Grain Boundary Diffusion of Iron , Cobalt and Chromium in High Purity Iron

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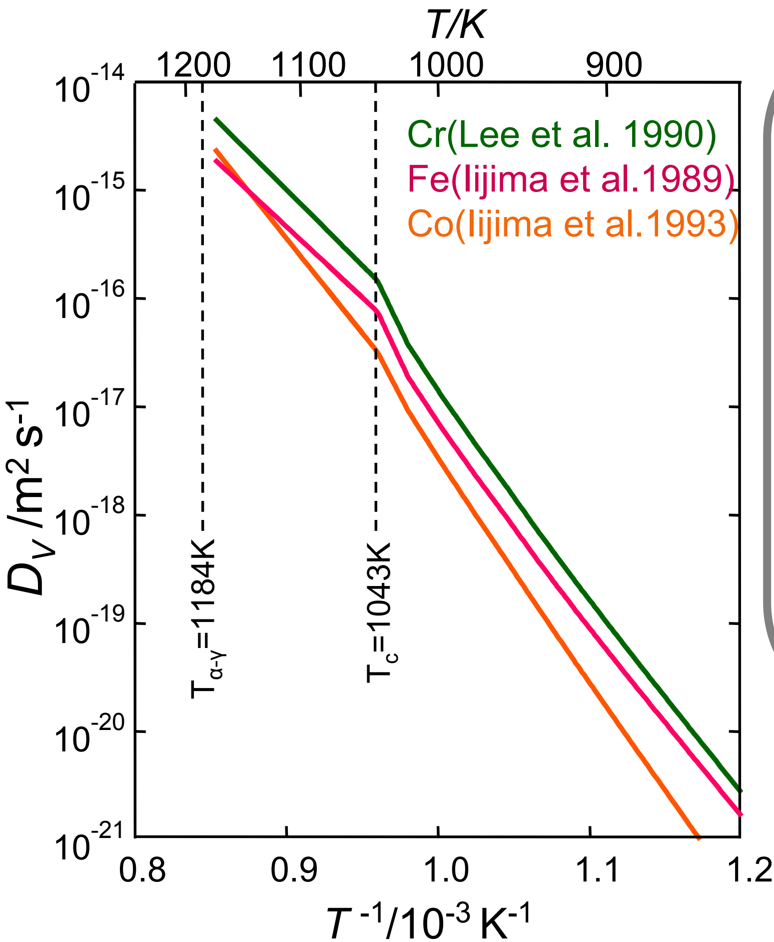
Introduction *Volume diffusion in High Purity Iron*



