2018.7.5　17th ALEMI Meeting @ Citadelle Hotel, Metz, France

Nucleation of Vanadium Carbide Interphase Precipitation with Different Ferrite Growth Rate in Low Carbon Steels

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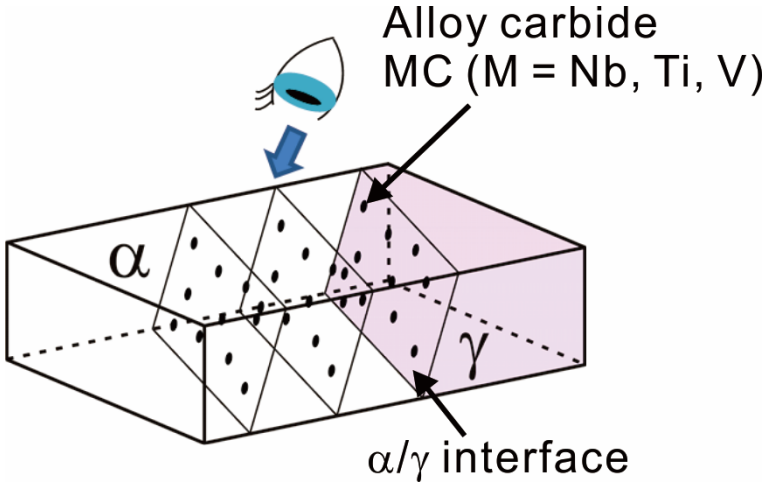
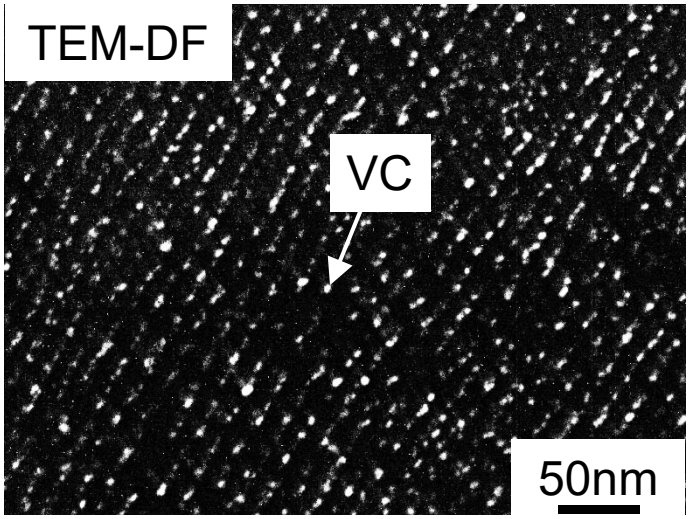
Interphase precipitation

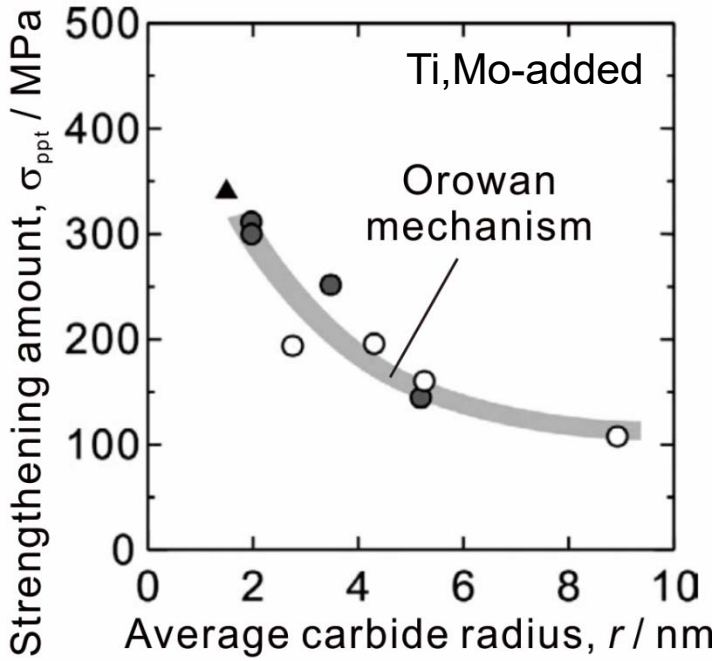


Periodic nucleation at migrating interface

V-added low carbon steel



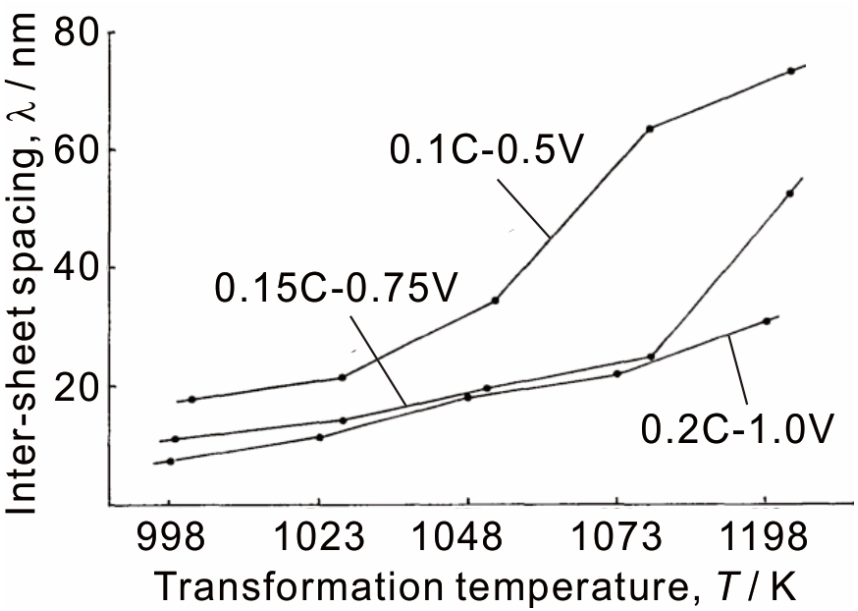
Precipitation strengthening

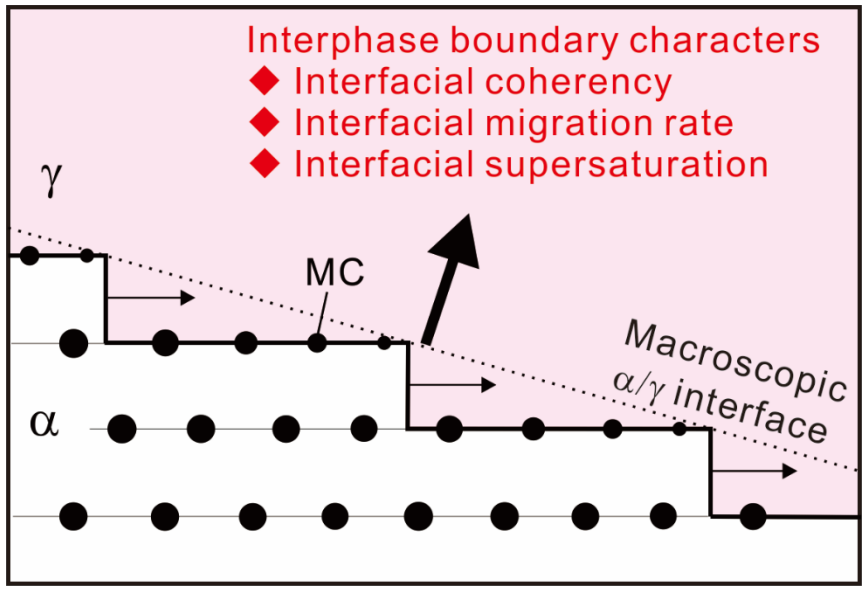


N. Kamikawa et al., *ISIJ Int.* 54 (2014) 212.

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

Various factors on dispersion of interphase precipitation





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

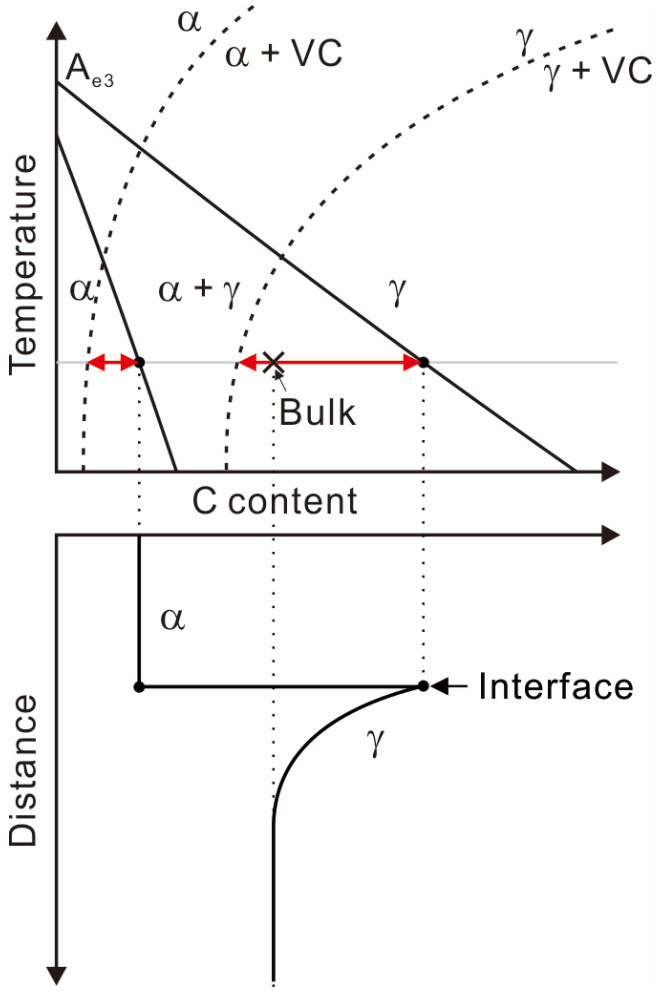
- Interfacial coherency → Density of defects
- Interfacial migration rate → Time
- Interfacial supersaturation → Driving force

} for nucleation

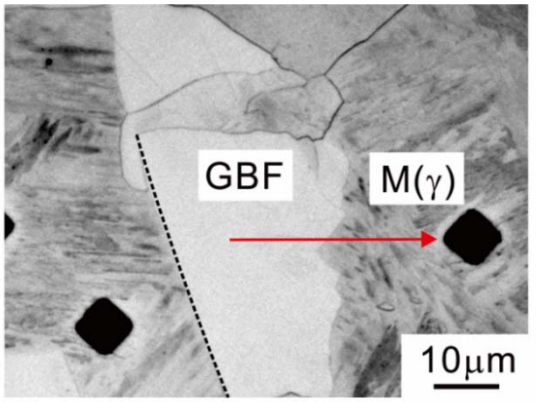
Variations in dispersion of interphase precipitation

Estimation of interfacial concentration

Phase diagram

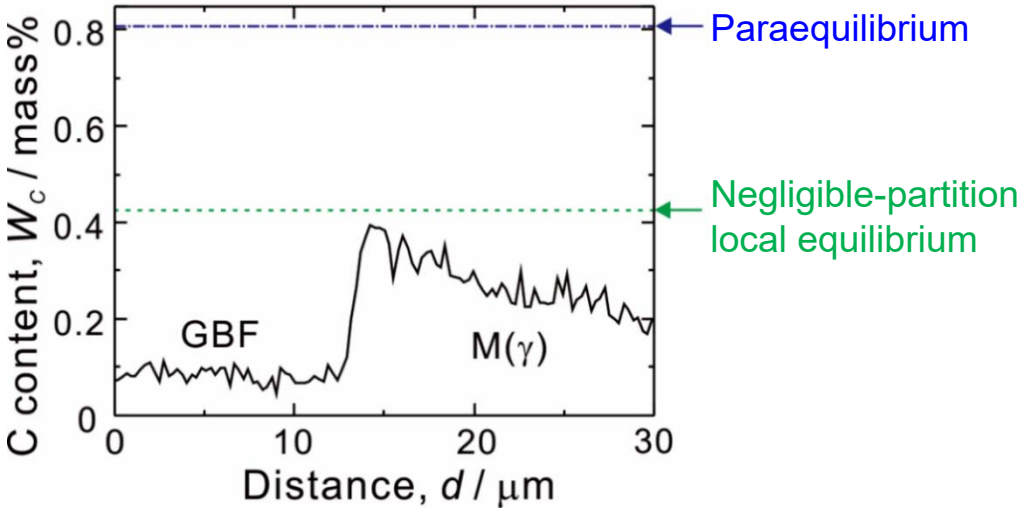


0.2C-0.4V, 963K, 0.3ks



GBF: grain boundary α;
M(γ): martensite

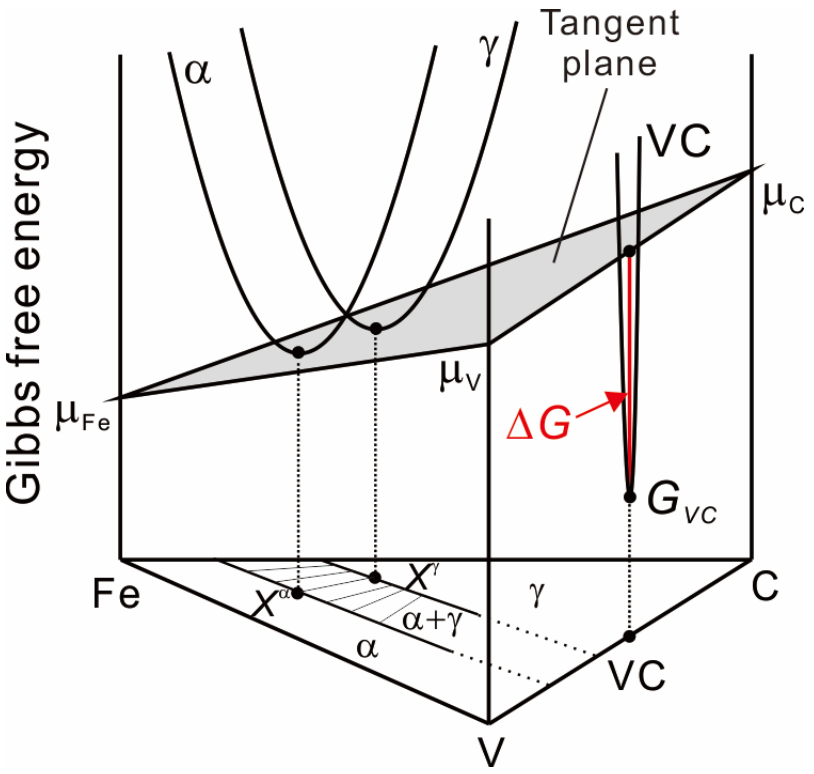
By electron probe microanalysis (EPMA)



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.

