

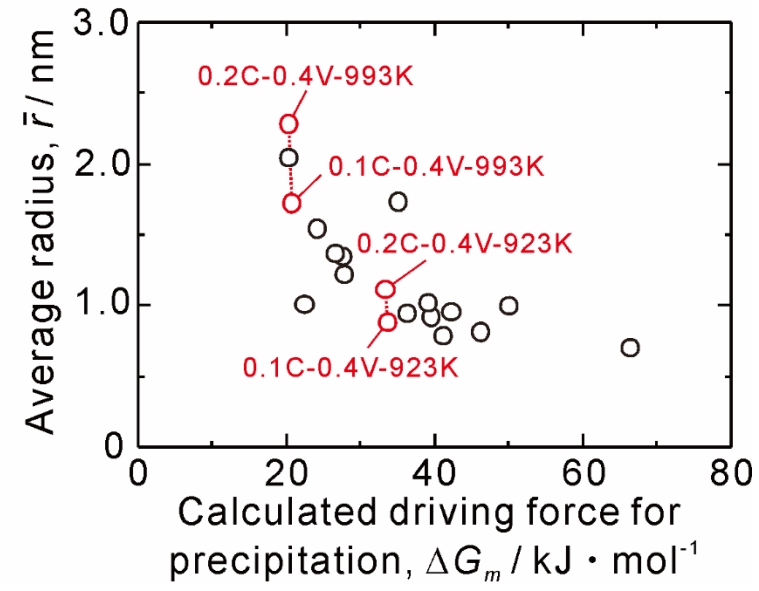
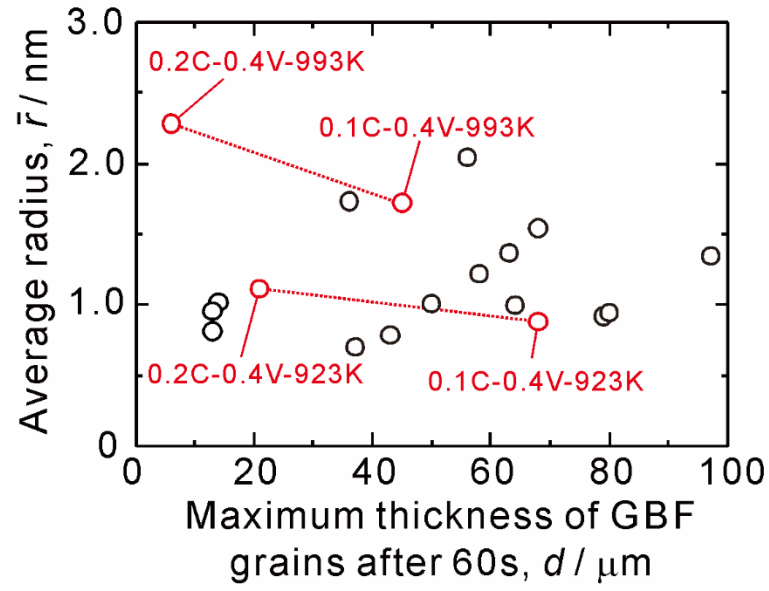
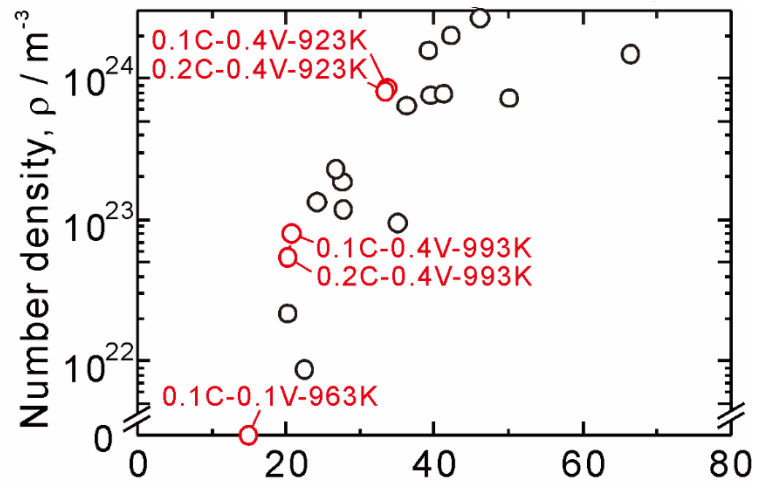
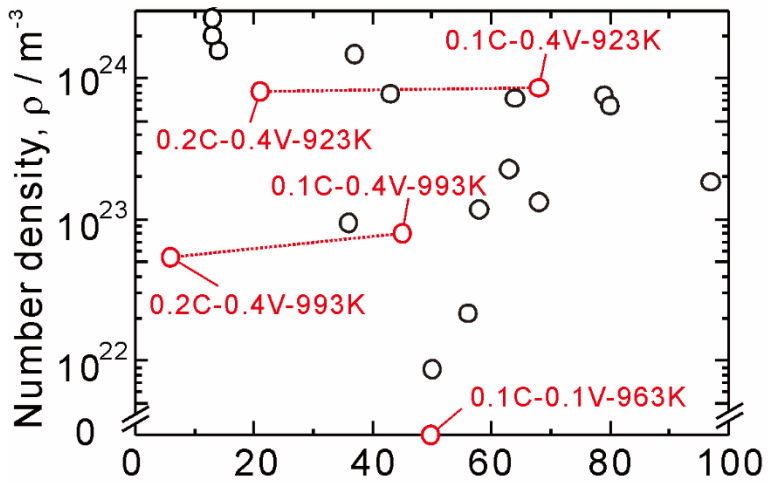
$$\Delta G = 0.5\mu_V + 0.5\mu_C - G_{VC}$$

- ΔG : driving force;
- μ_i : chemical potential of i ;
- G_{VC} : free energy

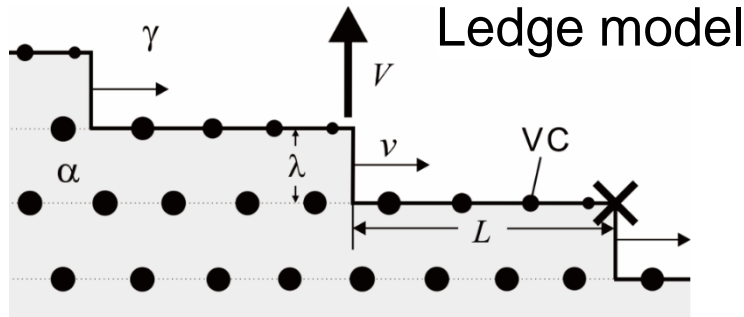
(Segregation is neglected for simplicity)

0.1C-0.4V, 923K, 172.8ks



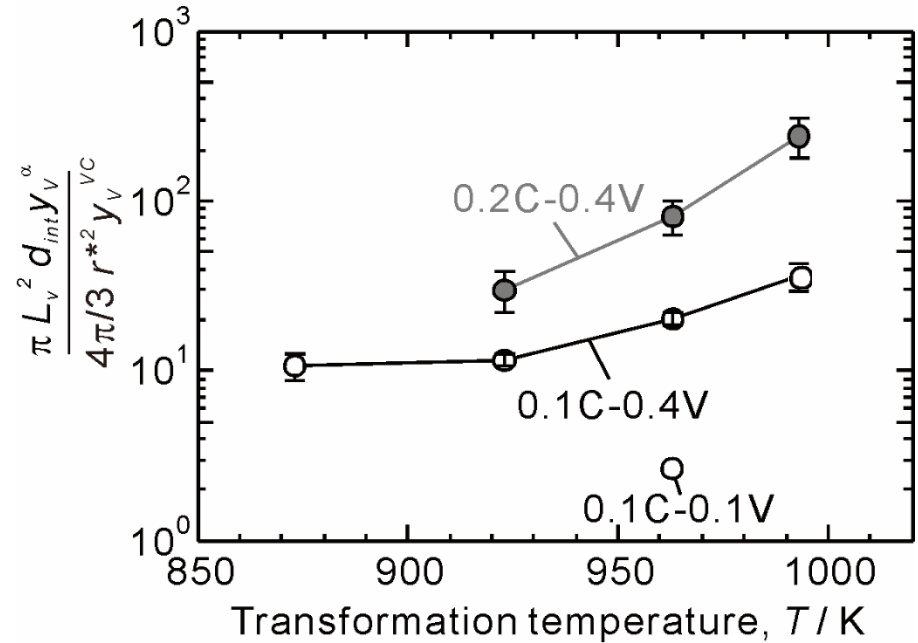
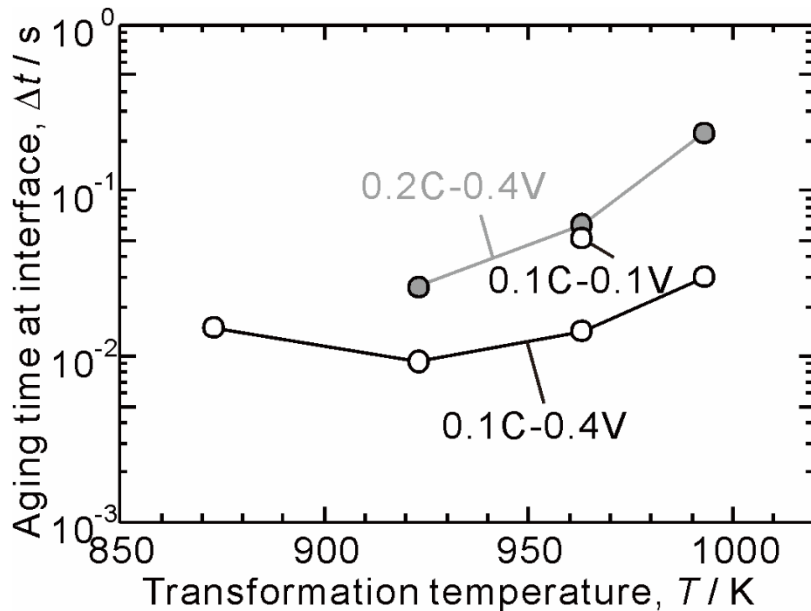
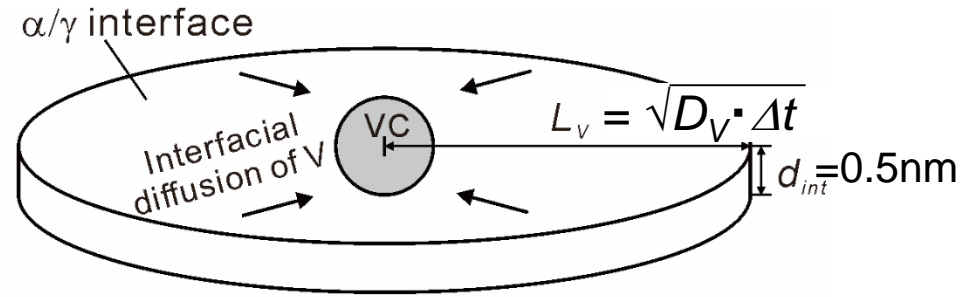


- Compared with α growth rate, dispersion of interphase precipitation shows better correlations with driving force for its precipitation.