Self-diffusion

→Downward deviation below T_c

Impurity diffusion

Magnetic influence

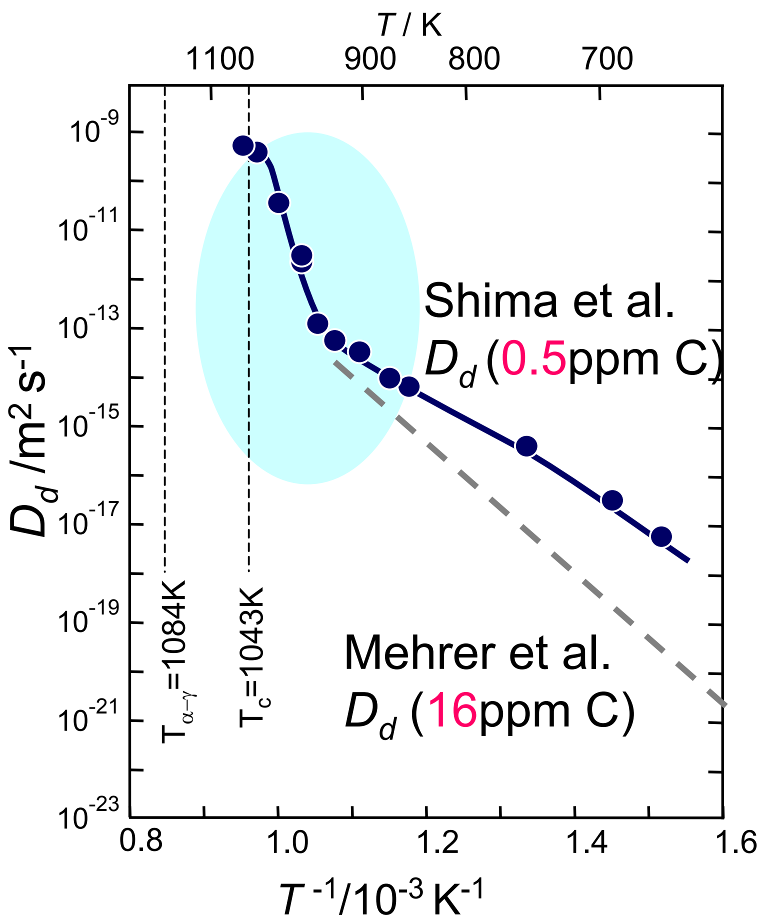
Co : larger
Cr : smaller } → than Fe

+

Isotope effect

The influence of magnetic spin ordering

Introduction *Self-diffusion along dislocation in Iron*



Dislocation diffusion

Mehrer (16ppm C)

→ Linearity

↕

Shima (0.5ppm C)

→ *decrease remarkably*

↑ Magnetic influence

↓

D_d : stronger than that on D_v

Grain boundary diffusion

Large magnetic influence

↕

High purity iron : not studied

Objective

Accurate determination of the grain boundary diffusion

and the influence of magnetic spin ordering

on grain boundary diffusion in high purity iron

Preparation of Specimens

High purity electrolytic iron (.1)

↓

Induction-melting
(in a cold-cupper crucible)

↓

Hot-forging and machining (..)

↓ Grain size.500μm

Electro-polishing

↓

Annealing
to stabilize grain boundary

↓ Grain size.2~3mm

Mechanical and electro-polishing

↓

Annealing (.3)

Table1, Chemical composition [mass ppm]

..	**C**	**N**	**O**	**P**	**S**		
	8	**5**	**40**	**1**	**2**		
	Ni	Cr	Si	B	Cd	Cu	
	8	1	2	1	1	1	
	Co	H	Mn	As	Sn		
	36	2	5	1	1		
.2	**C**	**N**	**O**	**P**	**S**	Ni	Si
	9	**<5**	**14**	**<1**	**<1**	7	0.2
.3	**C**	**N**	**O**	**P**	**S**		
	<0.7	**1.0**	**2.0**	**<0.5**	**1.0**		

Experimental Procedure

Electroplating

↓

Diffusion annealing

↓

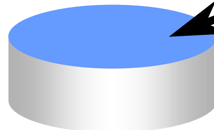
Serial sectioning

↓

Measurement of emitted radioactivities

↓

Penetration profiles

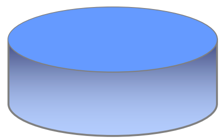


The radioactive tracers

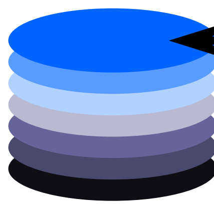
^{59}Fe (γ-ray 1.095 and 1.292MeV, half-life 3.84Ms)

^{57}Co (γ-ray 0.122MeV, half-life 23.4Ms)

^{51}Cr (γ-ray 0.3205MeV, half-life 2.39Ms)



523~1173K

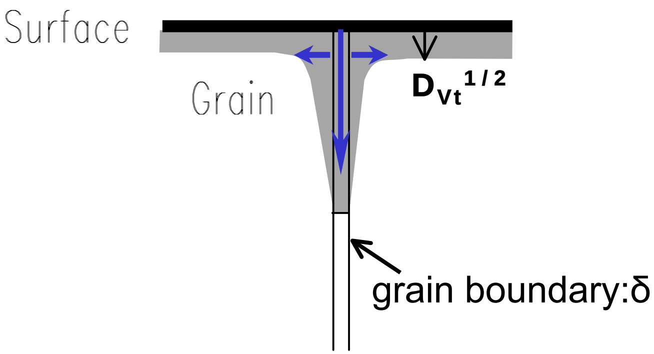


Rate: 0.2~5μm/section

Analysis of Grain Boundary Diffusion

<Type B> $100\delta < (D_v)^{1/2} < d/20$

High Temperature
Long annealing time

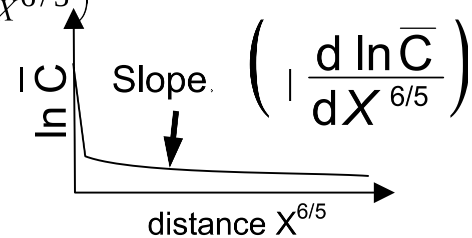


Suzuoka's equation

$$s\delta D_{gb} = 1.206\left(\frac{D_V^{0.585}}{t^{0.605}}\right)^{\frac{1}{1.19}}\left(\frac{d\ln\bar{C}}{dX^{6/5}}\right)^{\frac{5}{2.975}} \quad (10^2 < \beta < 10^4)$$

$$s\delta D_{gb} = 1.308\left(\frac{D_V}{t}\right)^{\frac{1}{2}}\left(\frac{d\ln\bar{C}}{dX^{6/5}}\right)^{\frac{5}{3}} \quad (10^4 < \beta)$$