Estimation of driving force for VC interphase precipitation



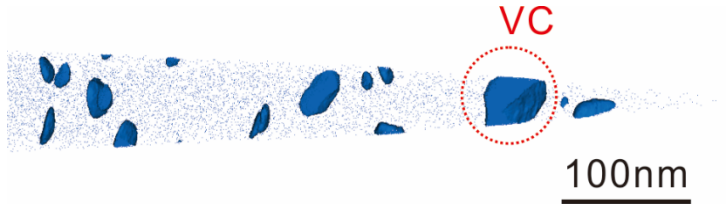
By assuming 50at% V and 50at% C:

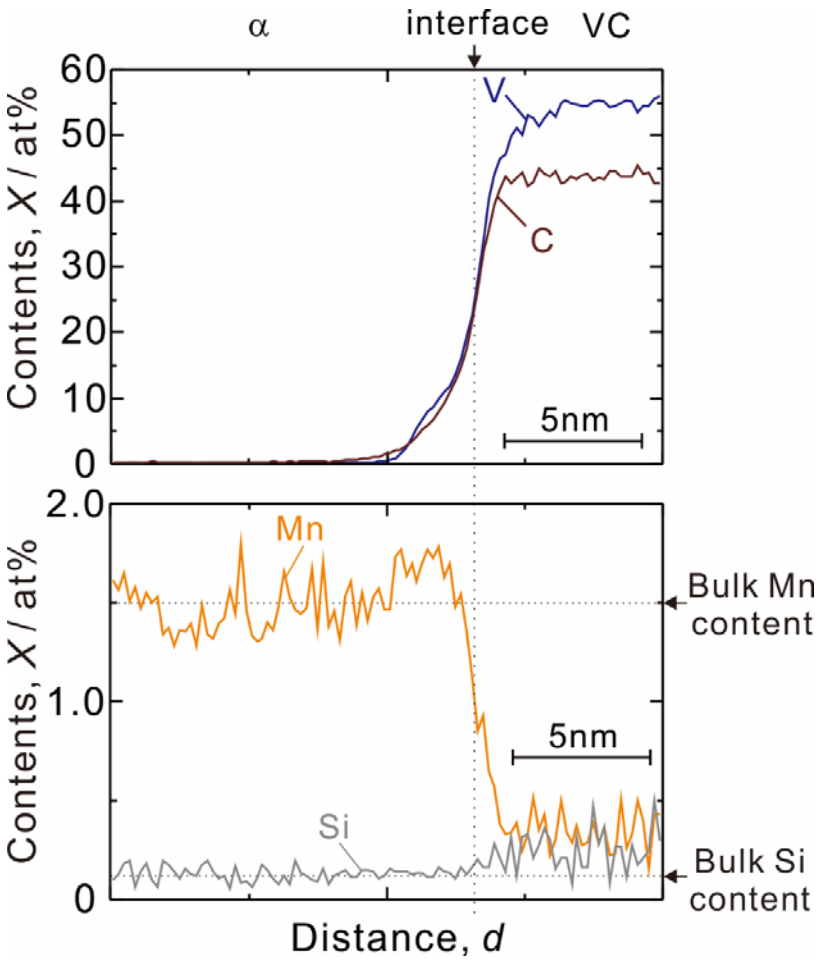
$$\Delta G = 0.5\mu_V + 0.5\mu_C - G_{VC}$$

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

(Segregation is neglected for simplicity)

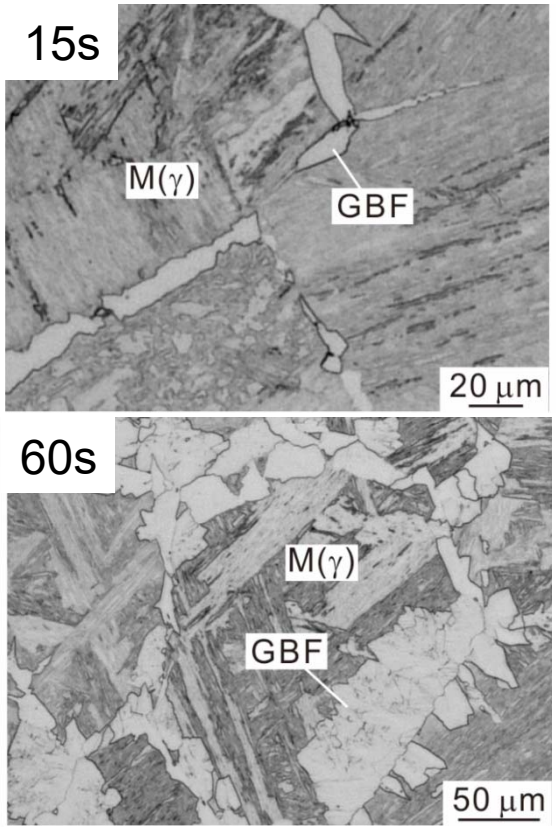
0.1C-0.4V, 923K, 172.8ks



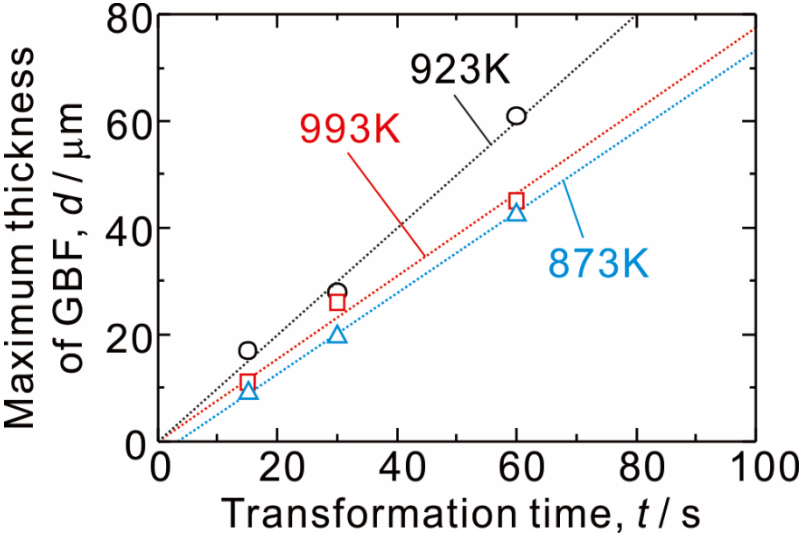


Estimation of α growth rate

0.1C-0.4V, 923K



GBF: grain boundary α; M(γ): martensite



- α growth rate can be approximately estimated from maximum thickness of GBF.

Objective

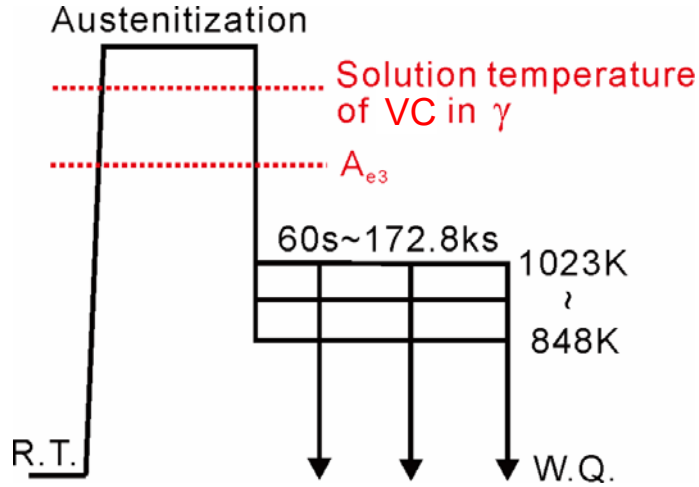
Through quantitative analysis on dispersion of VC interphase precipitation formed under different conditions, we aimed to clarify the effects of α growth rate and driving force on interphase precipitation.

- Alloys (mass%)

0.1C-0.1V: Fe-0.1C-1.5Mn-0.05Si-**0.1V**
0.1C-0.2V: Fe-0.1C-1.5Mn-0.05Si-**0.2V**
0.1C-0.4V: Fe-0.1C-1.5Mn-0.05Si-**0.4V (Base)**
0.1C-0.4V: Fe-0.1C-**0.7Mn**-0.05Si-0.4V **(Low Mn)**
0.1C-0.4V: Fe-0.1C-1.3Mn-**0.4Si**-0.4V **(High Si)**
0.2C-0.4V: Fe-**0.2C**-1.5Mn-0.05Si-0.4V
0.2C-0.9V: Fe-**0.2C**-1.5Mn-0.05Si-**0.9V**
0.3C-1.3V: Fe-**0.3C**-1.5Mn-0.05Si-**1.3V**

Effect of driving force
Effect of α growth rate
Effect of driving force

- Heat treatment



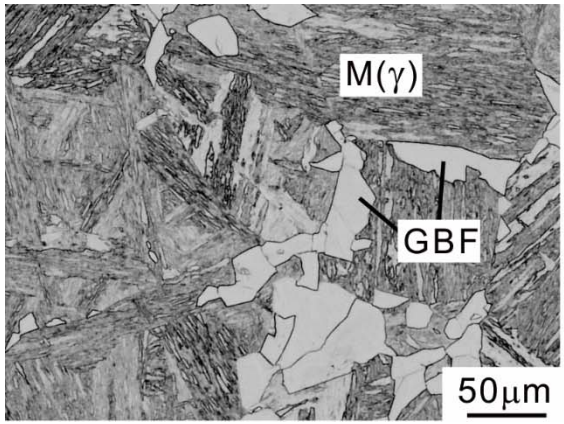
- Microstructural characterization
  - Optical microscopy (OM)
  - Scanning electron microscopy (SEM) / Electron backscatter diffraction (EBSD)
  - Three-dimensional atom probe (3DAP)

Effects of temperature and V, C contents on microstructure

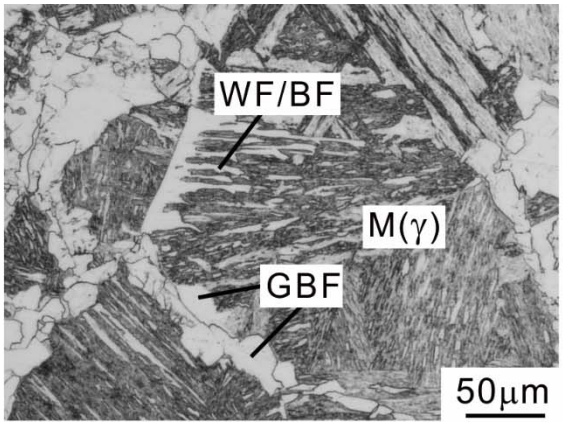
0.1C-0.4V (Base)

WF / BF: Widmanstatten / baintic α

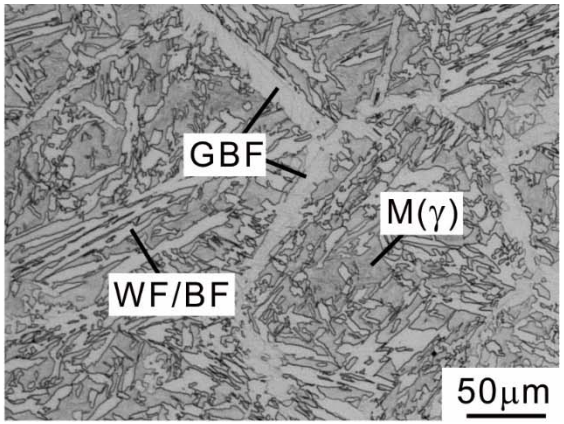
993K, 60s



923K, 60s



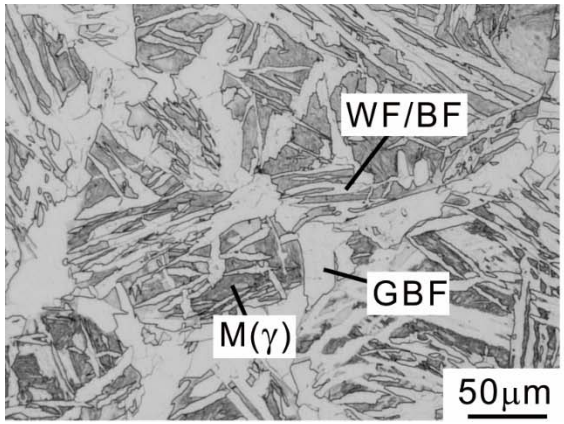
873K, 60s



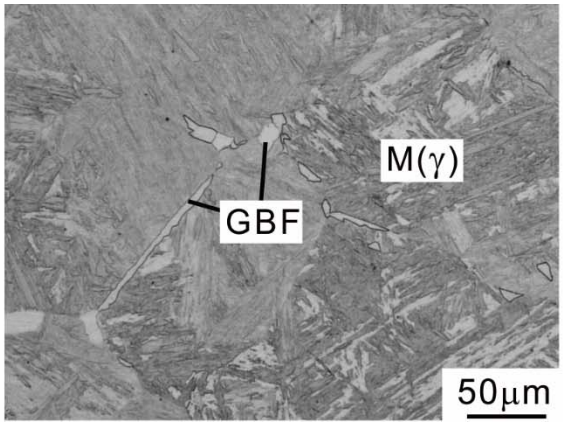
- α morphology changes from GBF into WF/BF by lowering temperature.