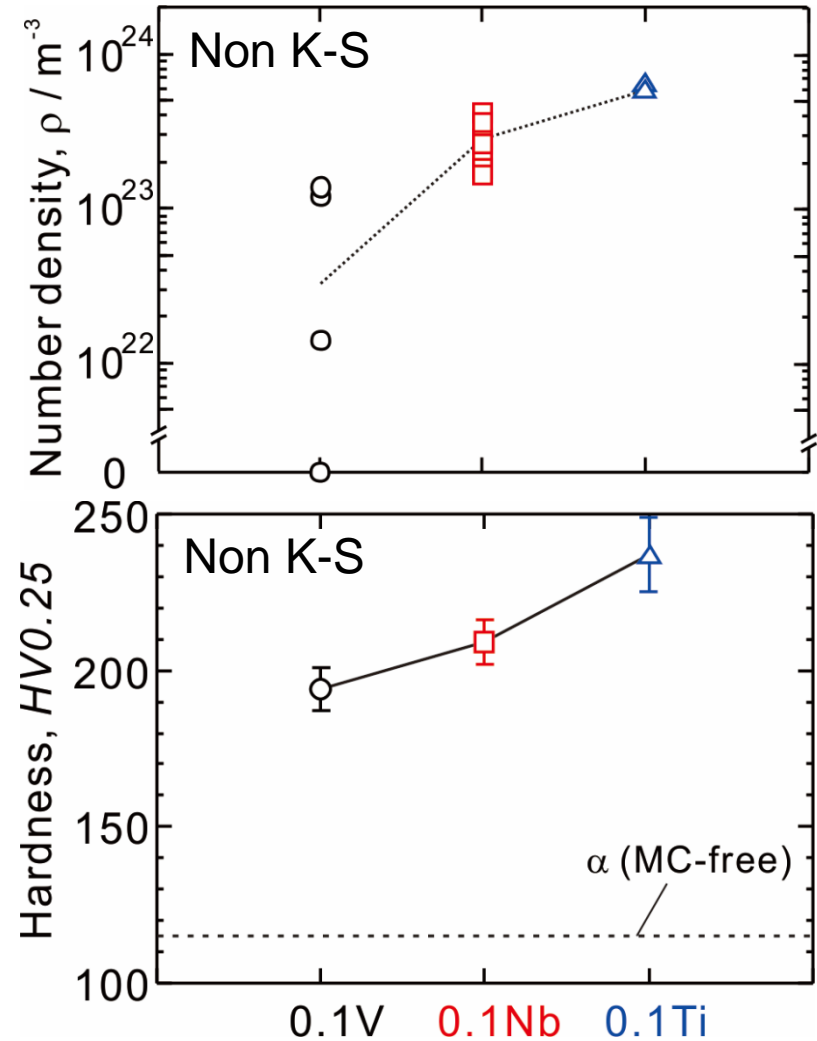
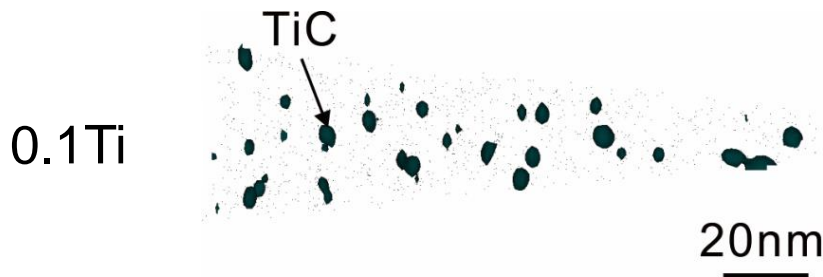
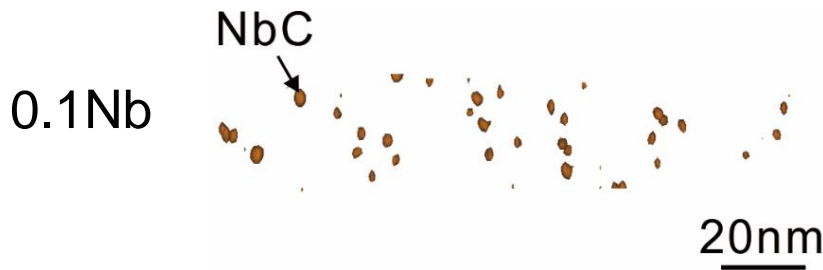
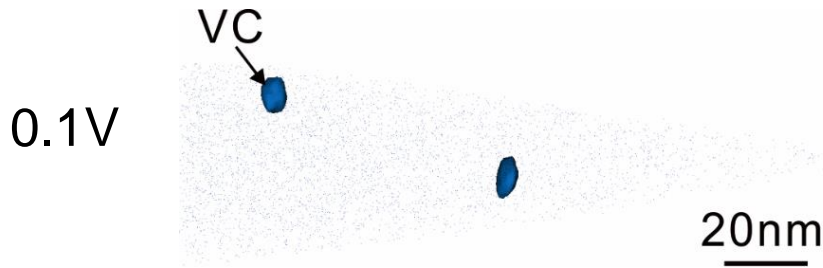
$$\Delta t = \frac{L}{v} \propto \frac{\lambda}{V}$$

V : α growth rate;
 v : ledge growth rate;
 λ : ledge height;
 L : ledge distance

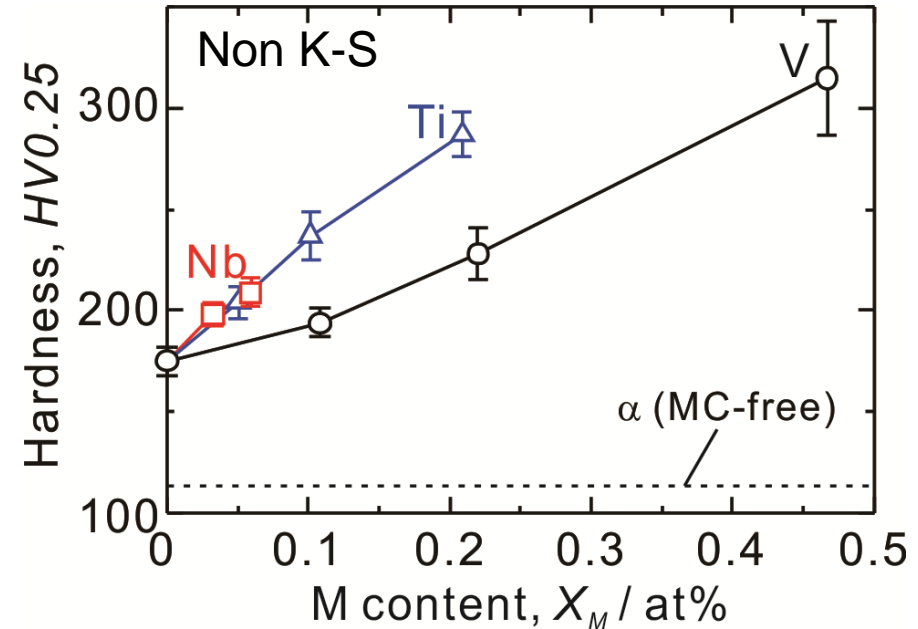
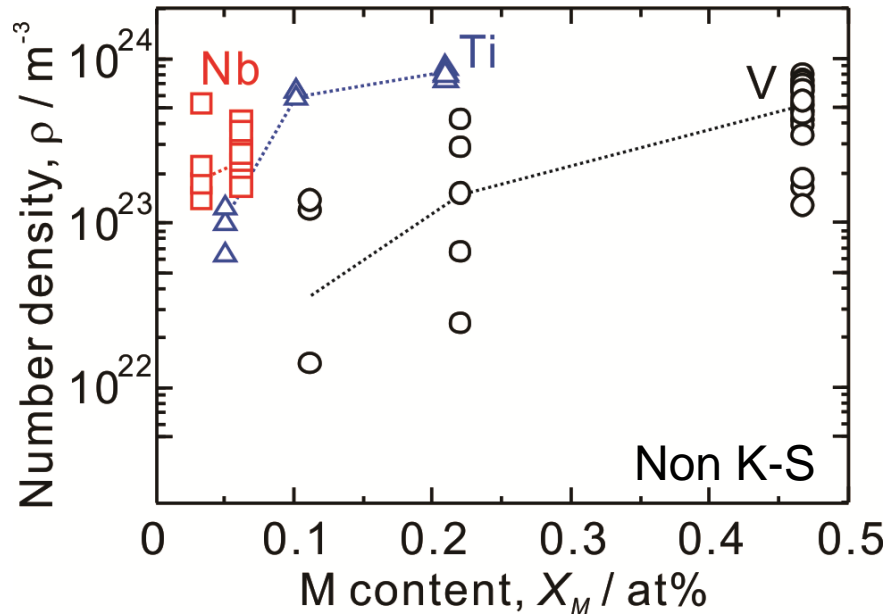


- Aging time at migrating α/γ interface is sufficient for nucleation of VC in most cases.

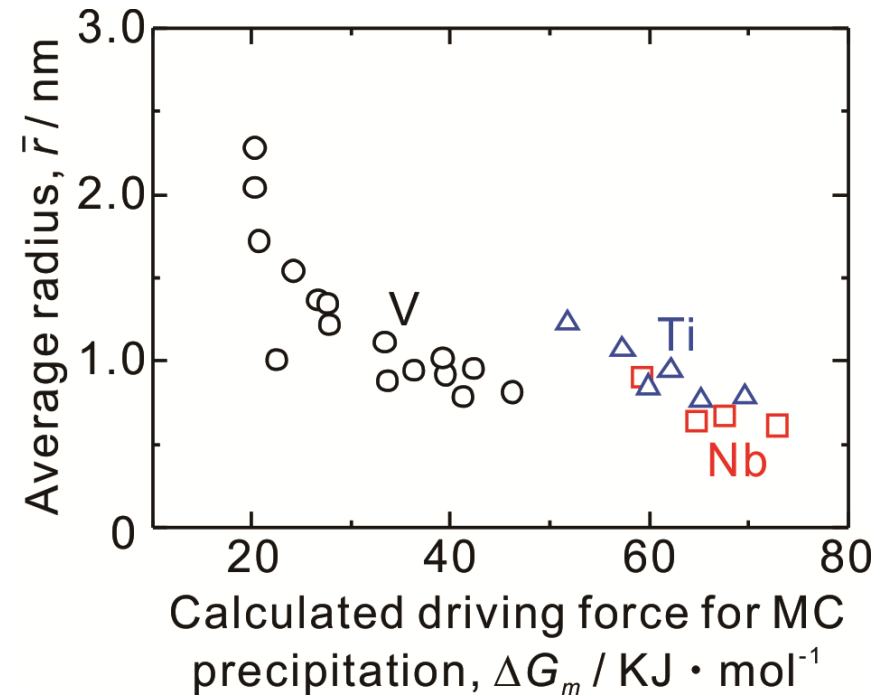
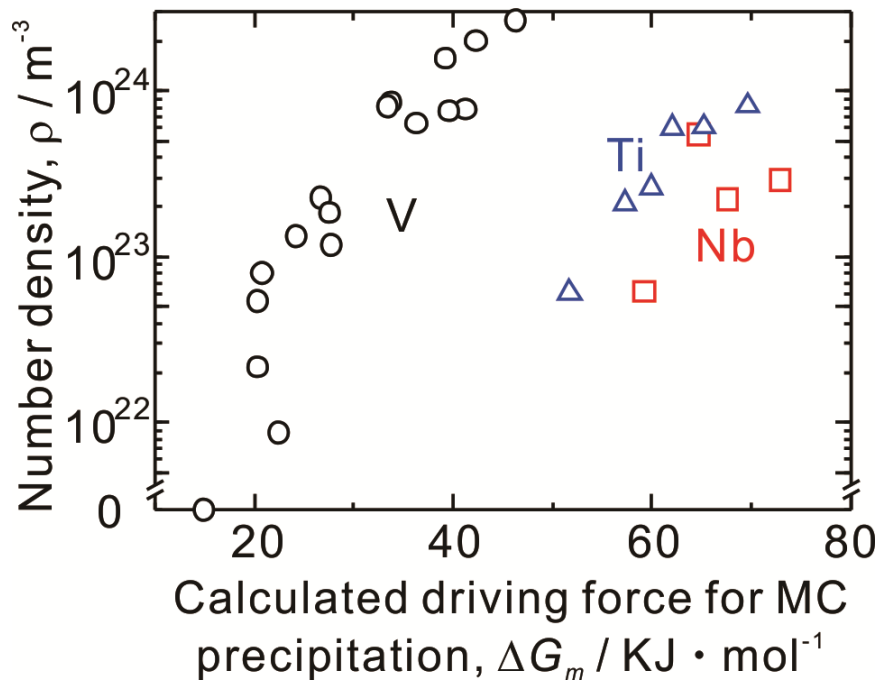
923K, 1.8ks, Non K-S



- With similar amount of addition, the dispersion of NbC and TiC is much finer than VC, resulting in higher hardness.