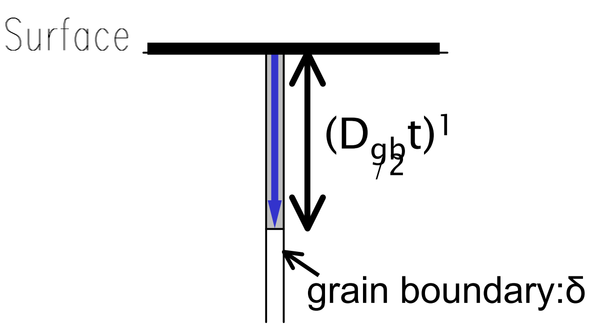
$$\beta = \frac{s\delta D_{gb}}{2D_V^{3/2}t^{1/2}}$$



penetration profile

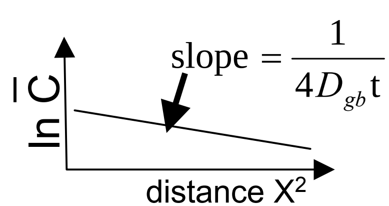
<Type C> $20\,(D_v)^{1/2} < \delta$

Low Temperature
short annealing time



The solution of Fick's second law

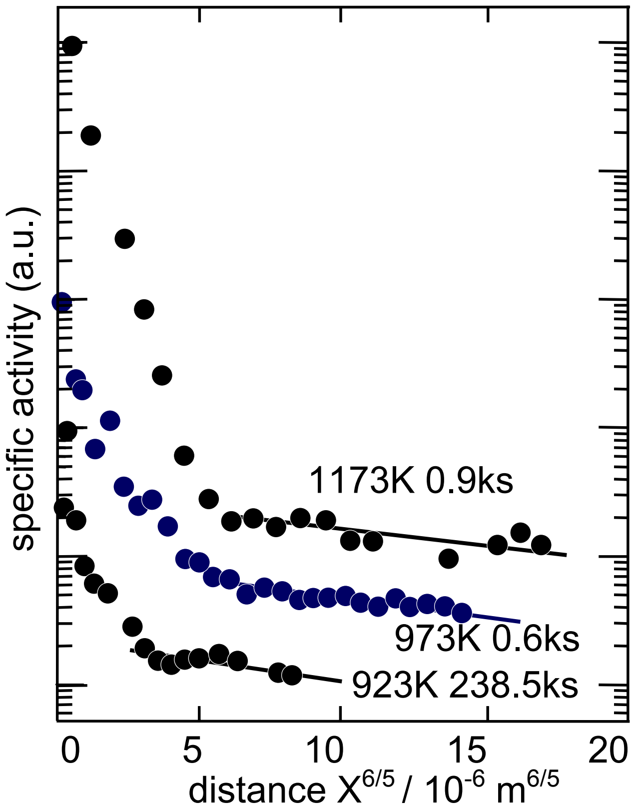
$$I(X,t) \propto \bar{C}(X,t) = \frac{M}{\sqrt{4D_{gb}t}}\exp\left(-\frac{X^2}{4D_{gb}t}\right)$$