923K, 60s

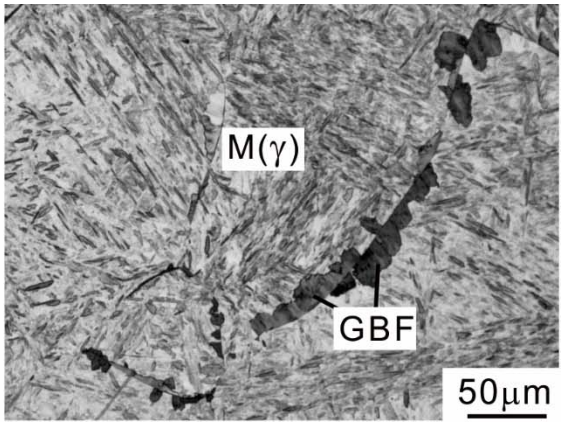
0.1C-0.1V



0.2C-0.4V

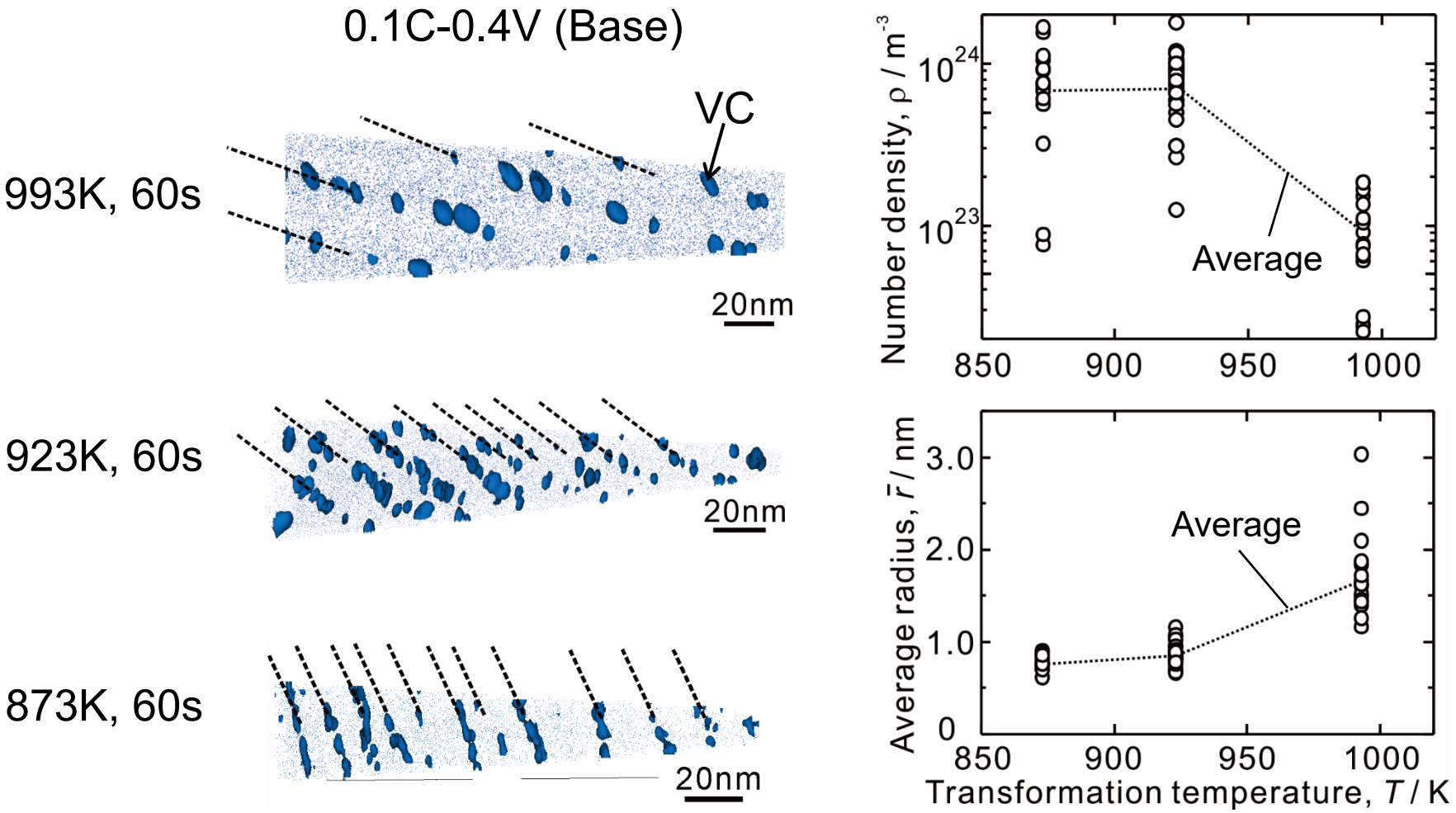


0.3C-1.3V



- Formation of WF/BF is suppressed by increasing V and C contents.

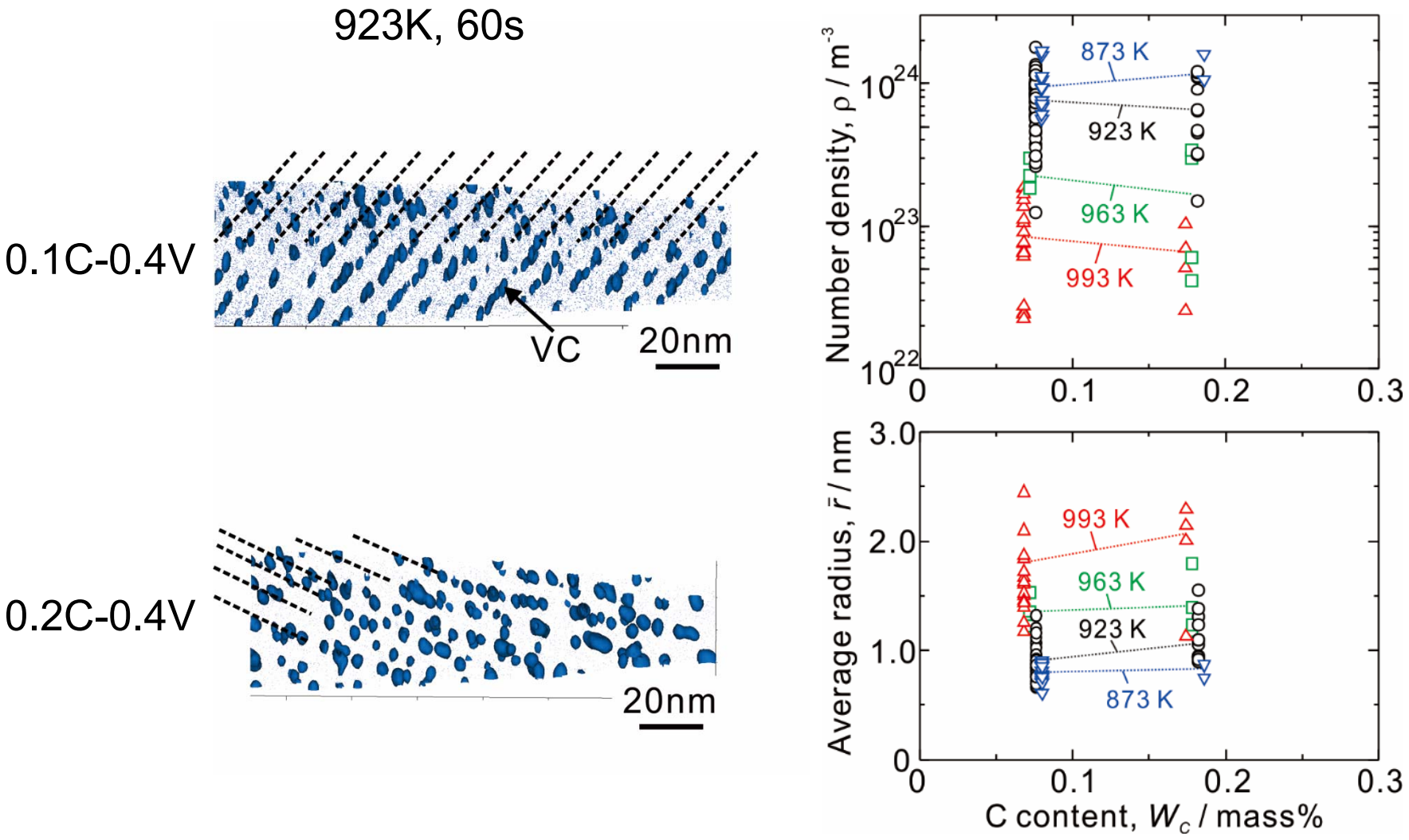
Effects of temperature on dispersion of VC



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

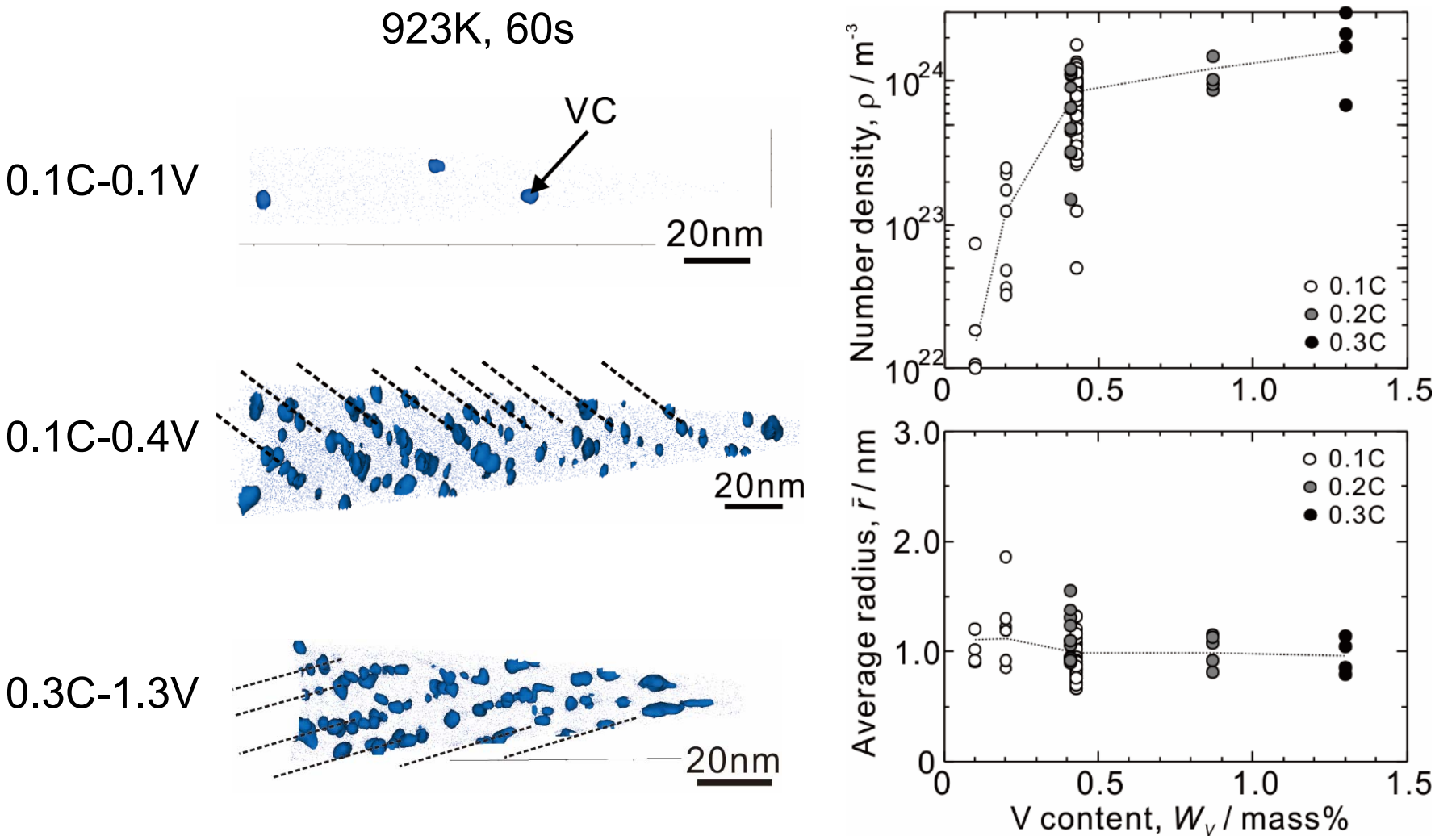
- Dispersion of VC becomes higher in number density and smaller in size by lowering transformation temperature.

Effects of C content on dispersion of VC



- Dispersion of VC is only slightly influenced by increasing bulk C content.