- Higher number density of NbC and TiC is also obtained by more addition, whose dispersion is much finer than VC.
- Although dispersion of NbC is slightly finer than TiC, their strengthening ability is similar but much stronger than VC.

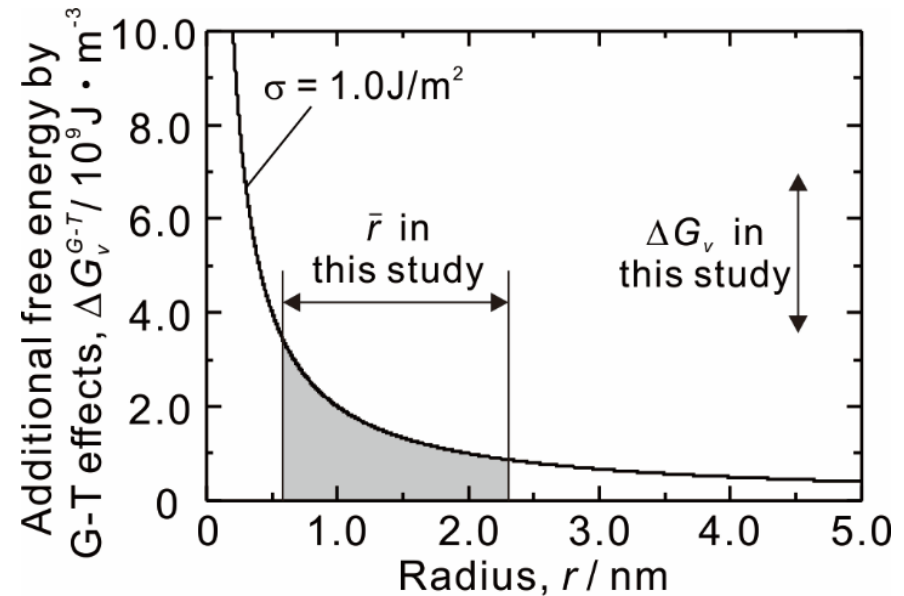
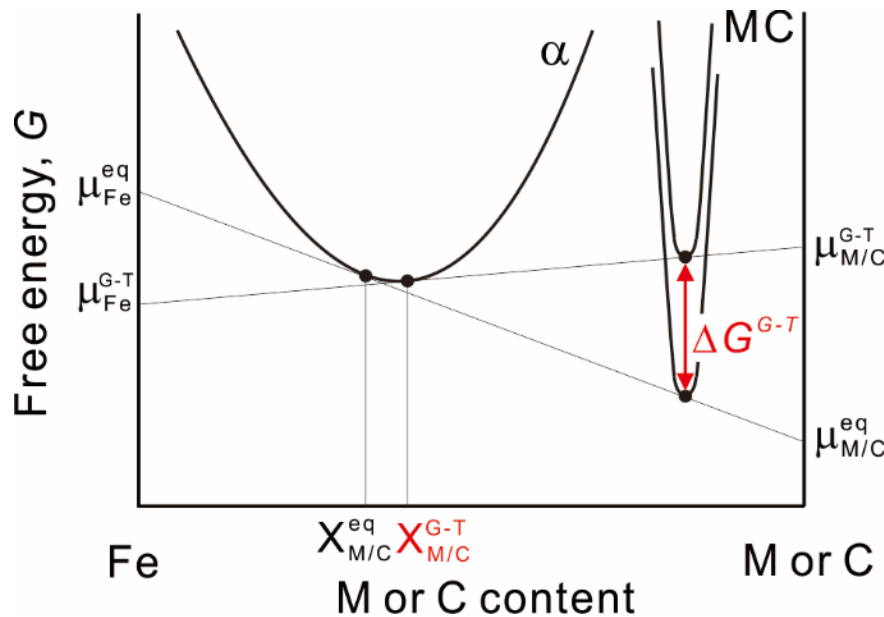


- Consistently with VC, dispersion of NbC and TiC becomes finer by enlarging the driving force for precipitation.
- Larger driving force for precipitation is necessary to obtain similar number density of NbC and TiC as VC.

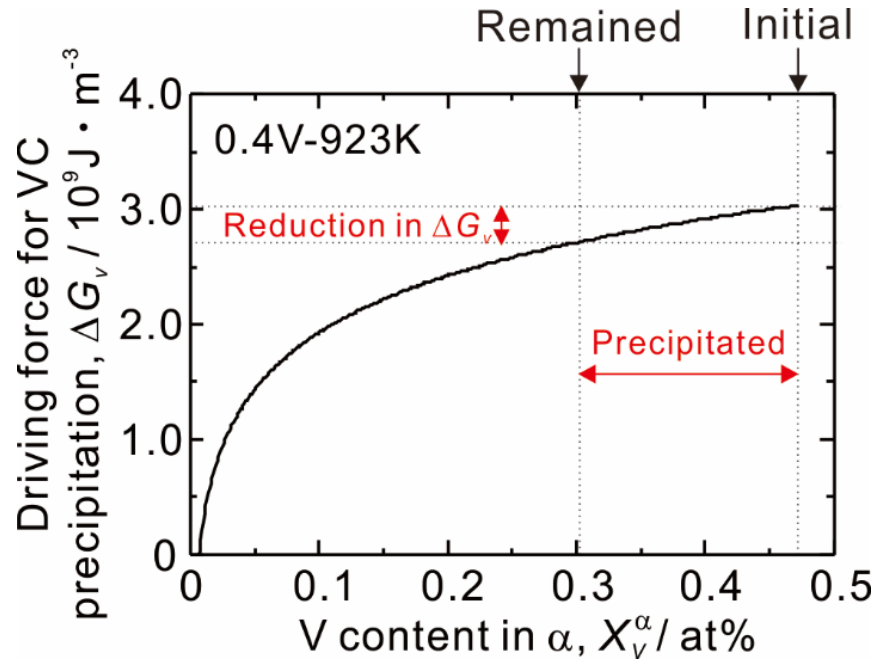
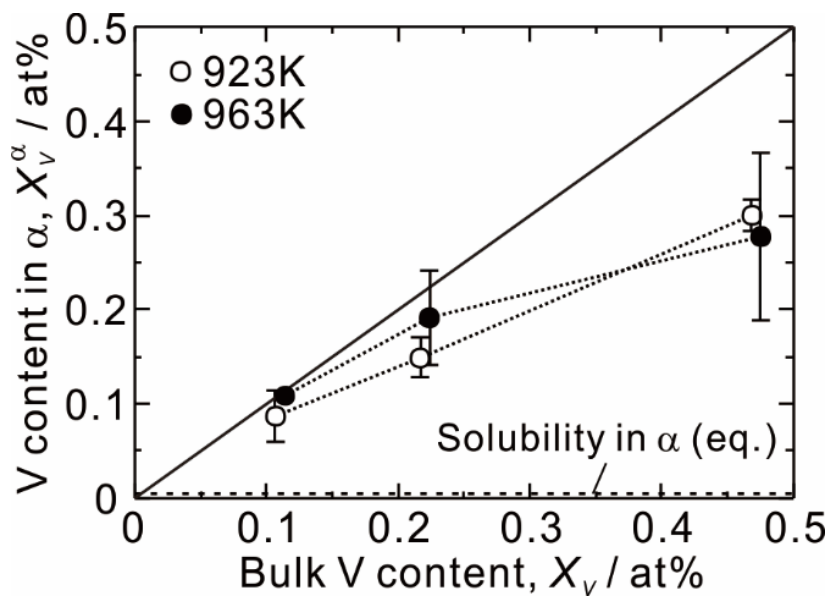
Additional free energy:

$$\Delta G_v^{G-T} = \frac{2\sigma}{r}$$

σ : α /MC interfacial energy;
 r : radius



- G-T effects cannot be neglected in the case of MC interphase precipitates with nano size.



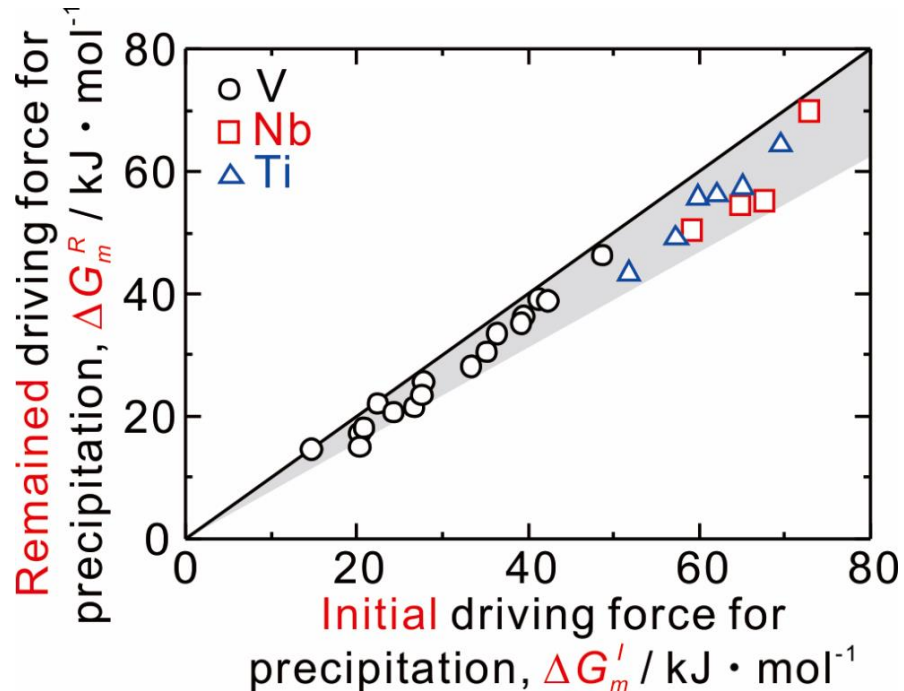
- Much higher content of V than its solubility still remains in α .
- More V and larger driving force remain with higher bulk content.

- Driving force is only slightly decreased after precipitation.