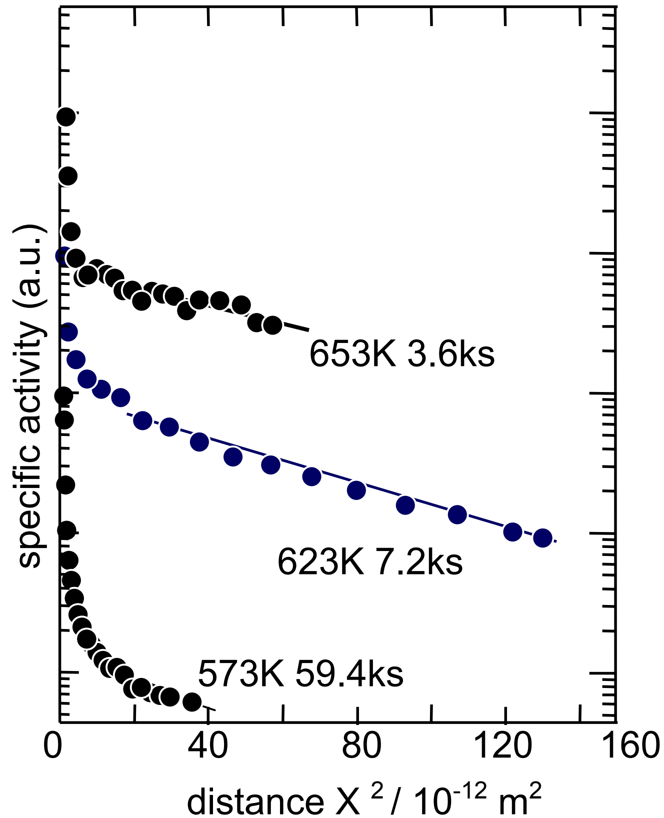
penetration profile

Results Penetration profiles of ^{59}Fe in High Purity Iron

a) Type B: 900~1173K



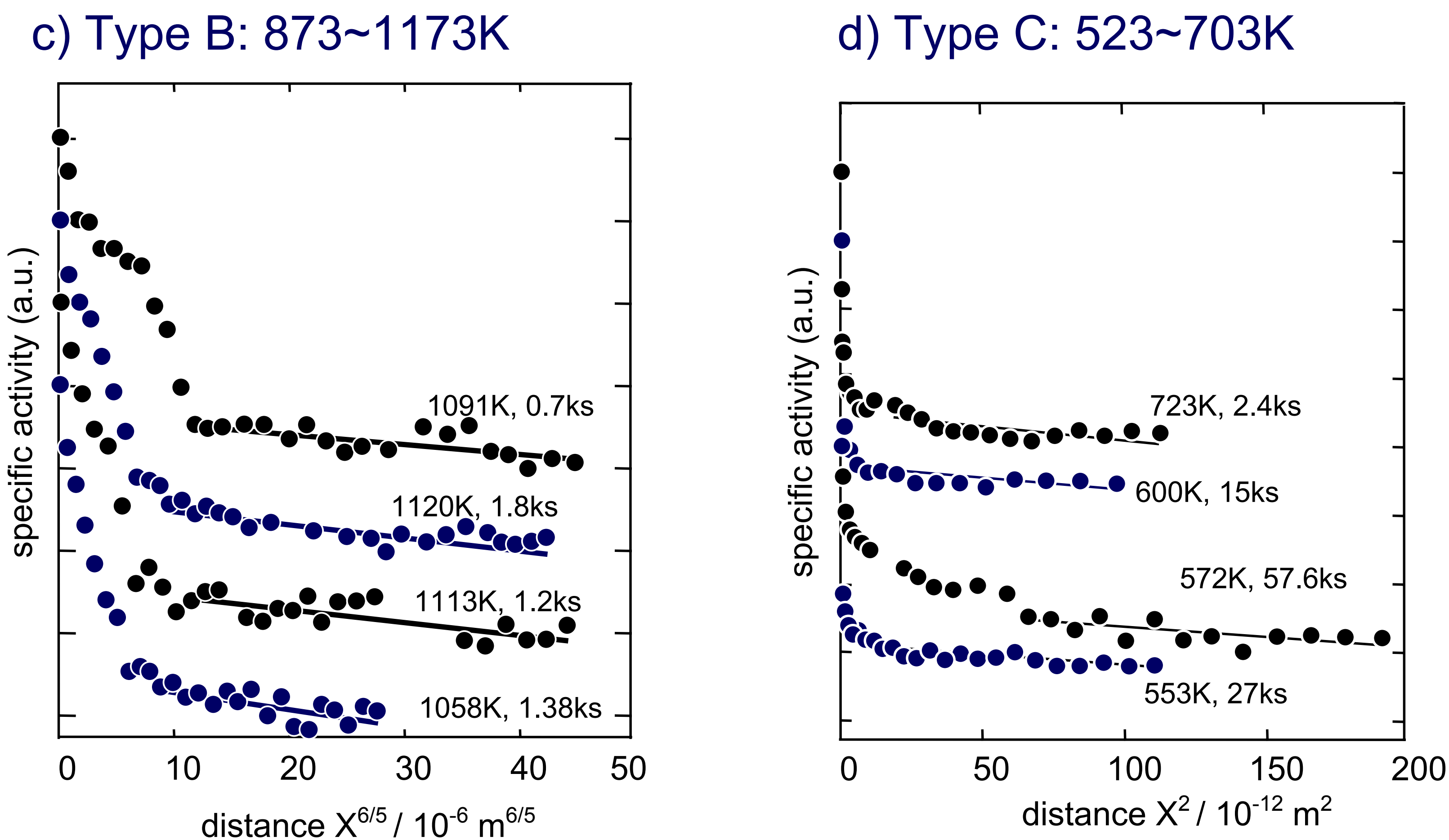
b)Type C: 500~850K



Examples of penetration profiles for grain boundary diffusion of ^{59}Fe in high purity iron

a) Type B (900~1173 K) and b) Type C (500~850K)