Effects of V content on dispersion of VC

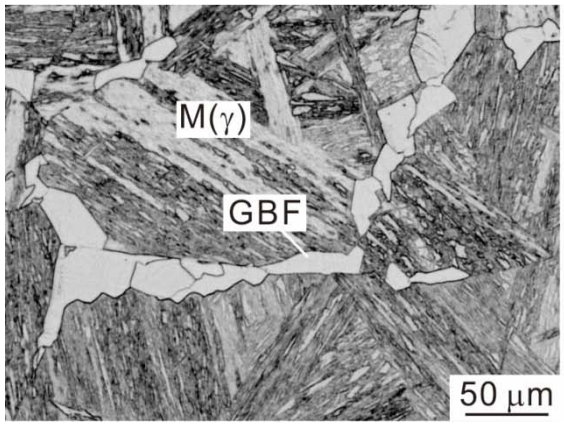


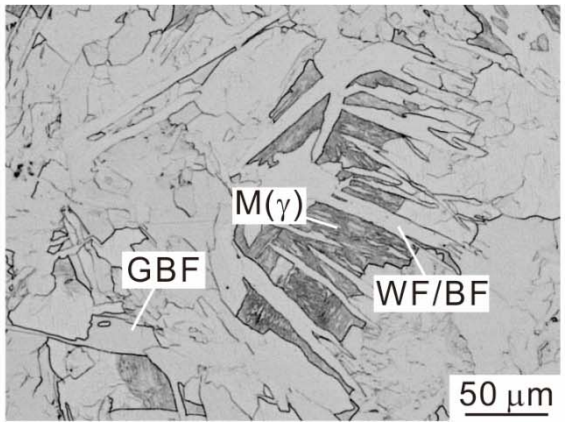
- Number density of VC is increased, while size of VC is slightly decreased by increasing V content.

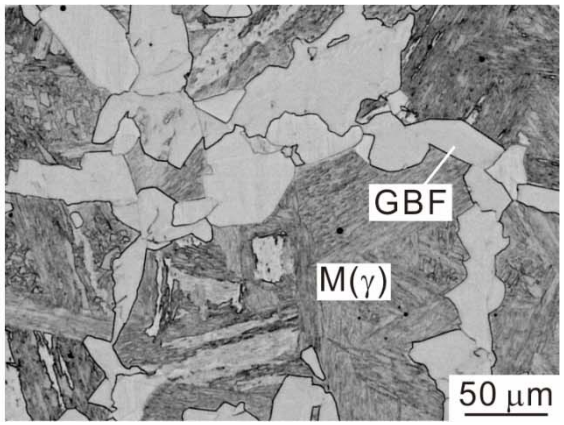
Effects of Mn and Si contents on microstructure

993K, 60s

0.1C-0.4V (Base) | 0.1C-0.4V (Low Mn) | 0.1C-0.4V (High Si)



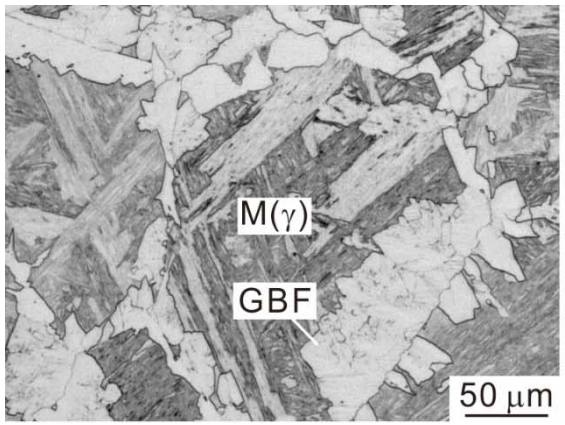


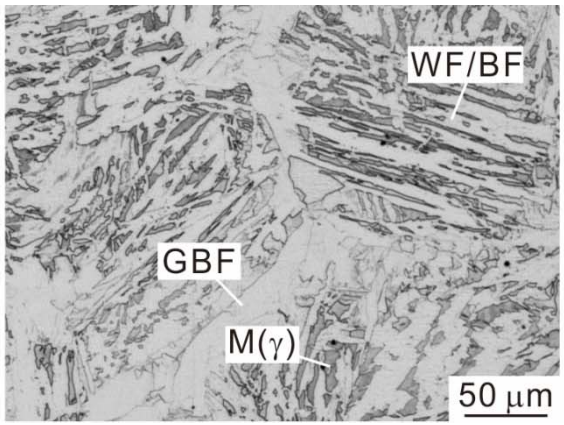


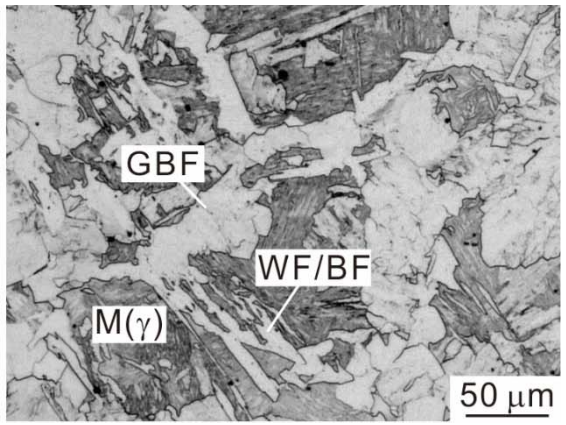
- α growth is greatly accelerated by reducing Mn or increasing Si content.

923K, 60s

0.1C-0.4V (Base) | 0.1C-0.4V (Low Mn) | 0.1C-0.4V (High Si)







- WF/BF formation is promoted by reducing Mn or increasing Si content.

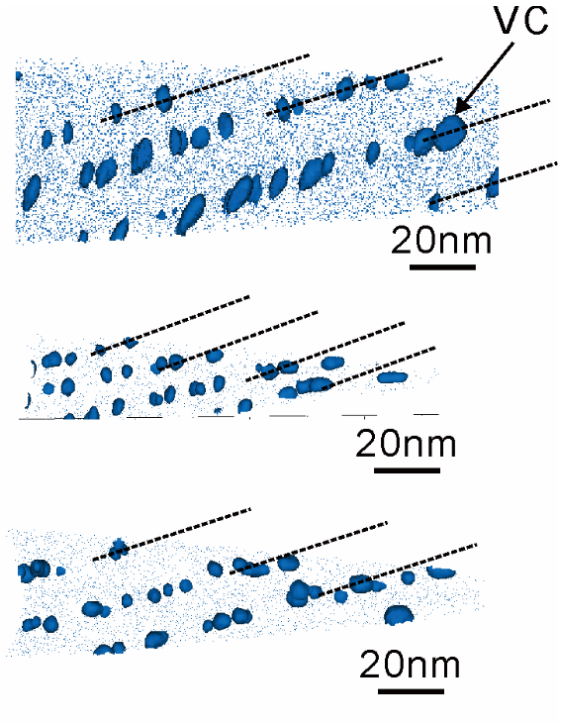
Effects of Mn and Si contents on dispersion of VC

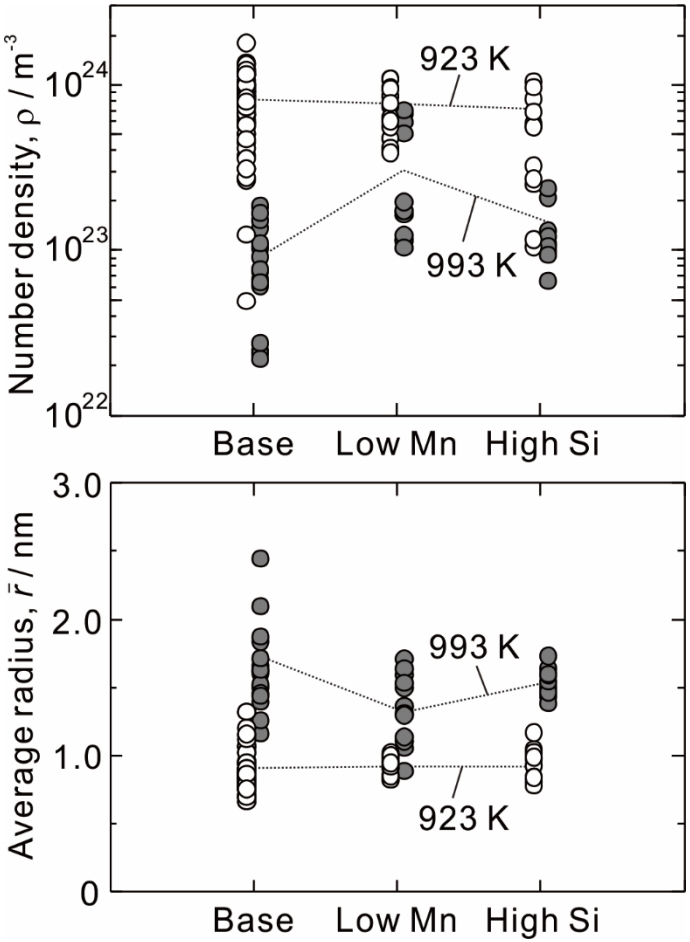
993K, 60s

0.1C-0.4V (Base)

(Low Mn)

(High Si)

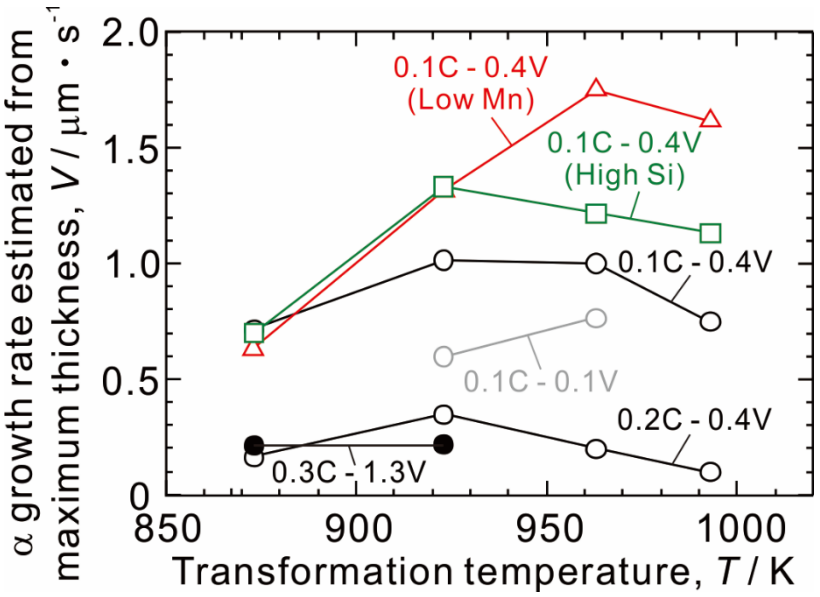




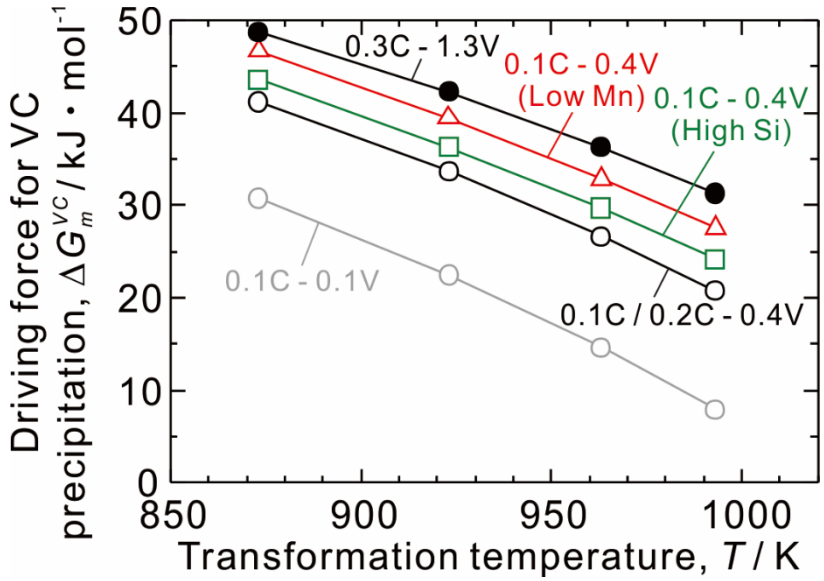
- Dispersion of VC is refined by reducing Mn or increasing Si content at higher temperature, but almost unchanged at lower temperature.