Ideal solution approximation: in α

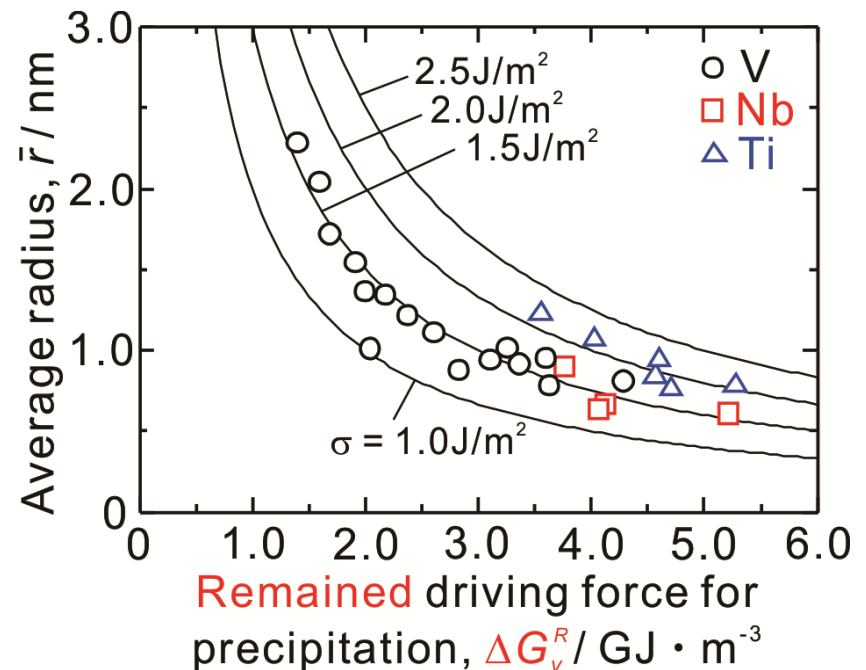
$$\Delta G = RT \ln \frac{X_C^\alpha \cdot X_V^\alpha}{X_C^S \cdot X_V^S} = RT \ln \frac{X_V^\alpha}{X_V^S}$$

solubility



- Remained driving force is nearly proportional to initial one under various conditions.

$$f \propto X_M^{ppt} = X_M^{bulk} - X_M^{\alpha} = X_M \left(1 - \exp \left(\frac{\Delta G^R - \Delta G^I}{RT} \right) \right)$$



- Observed radius is inversely proportional to remained driving force under G-T effects with various interfacial energies.

$$r = \frac{2\sigma}{\Delta G^R} \propto \frac{2\sigma}{\Delta G^I}$$

$\sigma_{\alpha/VC} = 1.5 \text{ J/m}^2;$
 $\sigma_{\alpha/NbC} = 1.5 \text{ J/m}^2;$
 $\sigma_{\alpha/TiC} = 2.1 \text{ J/m}^2.$

G-T effects

Reduction in driving force

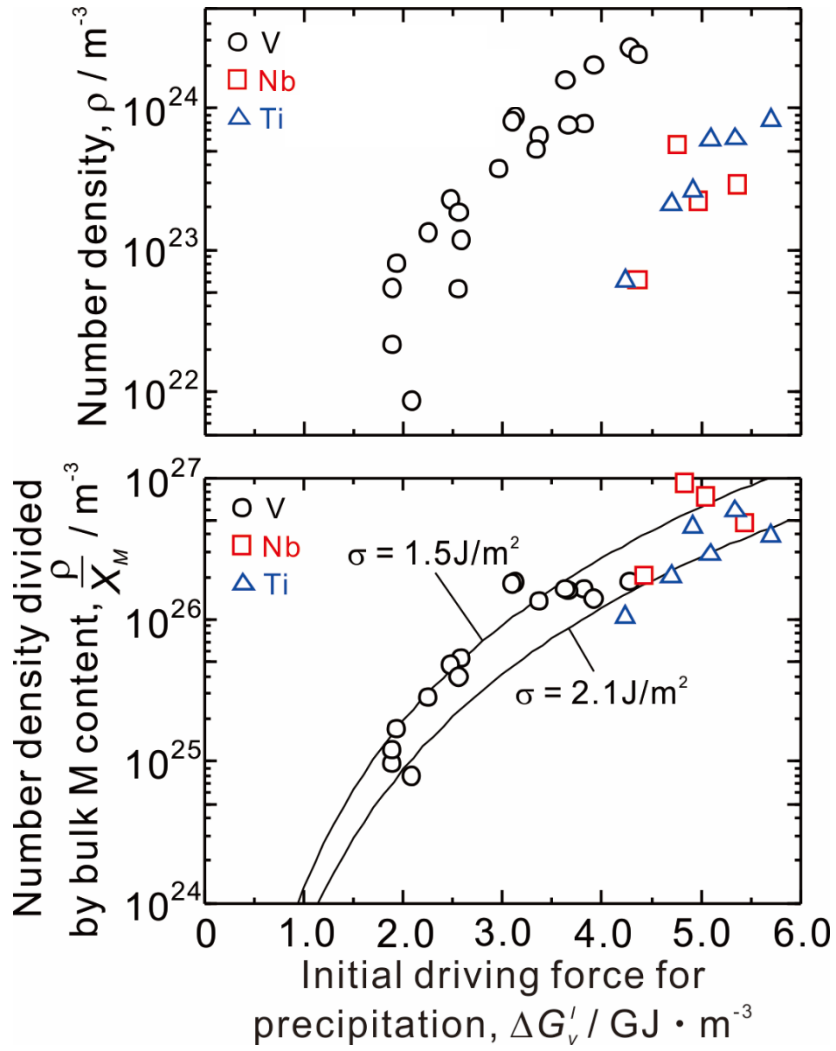
$$\rho \cdot \frac{4}{3} \pi r^3 = f$$



Number density is estimated as:

$$\rho \approx k X_M \frac{\Delta G_V^I{}^4}{\sigma^3}$$

- k : constant;
- X_M : bulk M content;
- ΔG_V^I : initial driving force for MC precipitation;
- σ : α /MC interfacial energy;

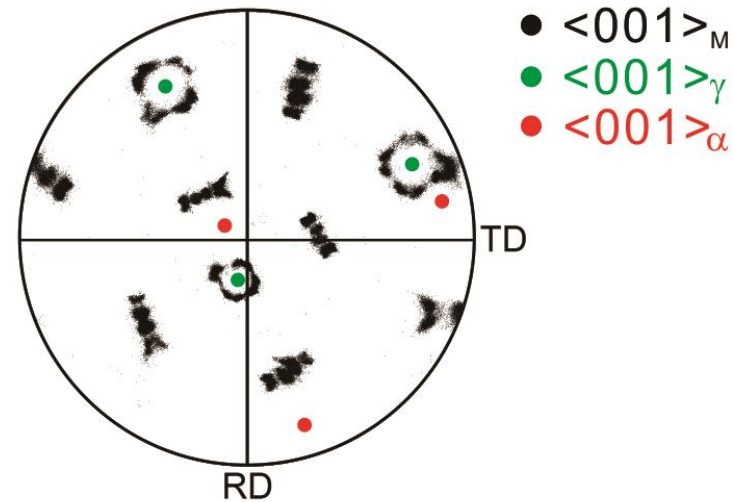
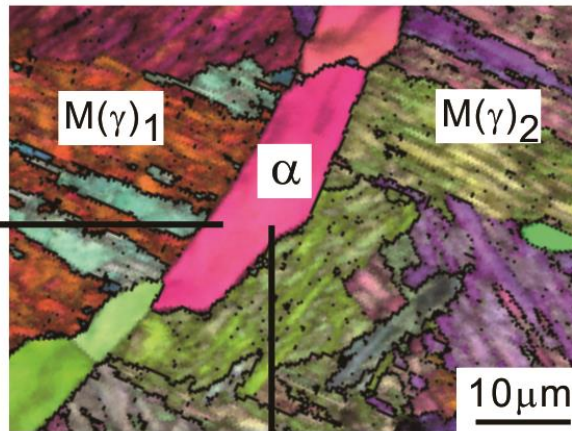


- Number density divided by bulk M content against driving force shows much smaller deviation, whereas the deviation between V, Nb and Ti can be explained by the difference in α /MC interfacial energy.

The effects of various factors on dispersion of interphase precipitation as well as its resultant precipitation strengthening in low carbon steels were systematically investigated in this study. Based on all the experimental results, this study is summarized as:

1. Interphase precipitation behaviors strongly depend on α/γ orientation relationship that large deviation from the exact K-S one promotes the formation of VC interphase precipitation.
2. α growth rate only has minor influence on the dispersion of interphase precipitation.
3. Transformation temperature and alloying elements affect the dispersion of interphase precipitation mainly by changing the driving force for its precipitation.
4. Finer dispersion of interphase precipitation results in higher hardness of α grains due to larger precipitation strengthening.

① EBSD → α -orientation map + 001_{bcc} pole figure → α/γ OR analyses:



Deviation angle from the exact K-S OR: $\Delta\theta$

Near K-S: $\Delta\theta \leq 5\text{deg.}$

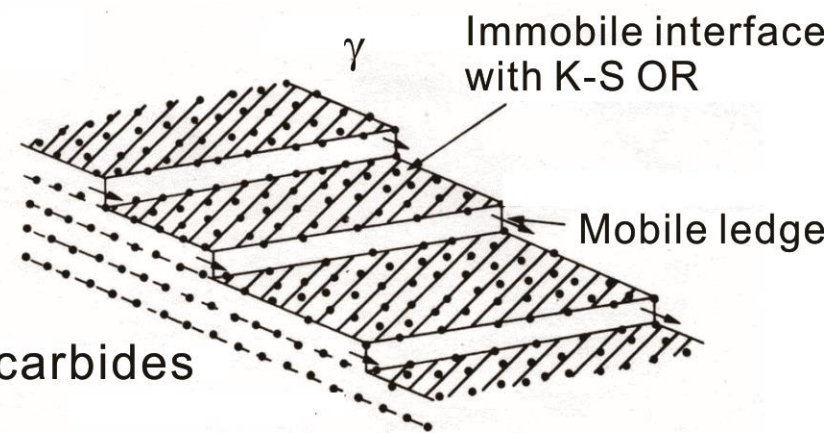
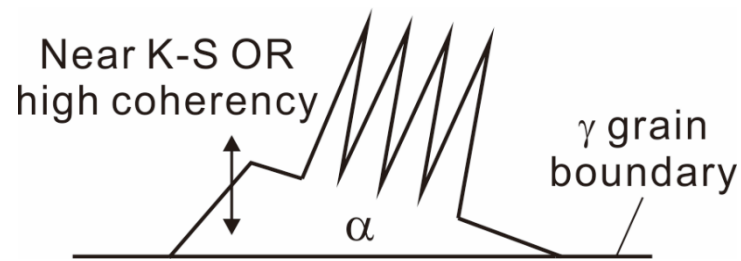
Non K-S: $\Delta\theta > 5\text{deg.}$

Micro-sampling by
focused ion beam

② 3DAP analyses → dispersion of VC precipitates

③ Nano-indentation → nano-hardness of the same α grain

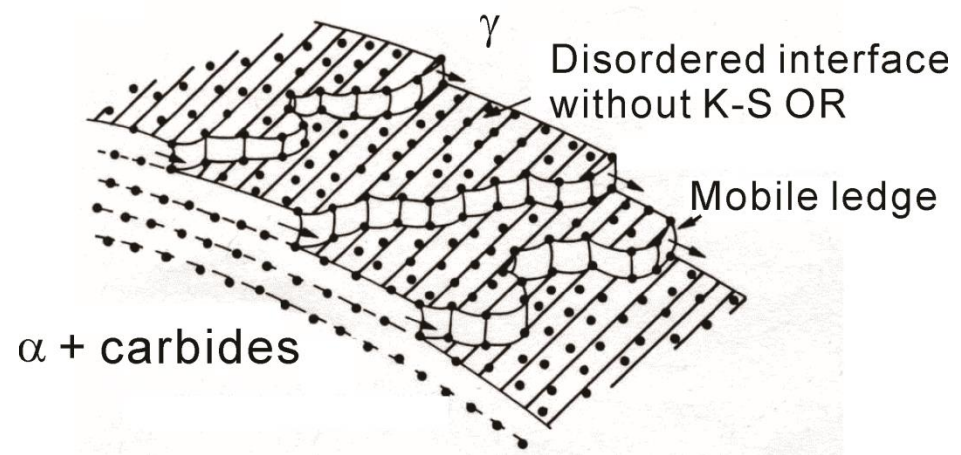
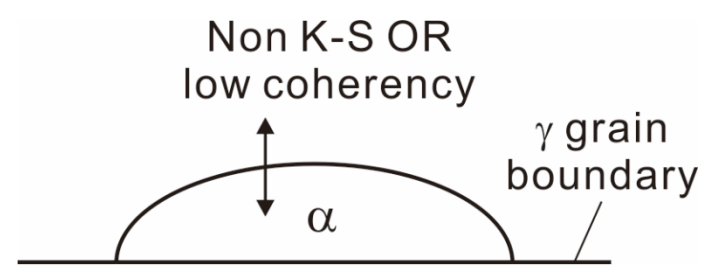
Ledge Mechanism



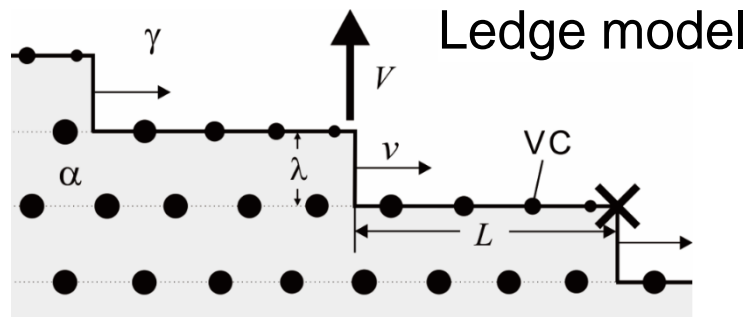
R.W.K. Honeycombe, *Metall. Mater. Trans. A* 7 (1976) 915.