Results Penetration profiles of ^{57}Co in High Purity Iron

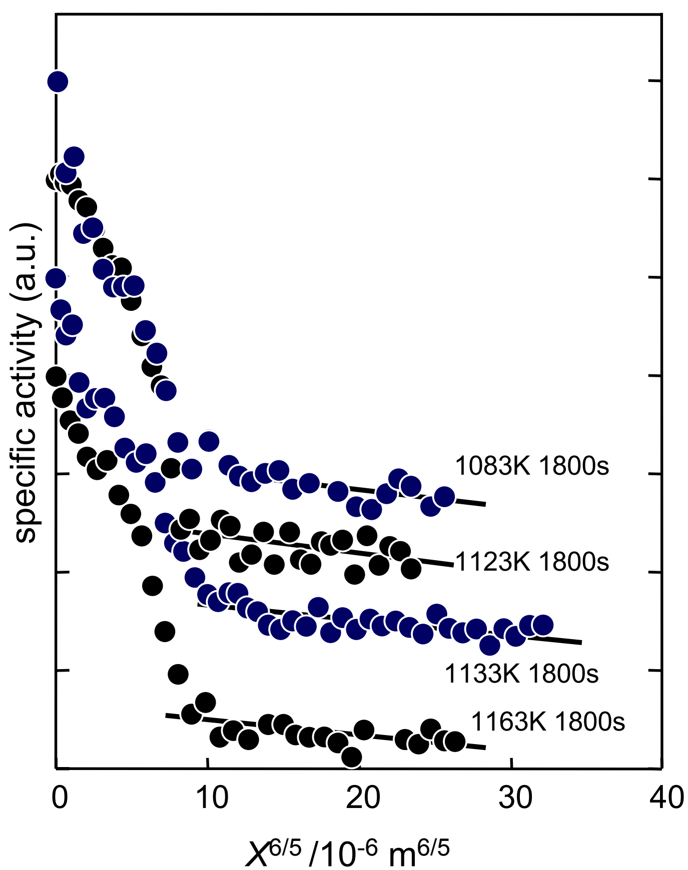


Examples of penetration profiles for grain boundary diffusion of ^{57}**Co** in high purity iron

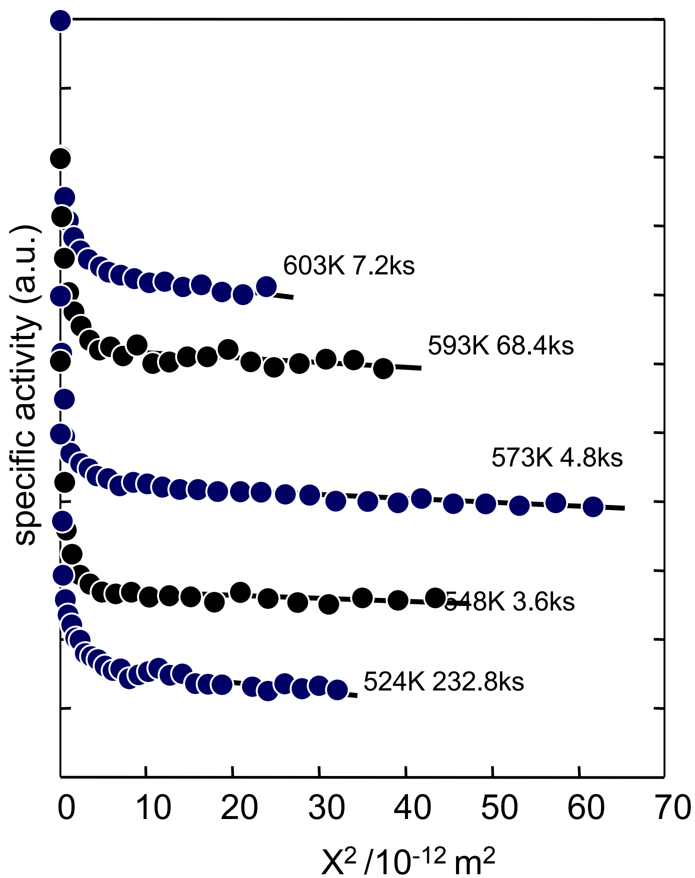
c) Type B(873~1173 K) and d) Type C(523~703K)