Estimated α growth rate and driving force for precipitation

From maximum α thickness:

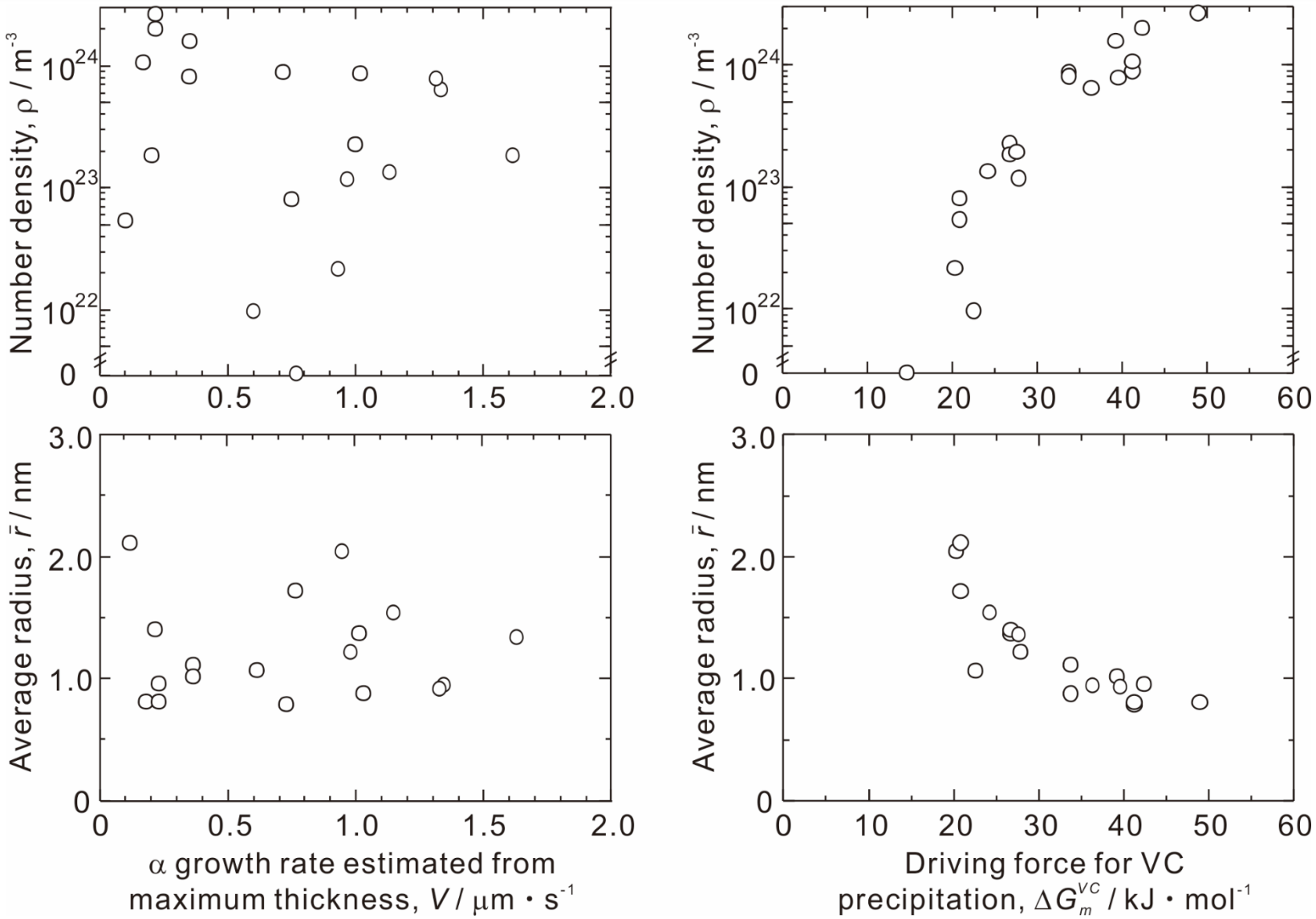


From interfacial composition:



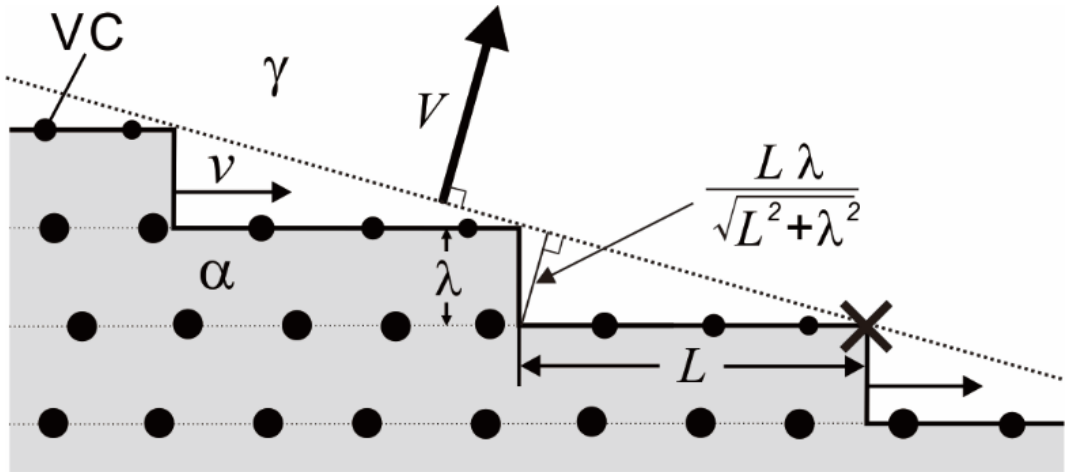
- α growth rate shows a peak at an intermediate temperature, becomes higher with lower Mn or higher Si content, and lower with higher C content.
- Driving force for precipitation is larger at lower temperature or with higher V, lower Mn or higher Si content, but not influenced by bulk C content.

Effects of α growth rate and driving force on dispersion of VC



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

Ledgewise α growth with VC interphase precipitation



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

Aging time at migrating α/γ interface:

$$\Delta t = \frac{L}{v} = \frac{\frac{L\lambda}{\sqrt{L^2+\lambda^2}}}{V} \approx \frac{\lambda}{V} \qquad \text{when} \quad L = 4\lambda$$

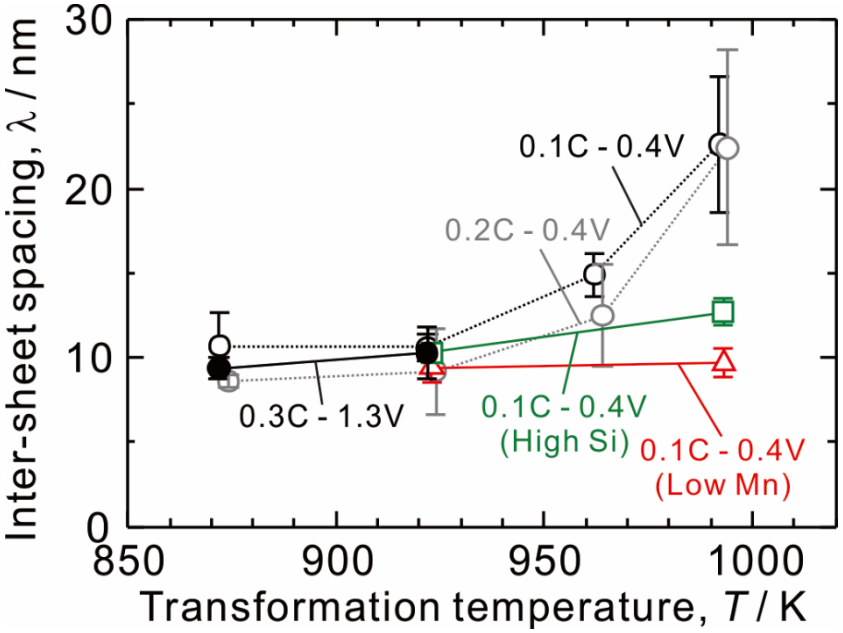
R. Okamoto al., *Acta Mater.*, 58 (2010) 4791.

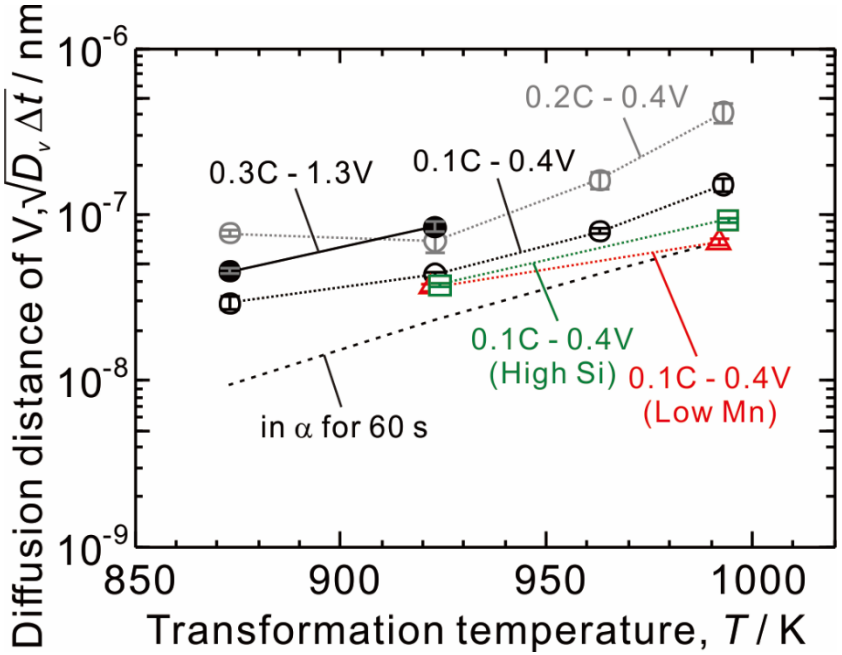
- Aging time at migrating α/γ interface for precipitation of VC can be estimated from inter-sheet spacing and macroscopic α growth rate.

Interfacial aging time at migrating α/γ interface

By using grain boundary diffusivity in Fe:

J. Fridberg et al., *Jernkontorets Ann.*, 153 (1969) 263.

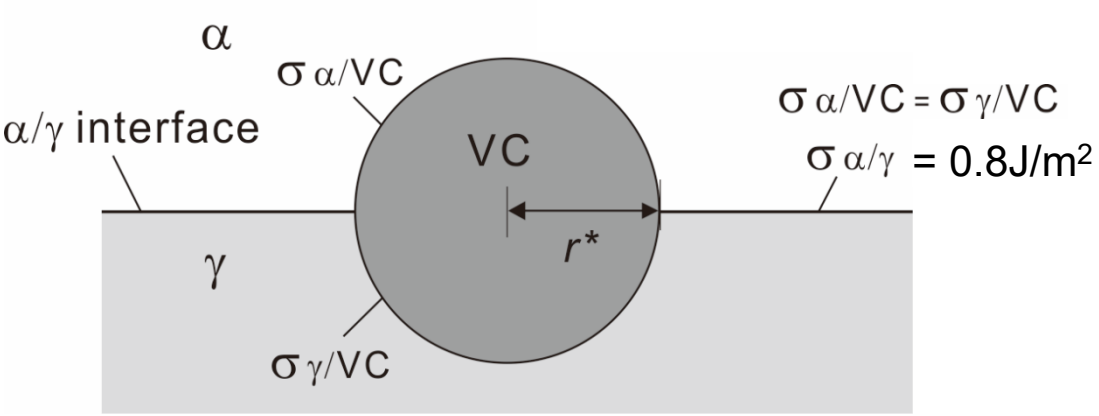




- Inter-sheet spacing becomes smaller by lowering temperature, reducing Mn or increasing Si content at higher temperature.

- Interfacial aging time tends to be shorter with larger α growth rate.
- Interphase precipitation is mainly controlled by interfacial diffusion of V.

By assuming spherical critical nucleus:



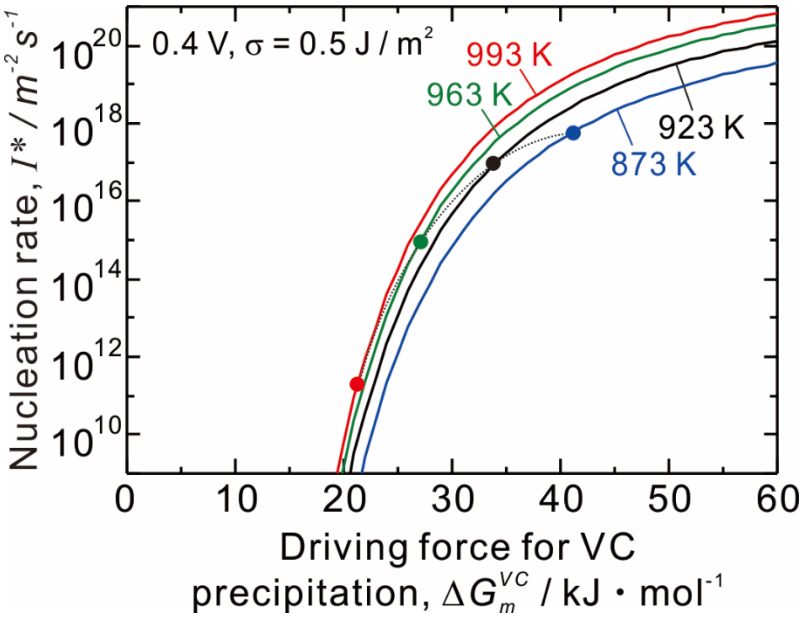
Nucleation rate:

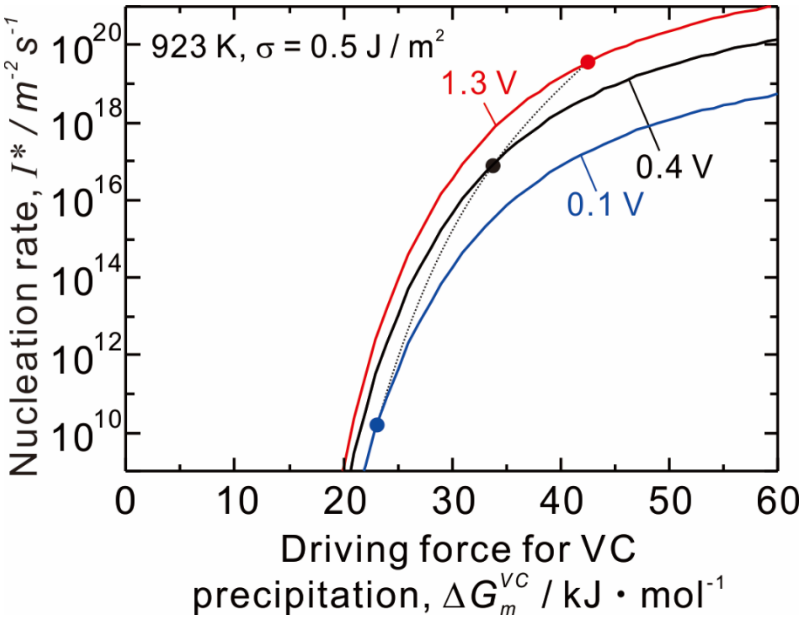
$$I^* = N\beta^* Z\, exp\,(-\frac{\Delta G^*}{kT})$$