Kurdjumov-Sachs (K-S)
orientation relationship (OR):
 $(111)_{\gamma} // (011)_{\alpha}, [\bar{1}01]_{\gamma} // [\bar{1}\bar{1}\bar{1}]_{\alpha}$

Quasi-ledge Mechanism

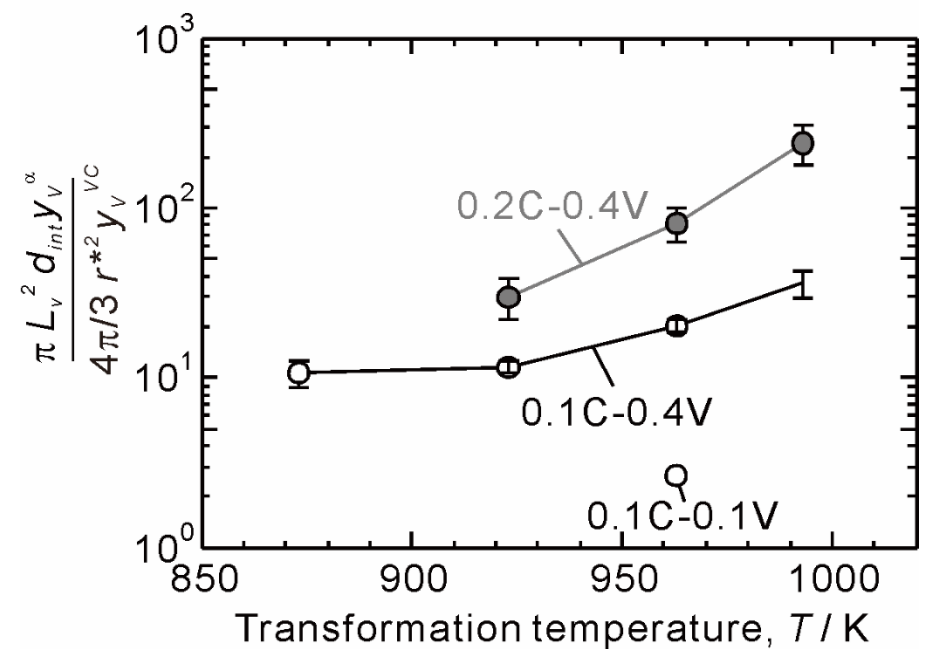
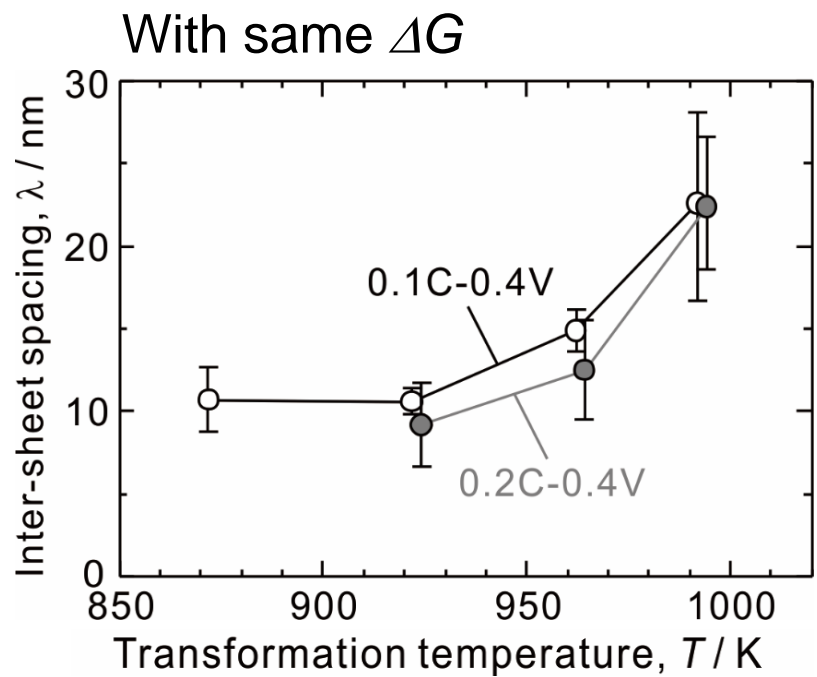
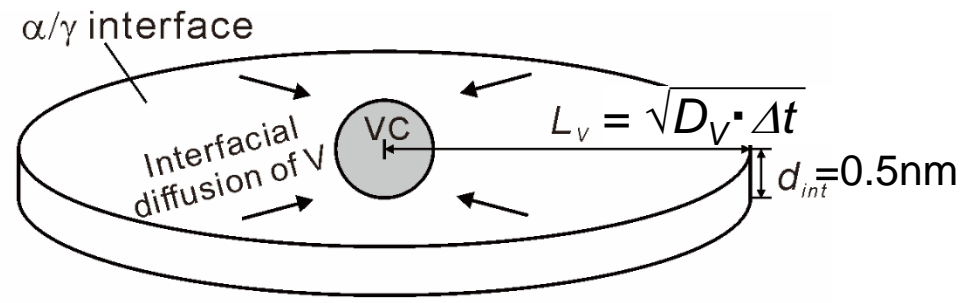


R.A. Ricks et al., *Acta Metall.* 31 (1983) 853.

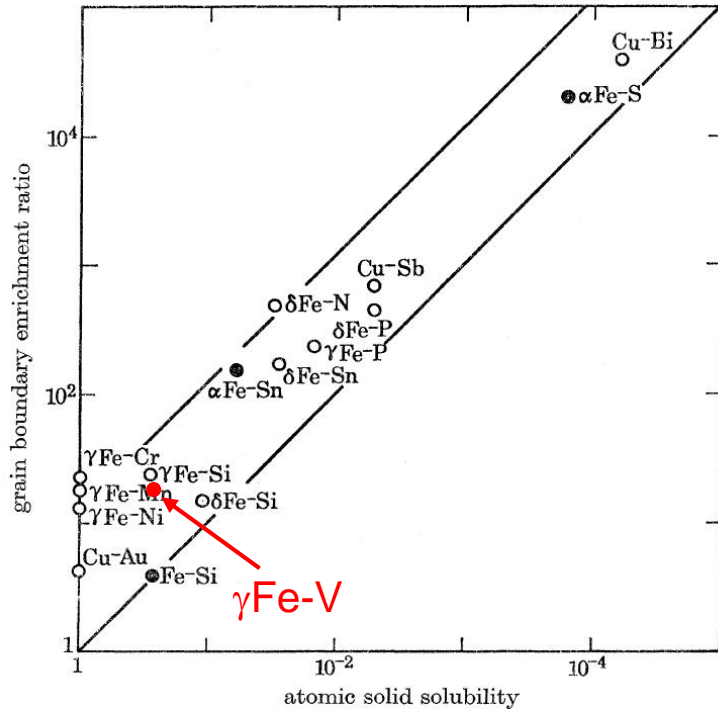


$$\Delta t = \frac{L}{v} \propto \frac{\lambda}{V}$$

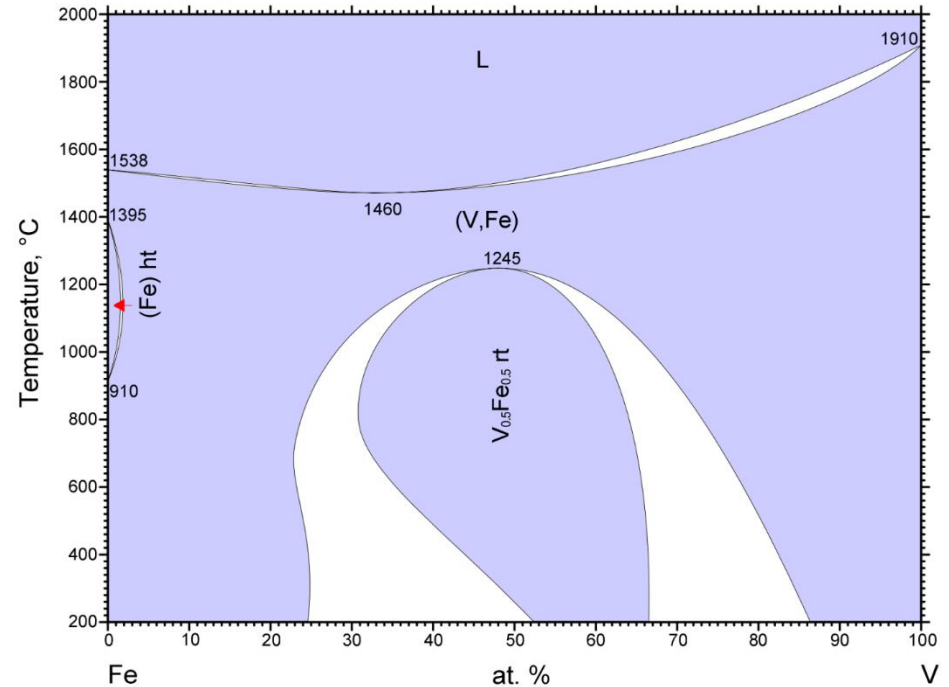
V : α growth rate;
 v : ledge growth rate;
 λ : ledge height;
 L : ledge distance



- Aging time at migrating α/γ interface is sufficient for nucleation of VC interphase precipitation.



Fe-V binary



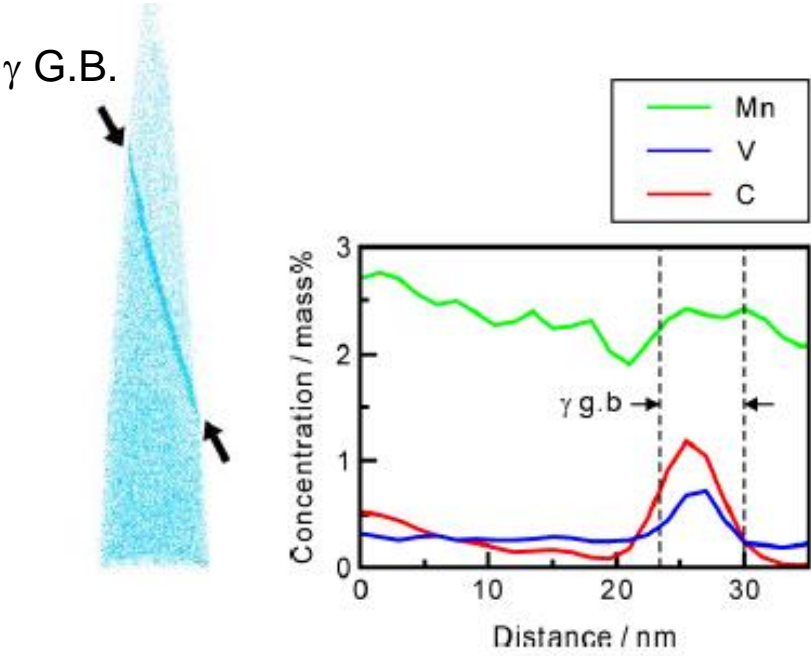
© ASM International 2006. Diagram No. 907267

M. P. Seah et al., *Proc. Royal Society of London* 335. (1973) 191.

- Alloying elements with lower solubility tend to be severely segregated at grain boundary.