Results
Penetration profiles of ^{51}Cr in High Purity Iron

e) Type B: 1053~1163K



f) Type C: 524~603K

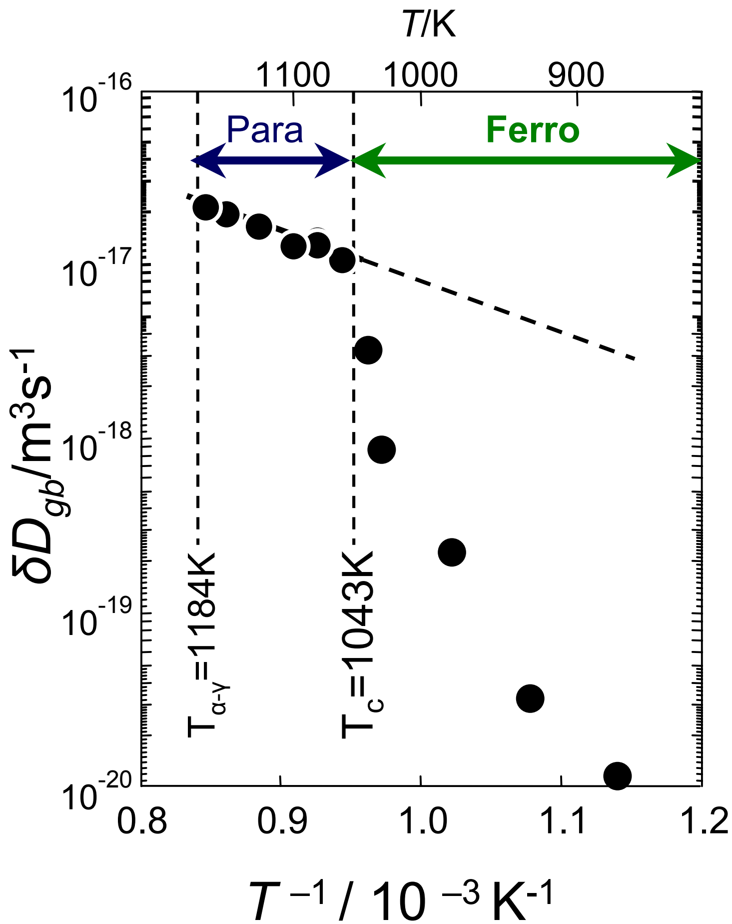


Examples of penetration profiles for grain boundary diffusion of **^{51}Cr** in high purity iron

e) Type B (1053~1163K) and f) Type C (524~603K)

Results Grain Boundary Diffusion of Fe in High Purity iron

Arrhenius plots of δD_{gb} of **Fe**
in Type B kinetics regime



Paramagnetic state

Linearity

Q^P=55.7kJmol^{-1}

$\delta D_{gb,0}$=6.53×10^{-15}m^{3}s^{-1}

Ferromagnetic state

Downward deviation

Grain Boundry Diffusion in iron

is affected by

Magnetic Spin Ordering

Results Grain Boundary Diffusion of Fe in High Purity iron

Volume diffusion

Ruch et al. 1976

$$D/\mathrm{m^2s^{-1}} = D^{\mathrm{P}}_{\mathrm{gb,0}} \exp\left[-\frac{Q^{\mathrm{P}}(1+\alpha M^2)}{\mathrm{R}T}\right]$$