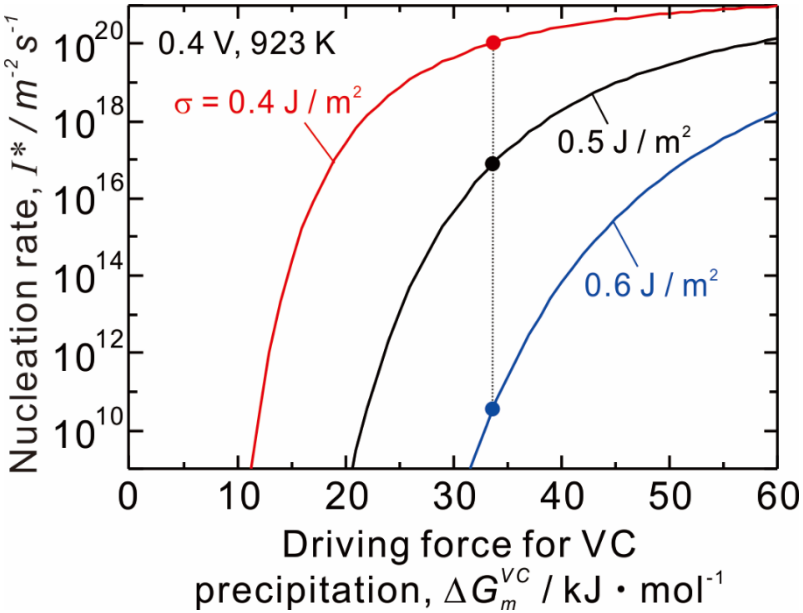
N : density of nucleation site;
β^*: frequency factor;
Z : Zeldovich factor;
ΔG^*: activation energy

- N becomes larger with higher **bulk V content**.
- β^* becomes larger mainly by increasing **temperature**.
- Z becomes larger with larger **driving force for precipitation**, or with smaller **α/VC and γ/VC interfacial energy**.
- ΔG^* becomes smaller with larger **driving force for precipitation**, or with smaller **α/VC and γ/VC interfacial energy**.

Influencing factors on nucleation rate

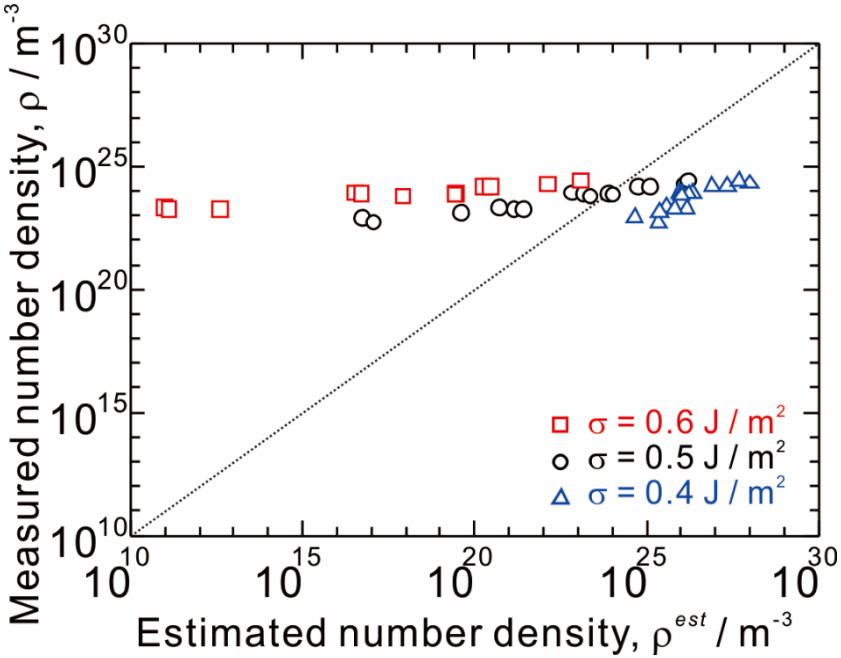


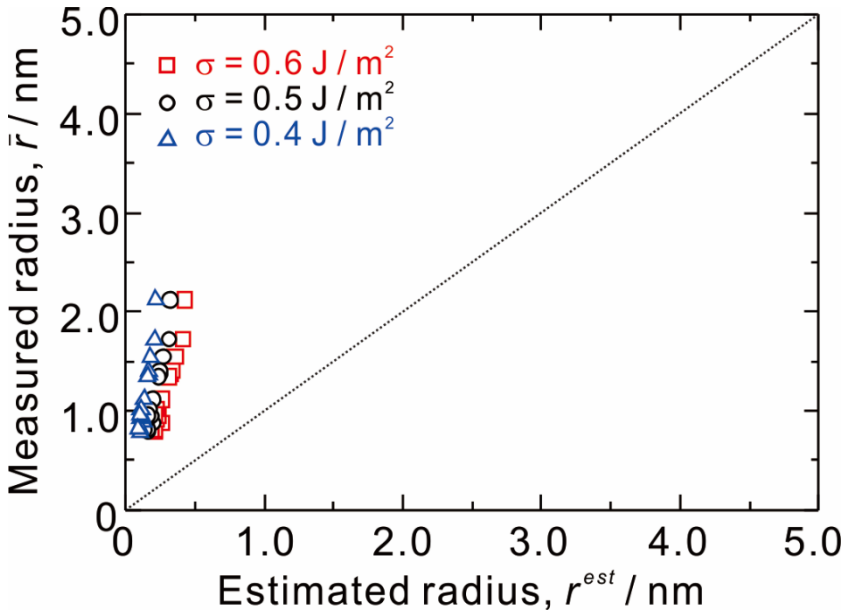




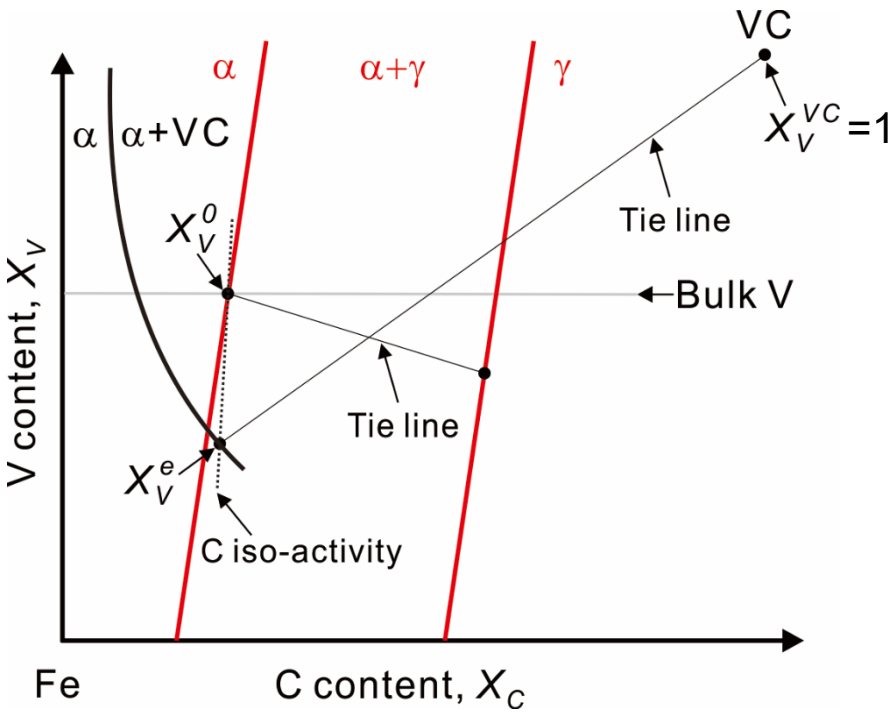
- Nucleation rate is significantly increased by lowering temperature, increasing V content, or lowering interfacial energy.

Comparison of estimated and measured dispersion of VC

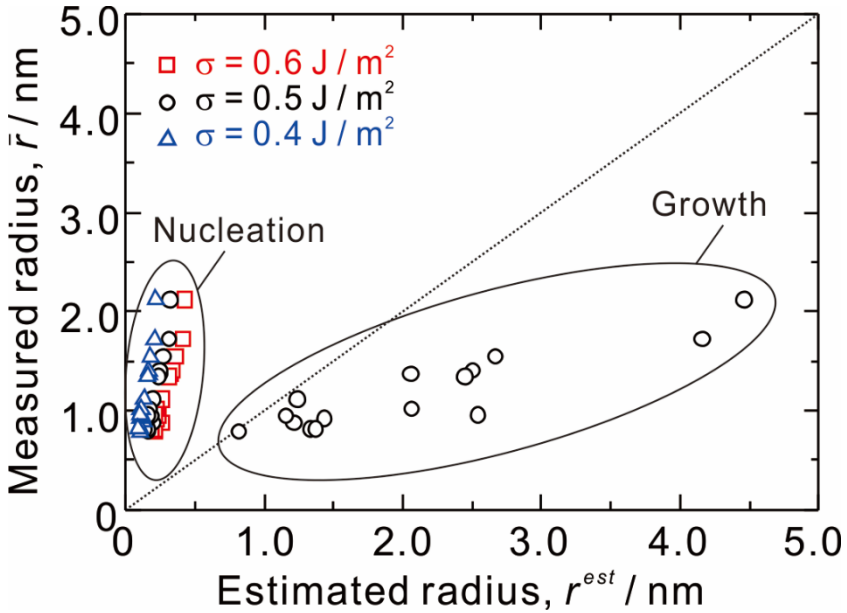




- Larger interfacial energy cannot reproduce variation range of number density, while small interfacial energy overestimate absolute amount.
- Regardless of interfacial energy, estimated radius is significantly smaller than measured ones.



By using interfacial diffusivity and aging time:



Radius after growth:

$$r = \sqrt{2\,\frac{X_V^0 - X_V^e}{X_V^{VC} - X_V^e}\,D_V\,t}$$

X_V : V content;
D_V : interfacial diffusivity of V

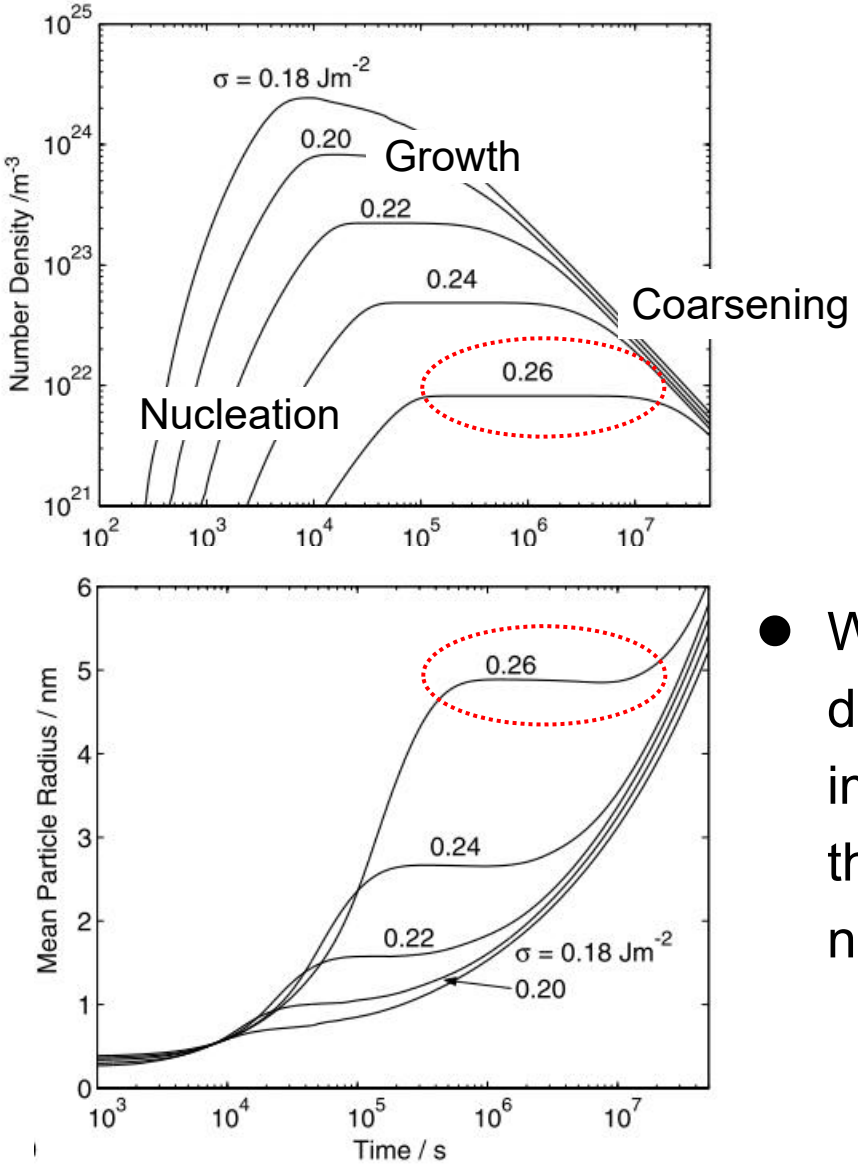
- Measured radius falls between those predicted ones for nucleation and growth.

Possible growth at migrating α/γ interface

Possible growth stage of interphase precipitation

Simulation of precipitation by aging (*N* model):

J.D. Robson, *Acta Mater.*, 52 (2004) 4669.



- Weak influence of α growth rate on dispersion of VC observed in this study implies that interphase precipitation is at the growth stage with plateau in both number density and size.