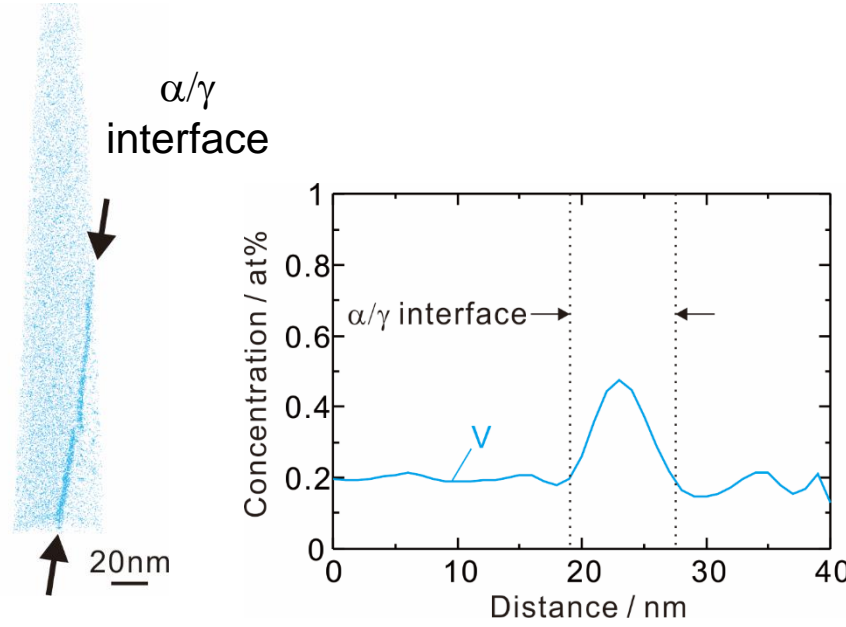
Fe-0.2C-2.0Mn-0.3V:
Aging @1173K, 3.6ks

V map:



Fe-0.1C-1.5Mn-0.1V:
 α transformation @923K, 60s

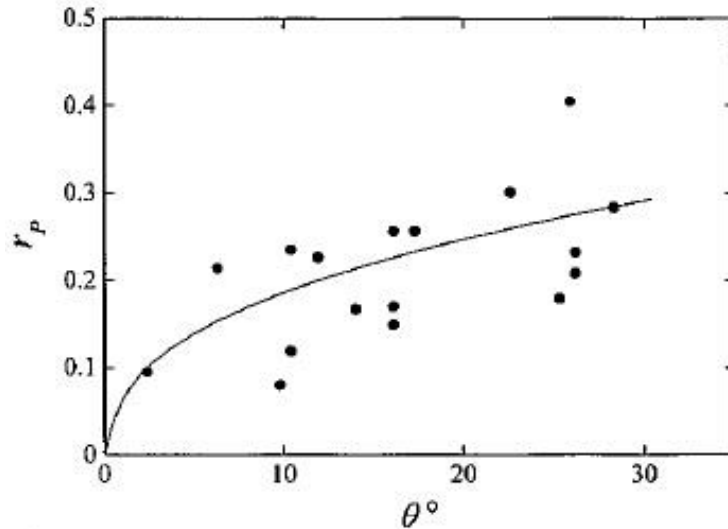
V map:



- V segregation occurs both at γ grain boundary and at α/γ interface.

By Auger:

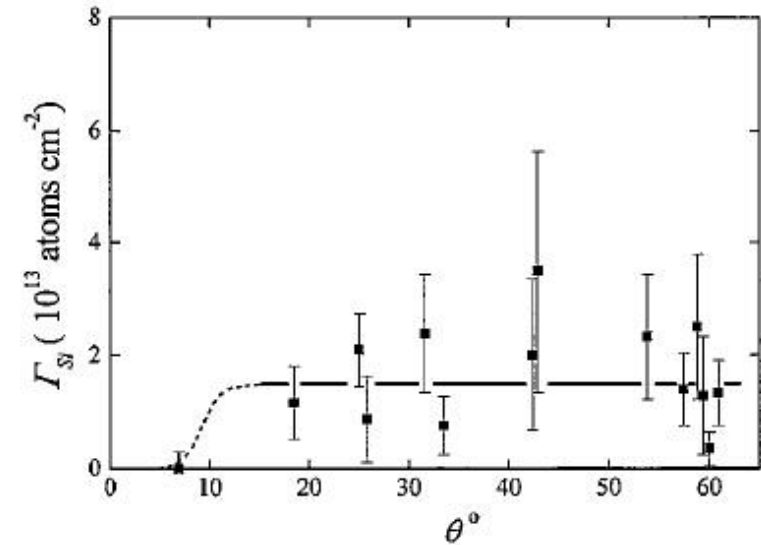
P in bcc Fe



K. Tatsumi, et al., *Trans. JIM* 27 (1986) 427.

By FIM:

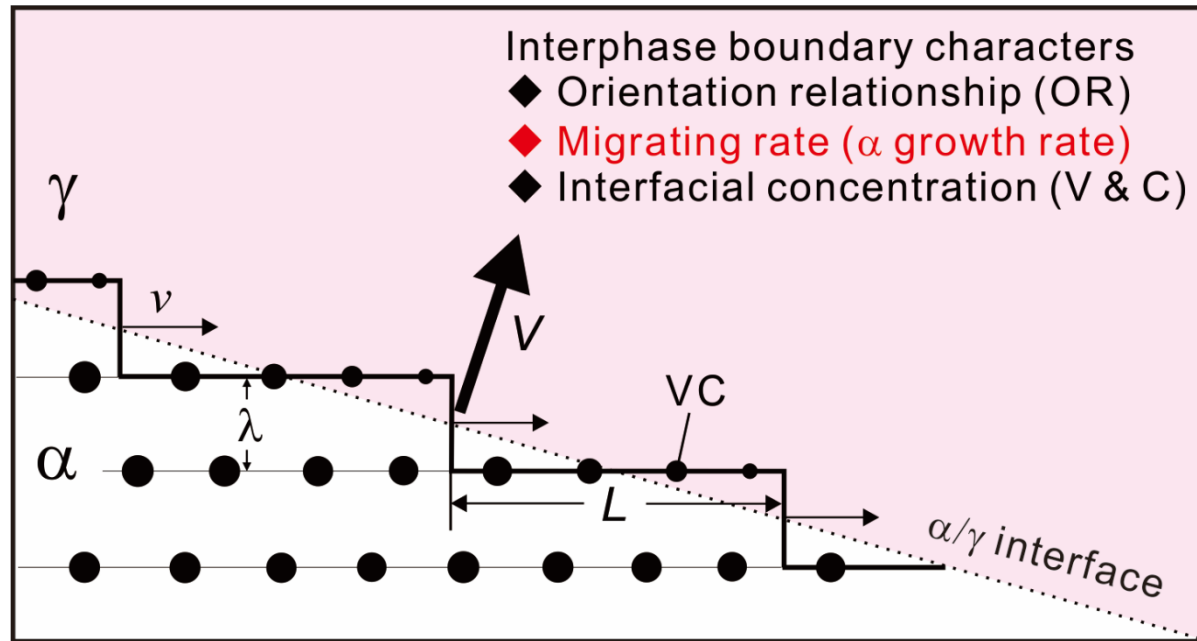
Si in bcc Fe



θ : misorientation angle

B.W. Krakauer et al. *Metal. Sci. Forum* 126-128 (1993) 161.

- Larger misorientation results in severer segregation possibly due to lower coherency with larger free volume.



Aging time at α/γ interface:

$$\Delta t = \frac{L}{v} \propto \frac{\lambda}{V}$$

V : macroscopic α growth rate
 v : microscopic ledge growth rate;
 λ : ledge height;
 L : ledge distance

- Aging time at migrating α/γ interface is reversely proportional to macroscopic α growth rate.
- Similar dispersion of VC in alloys with different C contents indicates that aging time does not have large influence on interphase precipitation.

Ashby-Orowan model:

$$\Delta\tau = 0.84 \left(\frac{1.2Gb}{2\pi L} \right) \cdot \ln \frac{x}{2b}$$

$$x = 2\bar{r} \sqrt{\frac{2}{3}}$$

G : shear modulus of α ;

b : Burgers vector of α ;

L : inter-particle spacing of MC on slip plane;

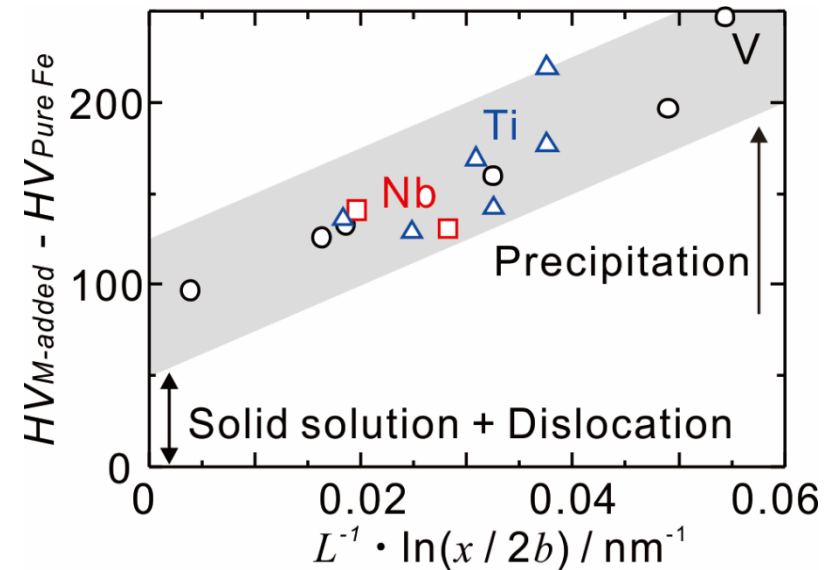
x : average diameter of MC on slip plane;