M : the ratio of the spontaneous magnetization

α : extent of the influence of the magnetic spin ordering on diffusion

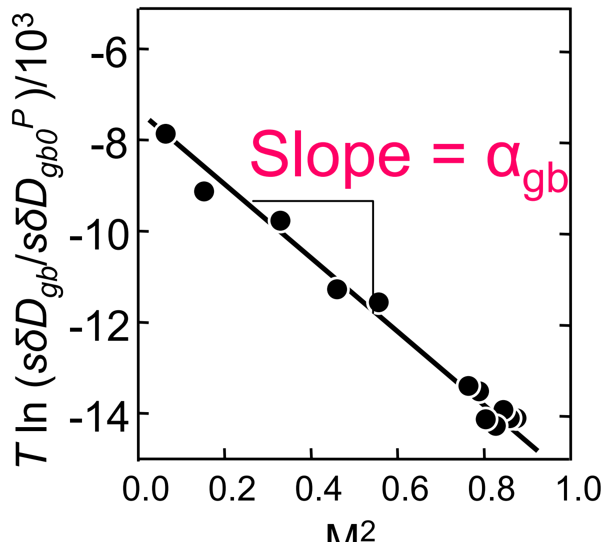
Extension

Grain boundary diffusion

$$\delta D\ /\mathrm{m^3s^{-1}} = \delta D^{\mathrm{P}}_{\mathrm{gb,0}} \exp\left[-\frac{Q^{\mathrm{P}}(1+\alpha M^2)}{\mathrm{R}T}\right]$$

$$\frac{RT}{Q^P}\ln\frac{\delta D}{\delta D^{\mathrm{P}}_{\mathrm{gb,0}}} = -(1+\alpha M^2)$$

$\alpha_{gb} = 1.28$



Results *Grain Boundary Diffusion of Fe in High Purity iron*

Grain boundary diffusion : δD_{gb}

$$\delta D\ /\mathrm{m^3s^{-1}} = \delta D^{P}_{gb,0} \exp\left[-\frac{Q^{P}(1+\alpha M^{2})}{RT}\right]$$

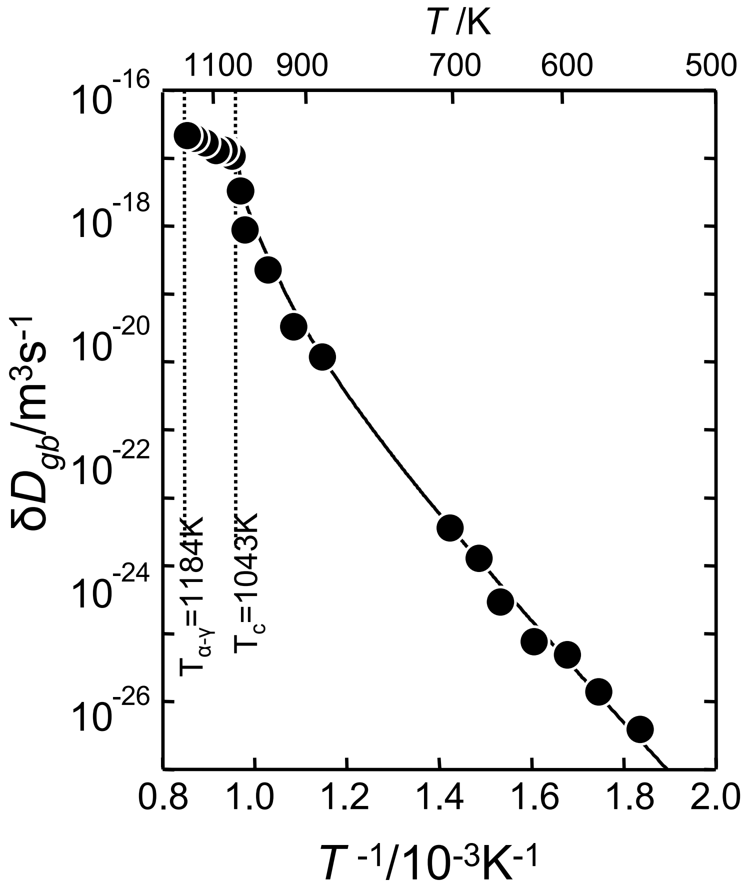
Q^P=55.7kJmol^{-1}

$\delta D_{gb,0}$=6.53×10^{-15}m^{3}s^{-1}

α_{gb} =1.28

$$\delta D_{gb}/\mathrm{m^3s^{-1}} = 6.53\times10^{-15} \times \exp\left[-\frac{55.7_{[\mathrm{kJ/mol}]}(1+1.28M^{2})}{RT}\right]$$