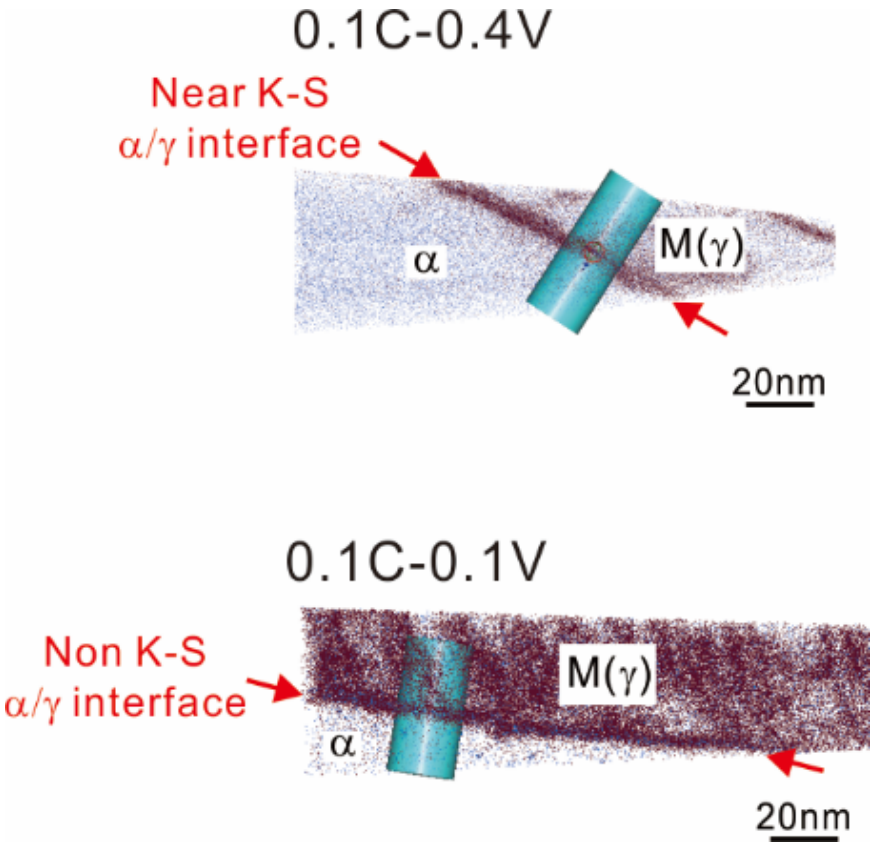
The effects of α growth rate and driving force for precipitation on dispersion of VC interphase precipitation were investigated.

This study can be summarized as:

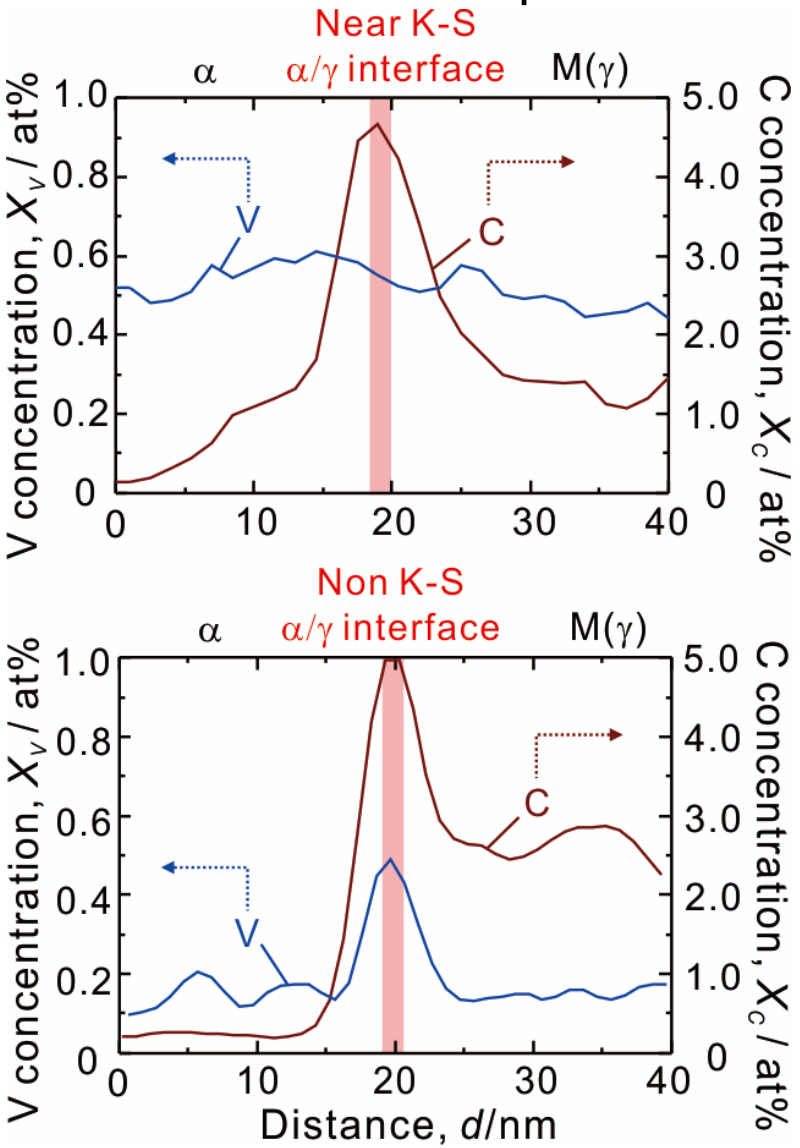
- Finer dispersion of VC formed by interphase precipitation can mainly be explained by larger driving force, while α growth rate only plays a minor role in influencing the dispersion.
  This can be understood by considering both nucleation and growth kinetics of VC at migrating α/γ interface.

Segregation of V at non K-S α/γ interface

V + C atom map



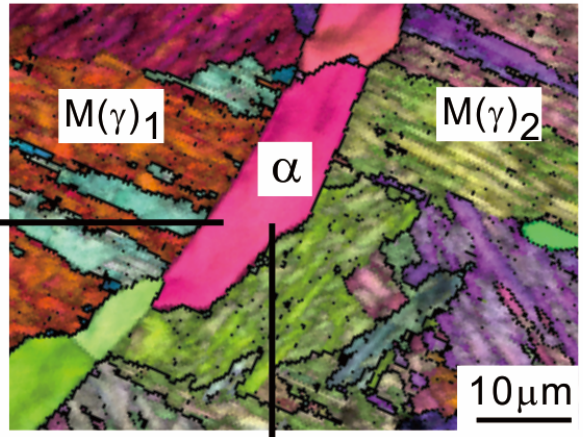
1D concentration profile

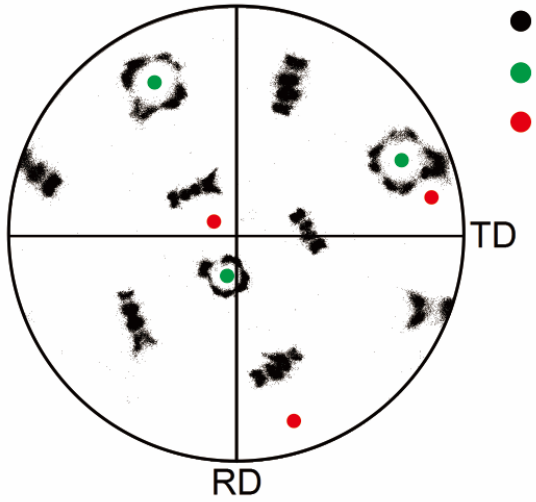


- In addition to C, V is also severely segregated at non K-S α/γ interface.

Combination of EBSD, 3DAP and nano-indentation

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





● <001>$_M$
● <001>$_\gamma$
● <001>$_\alpha$

Deviation angle from the exact K-S OR: Δθ

Near K-S: Δθ ≤ 5deg.

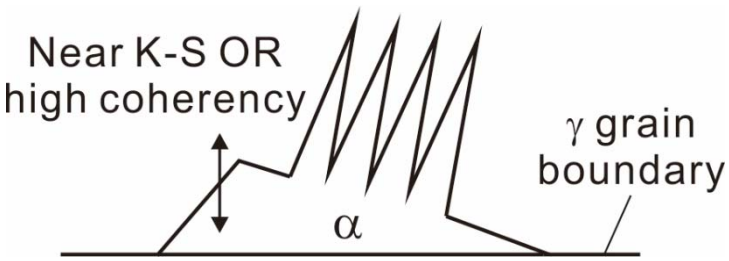
Non K-S: Δθ > 5deg.

Micro-sampling by focused ion beam

② 3DAP analyses → dispersion of VC precipitates

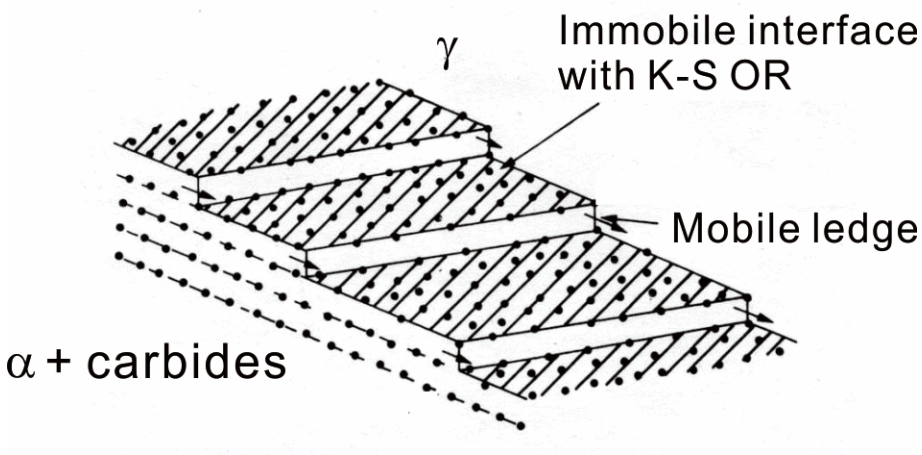
③ Nano-indentation → nanohardness of the same α grain

α/γ crystallography and mechanisms of interphase precipitation27

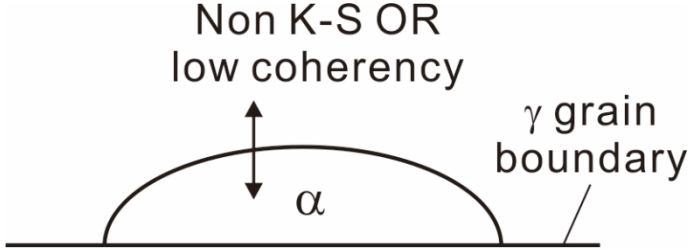


Kurdjumov-Sachs (K-S) orientation relationship (OR):
$(111)_\gamma$ // $(011)_\alpha$, $[\bar{1}01]_\gamma$ // $[\bar{1}\bar{1}1]_\alpha$

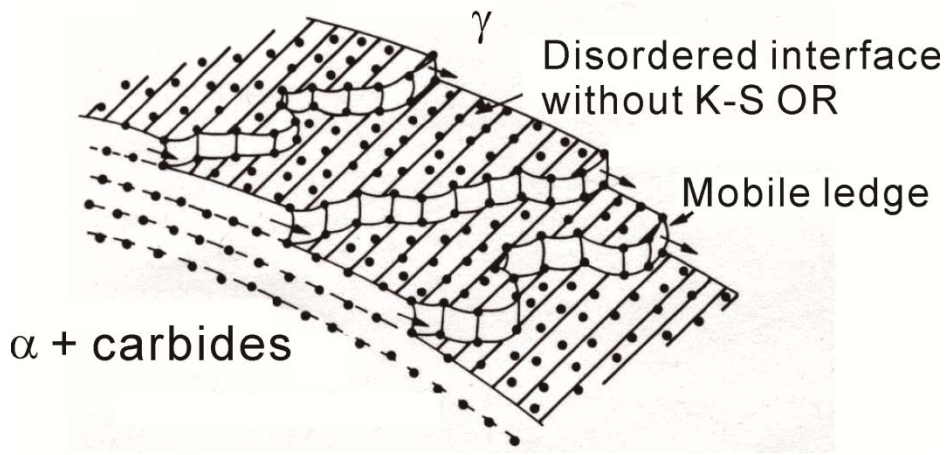
Ledge Mechanism



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



Quasi-ledge Mechanism



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

Ashby-Orowan model:

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

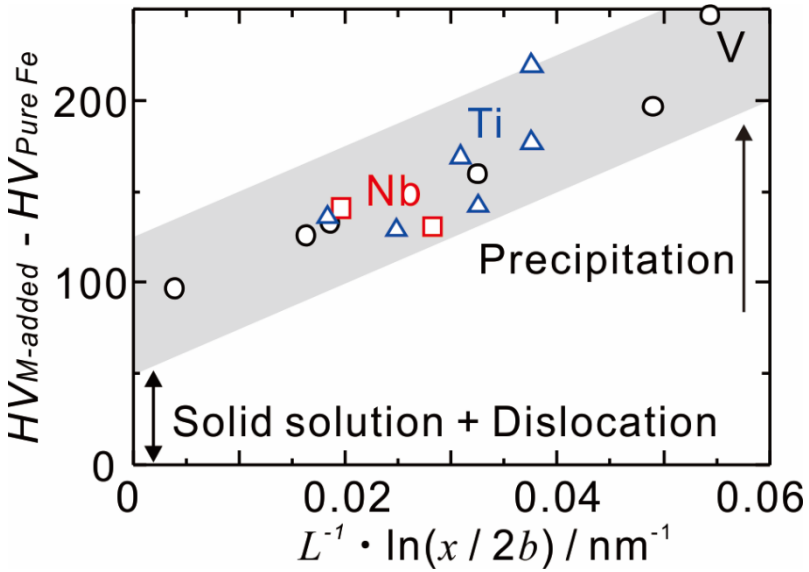
$$x = 2\bar{r}\sqrt{\frac{2}{3}}$$

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.