\bar{r} : average radius of MC

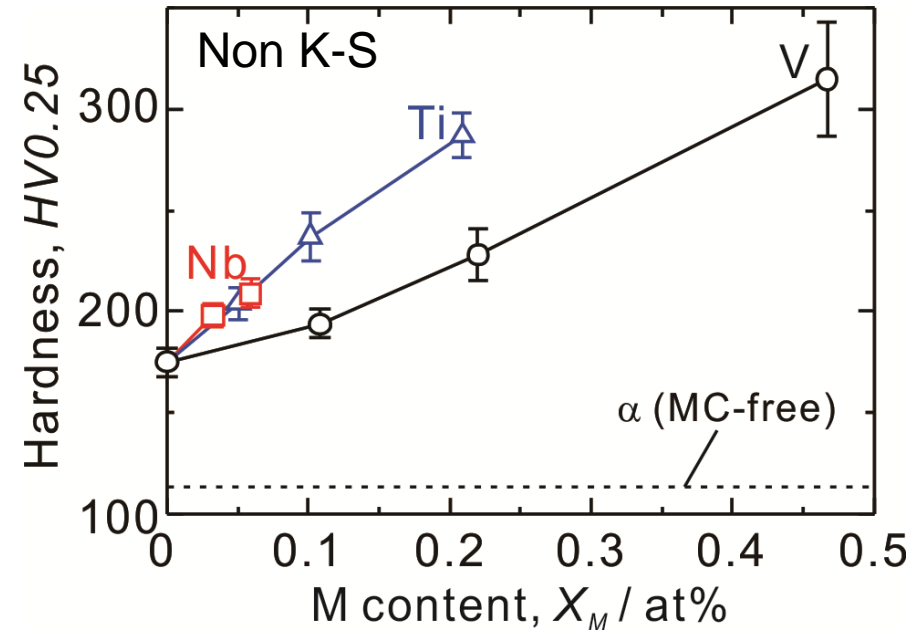
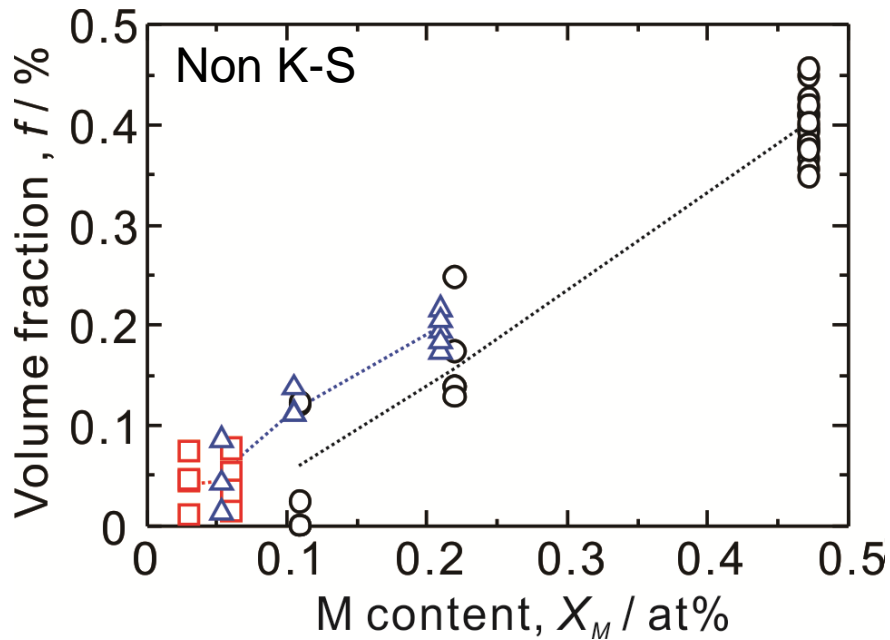
T. Gladman, *Mater. Sci. Tech.* 15 (1999) 30.

Hardness increment:

$$\begin{aligned} \Delta HV &= HV_{M-added} - HV_{Pure Fe} \\ &= HV_{ss} + HV_{disl} + HV_{ppt} \end{aligned}$$

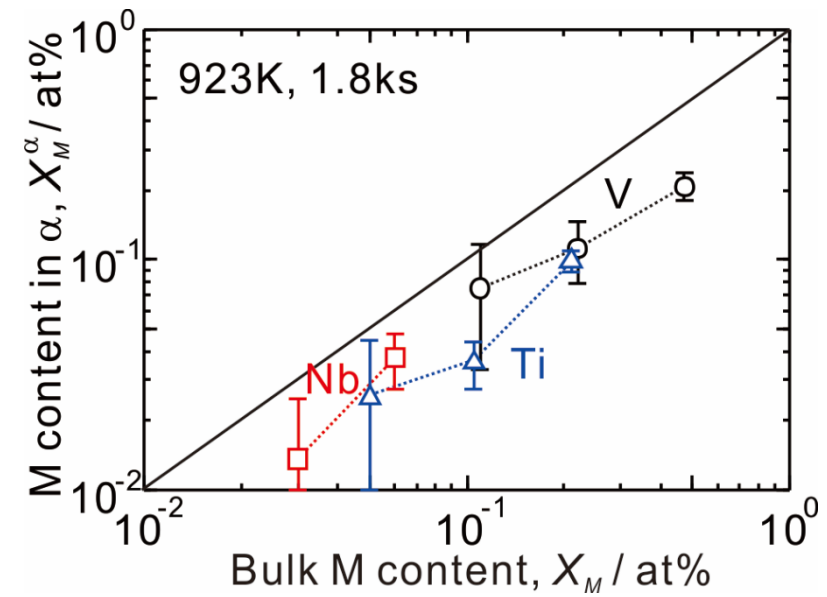
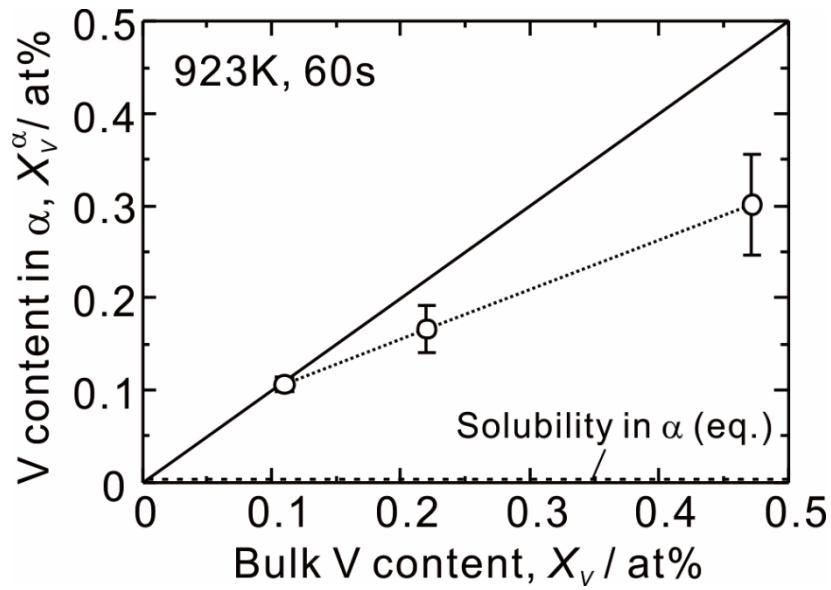


- Higher hardness increment of α by precipitation strengthening can be obtained by reducing the inter-particle spacing of MC.



- Higher number density of NbC and TiC is also obtained by more addition, whose dispersion is much finer than VC.
- Volume fraction of NbC and TiC also tends to be higher than VC, whose strengthening ability is much stronger than VC.

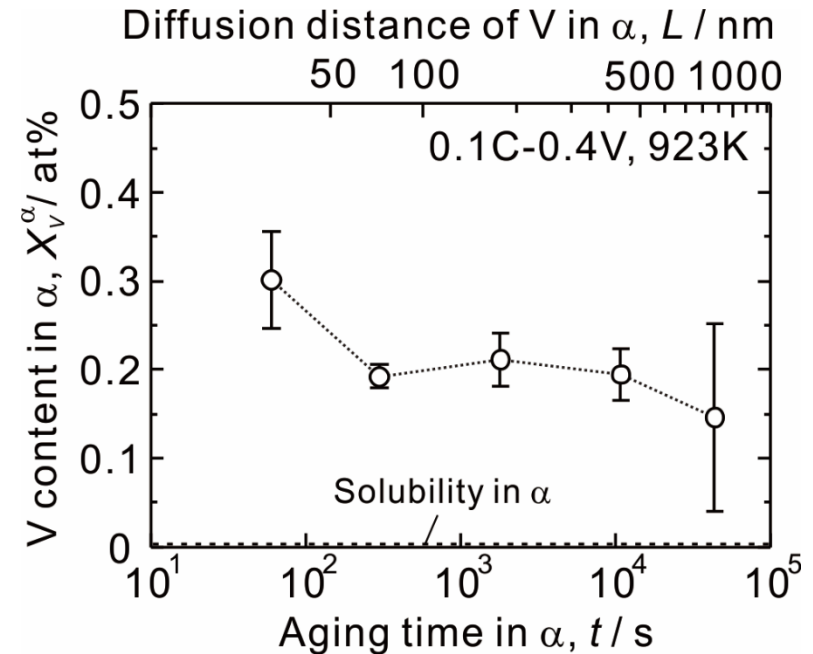
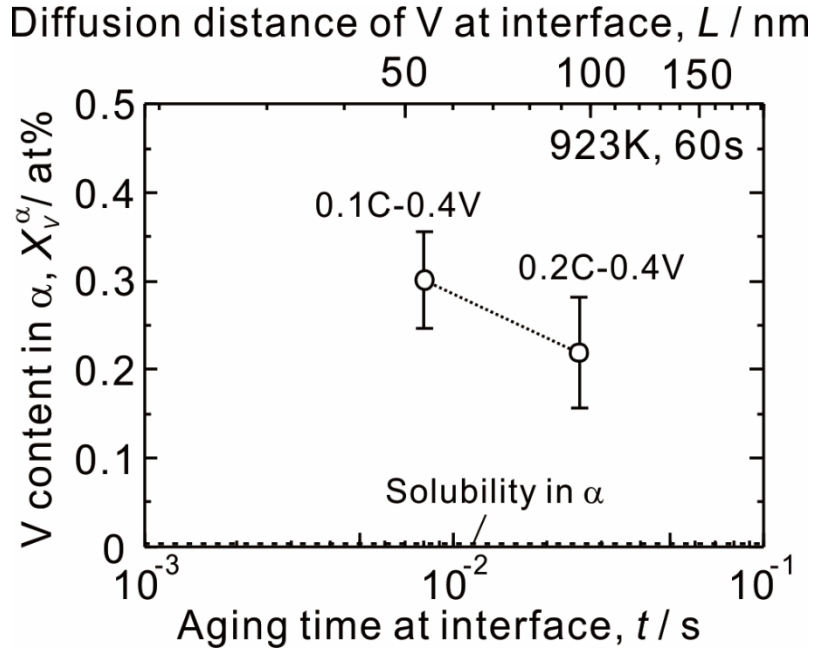
With different driving force for precipitation:



- More V remains in α in V-added alloys with higher bulk V content.
- Same phenomenon can also be observed in Nb and Ti-added alloys, although Nb and Ti contents in α tend to be lower than V content.

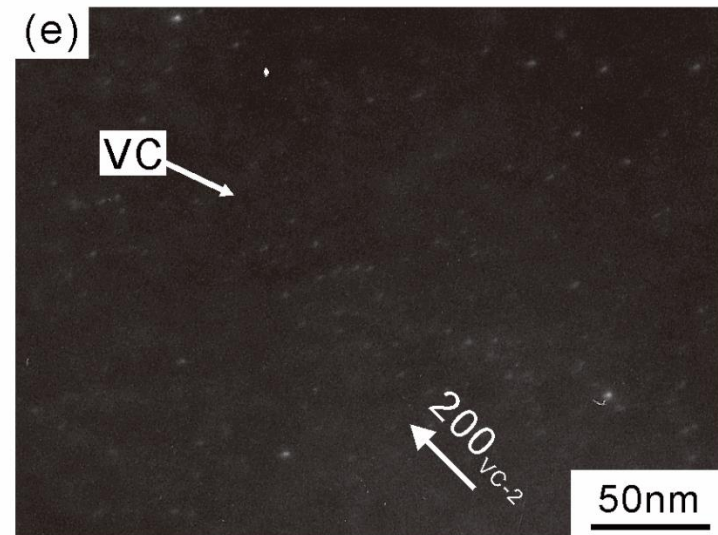
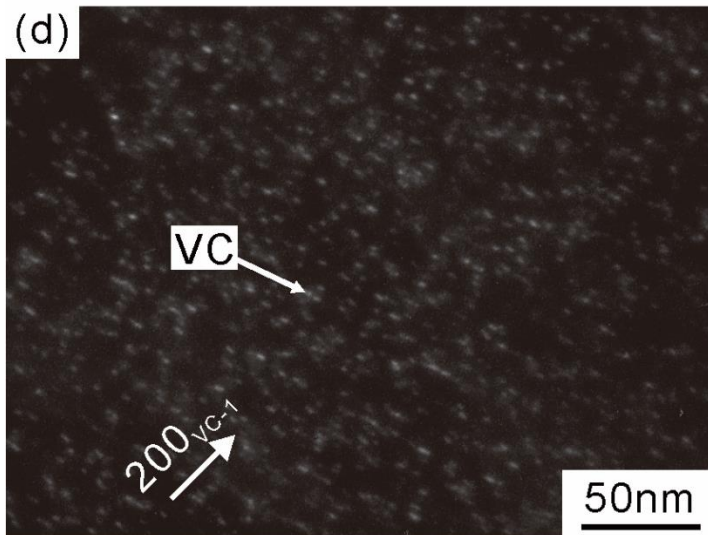
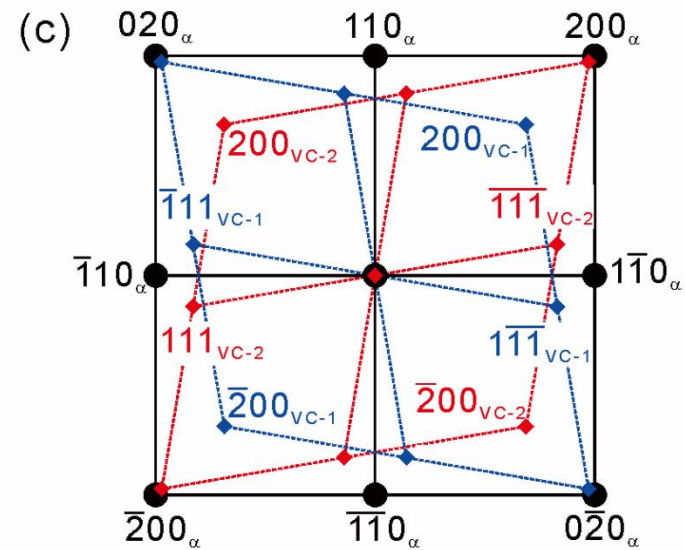
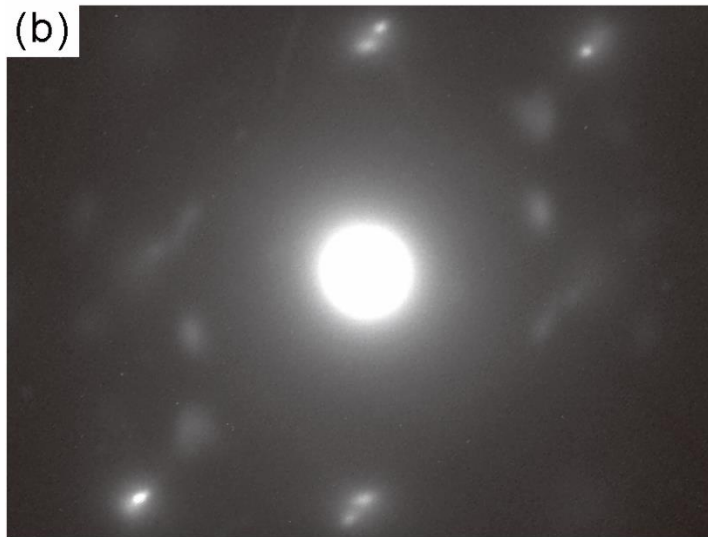
With same driving force for precipitation:

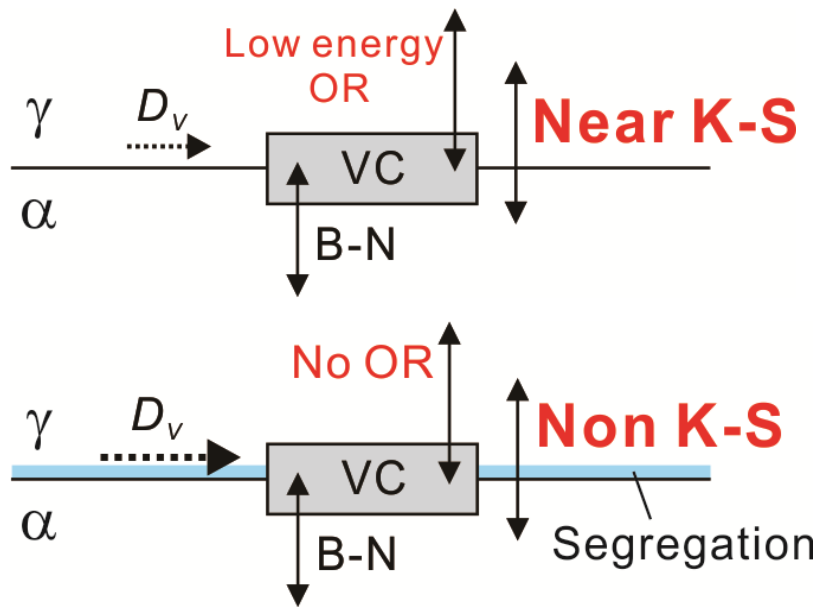
$$(L = \sqrt{2D_V t} \quad D_V: \text{diffusivity of V at interface / in } \alpha)$$



(Estimated from α growth rate and inter-sheet spacing)

- Both the aging times at α/γ interface and in α are not enough for V content in α to be decreased to its solubility.





Baker-Nutting (B-N) OR:
 $(001)_\alpha // (001)_{VC}, [110]_\alpha // [100]_{VC}$

$$\Delta\sigma \approx \sigma_{\alpha/VC} + \sigma_{\gamma/VC} - \sigma_{\alpha/\gamma}$$

$$= 2.2 \text{ J/m}^2 \quad \text{Near K-S case}$$

$$= 2.4 \text{ J/m}^2 \quad \text{Non K-S case}$$

- Promotion VC nucleation at non K-S interface is mainly caused by higher interfacial diffusivity and segregation of V, instead of higher α/γ interfacial energy.

	σ (J / m ²)	Exp. / Calc.	Ref.
α/γ K-S	~0.3	Calc.	[1]
α/γ random	~0.8	Exp.	[2]
γ/VC semi-coh.	~1.9	Calc.	[3]
γ/VC incoh.	~2.6	Calc.	[3]
α/VC semi-coh.	~0.6	Calc.	[4]

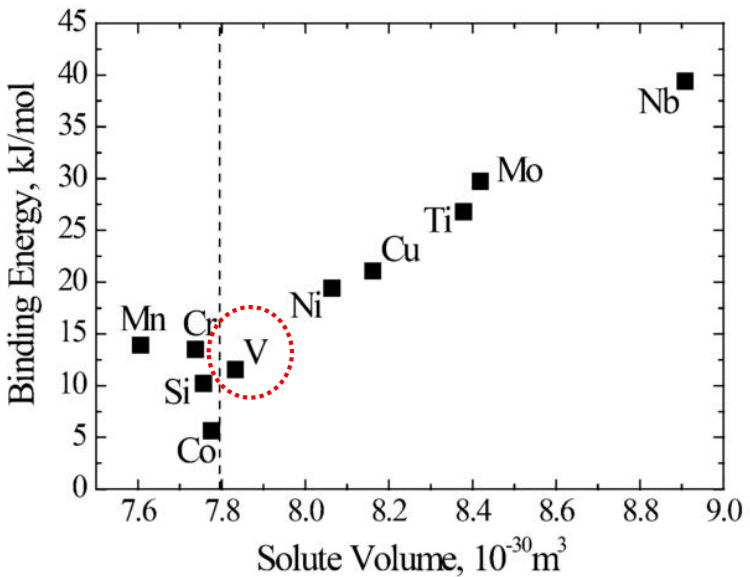
[1] M. Enomoto et al., *PTM* (2005) 67.

[2] L.E. Murr, *Int. Phen. in Metals and Alloys* (1975) 124.

[3] T. Furuhashi et al., *ISIJ Int.* 43 (2003) 1630.

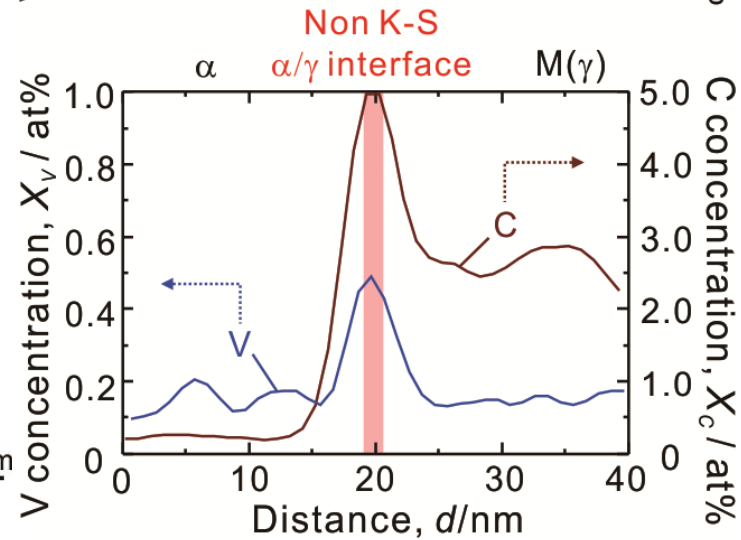
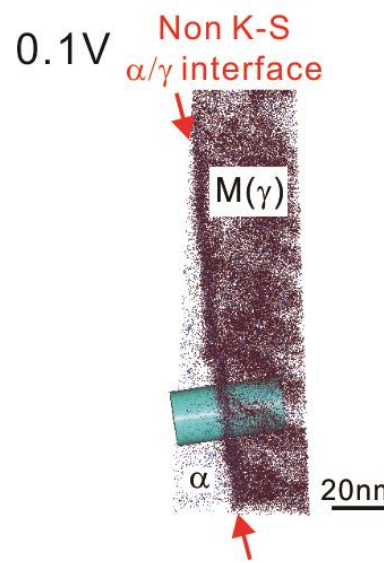
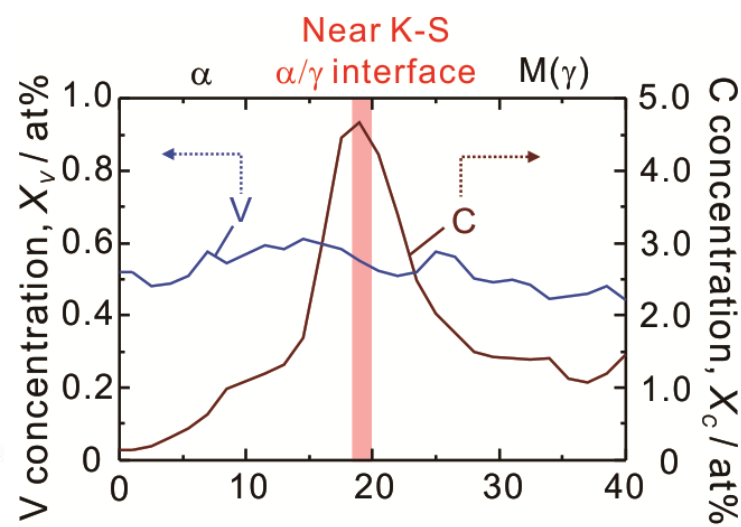
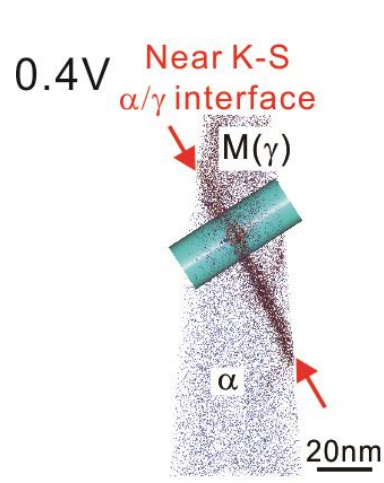
[4] D.H.R. Fors et al., *Phys. Rev. B.* 82 (2010) 195410.

Segregation tendency @ $\Sigma 5$ α grain boundary



M. Militzer et al., JOM 66 (2014) 740.

V + C atom map 1D concentration profile



- In addition to C, V is also severely segregated at non K-S α/γ interface.