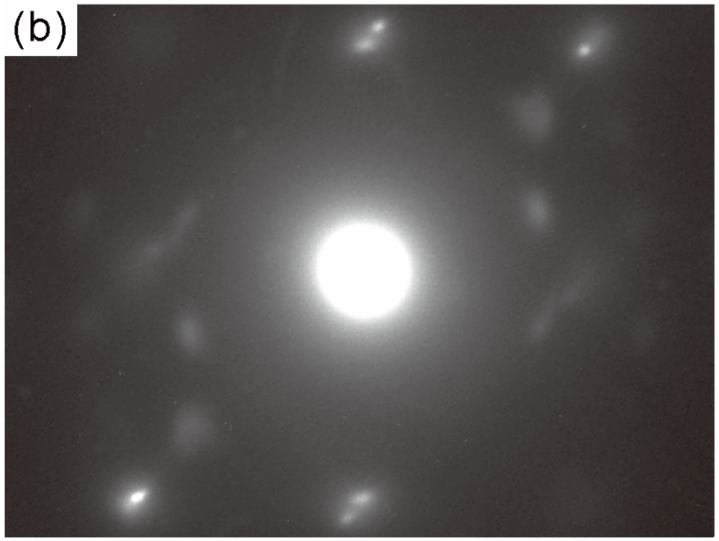
Hardness increment:

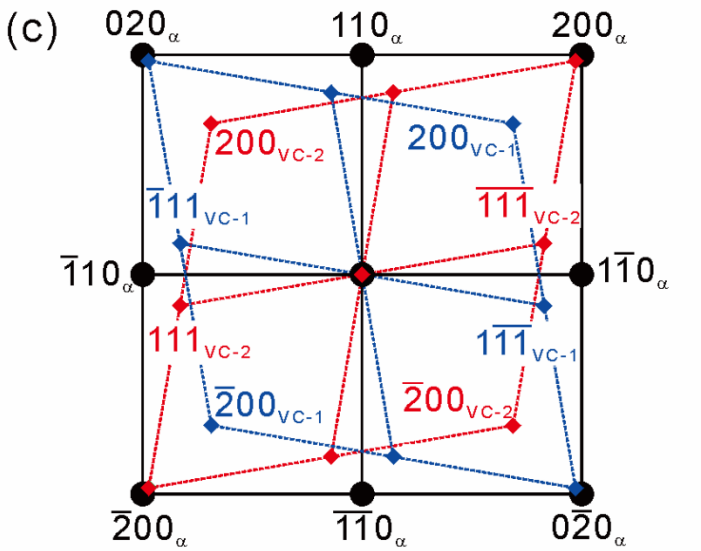
$$\Delta HV = HV_{M-added} - HV_{Pure\ Fe}$$
$$= HV_{ss} + HV_{disl} + HV_{ppt}$$

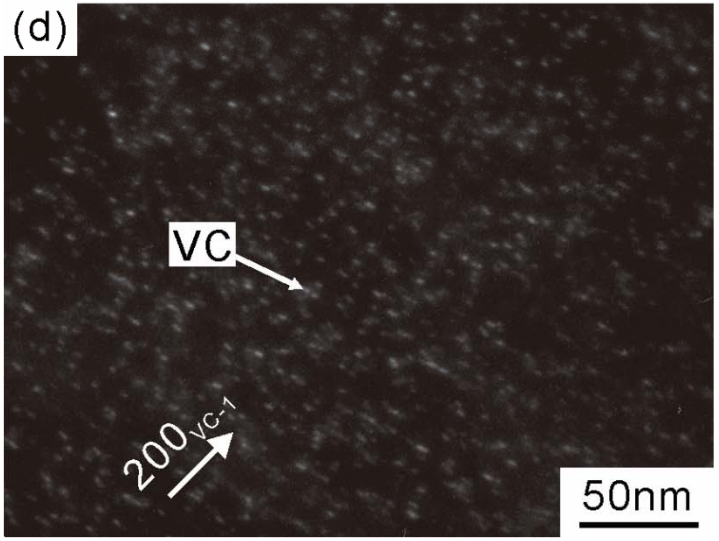


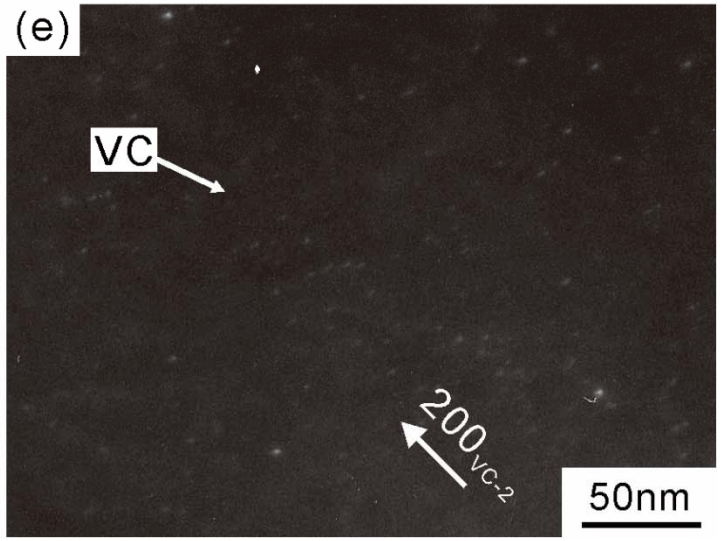
- Higher hardness increment of α by precipitation strengthening can be obtained by reducing the inter-particle spacing of MC.

Single variant of randomly dispersed VC precipitates

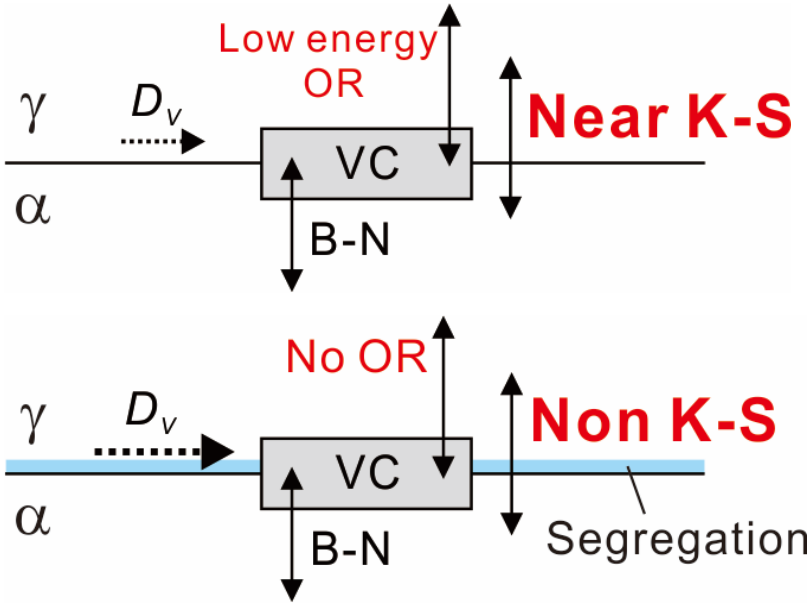








Promotion of VC nucleation at non K-S interface



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

	σ (J / m²)	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]

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

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

$= 2.4\ \mathrm{J/m^2}$ 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.

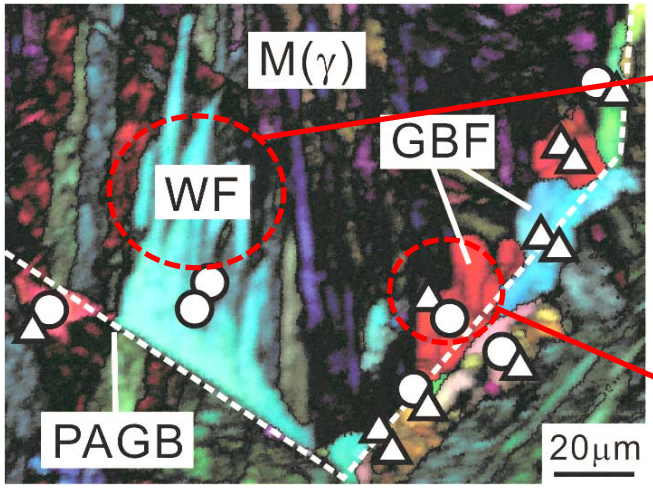
[1] M. Enomoto et al., *PTM* (2005) 67.
[2] L.E. Murr, *Int. Phen. in Metals and Alloys* (1975) 124.
[3] T. Furuhara et al., *ISIJ Int.* 43 (2003) 1630.
[4] D.H.R. Fors et al., *Phys. Rev. B.* 82 (2010) 195410.

VC precipitation in α with different α/γ orientation relationship

923K, 60s

α orientation map

○ : Near K-S (Δθ ≦ 5deg.);
△ : Non K-S (Δθ ＞ 5deg.)



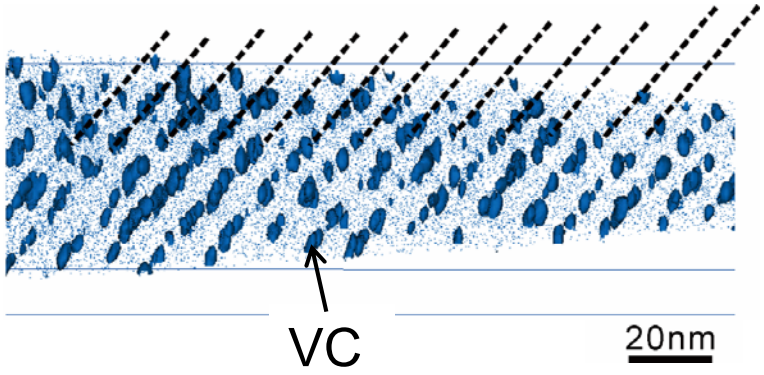
PAGB: prior γ grain boundary; M(γ): martensite;
GBF: grain boundary α; WF: Widmanstatten α;

Δθ: deviation angle from the exact Kurdjumov-Sachs orientation relationship (K-S OR)

Three-dimensional V atom map

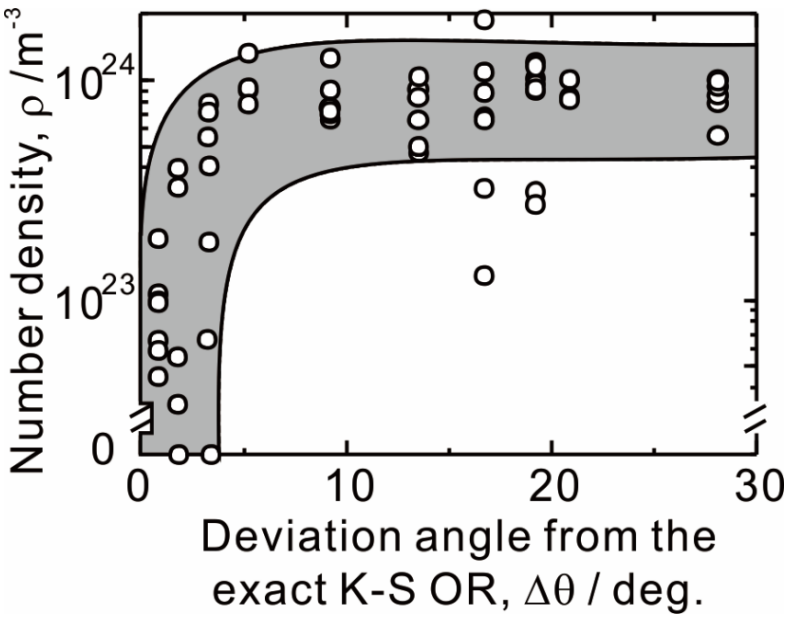
WF (Δθ = 0.8deg.)

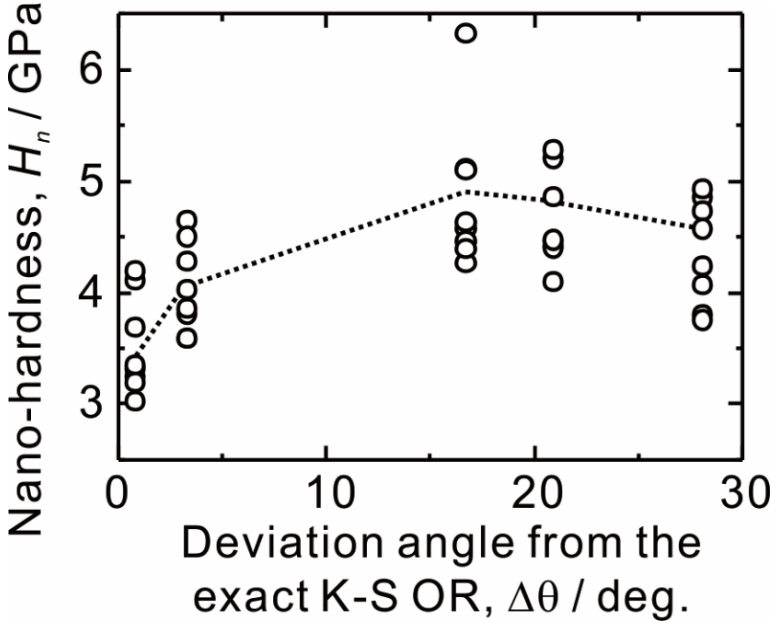
GBF (Δθ = 19.2deg.)



- 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.

Effects of α/γ OR on dispersion of VC interphase precipitation





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.