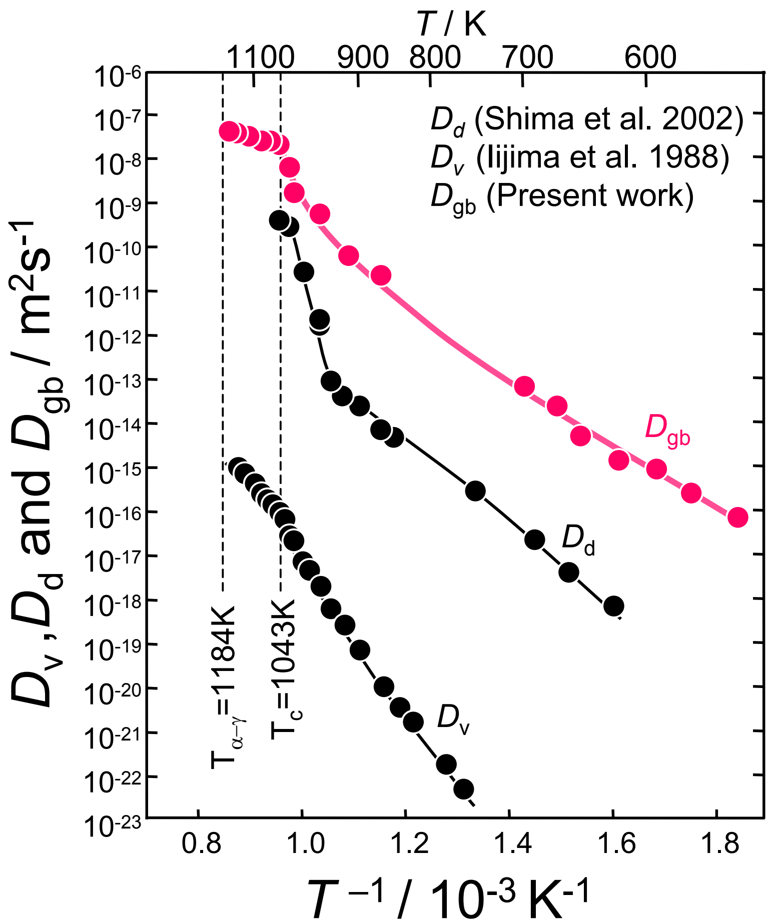
α_{gb}



Grain boundary diffusion in high purity iron

- The magnetic influence was observed *for the first time*

Results Self-Diffusion in High Purity iron



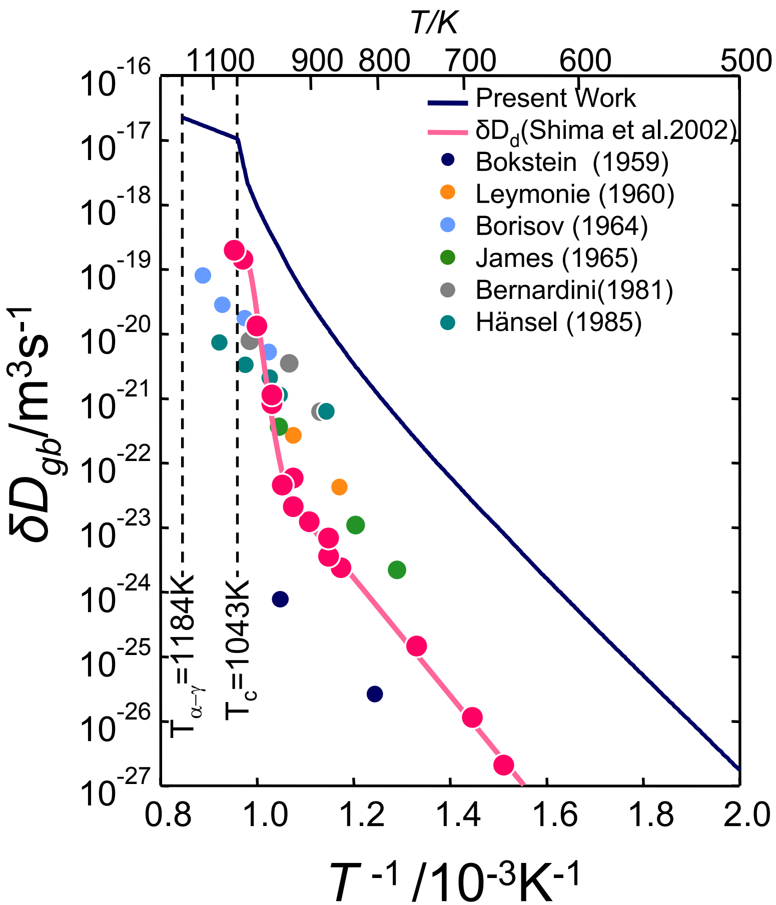
Self-diffusion in high purity iron

Affected by magnetic spin ordering

$\alpha_{gb} >> \alpha_V$

Results

Comparison with some previous works



Present work

Magnetic influence on D_{gb}

δD_{gb}:larger than the others

High purity iron

Previous works

δD_{gb}(past) ↔ D_d

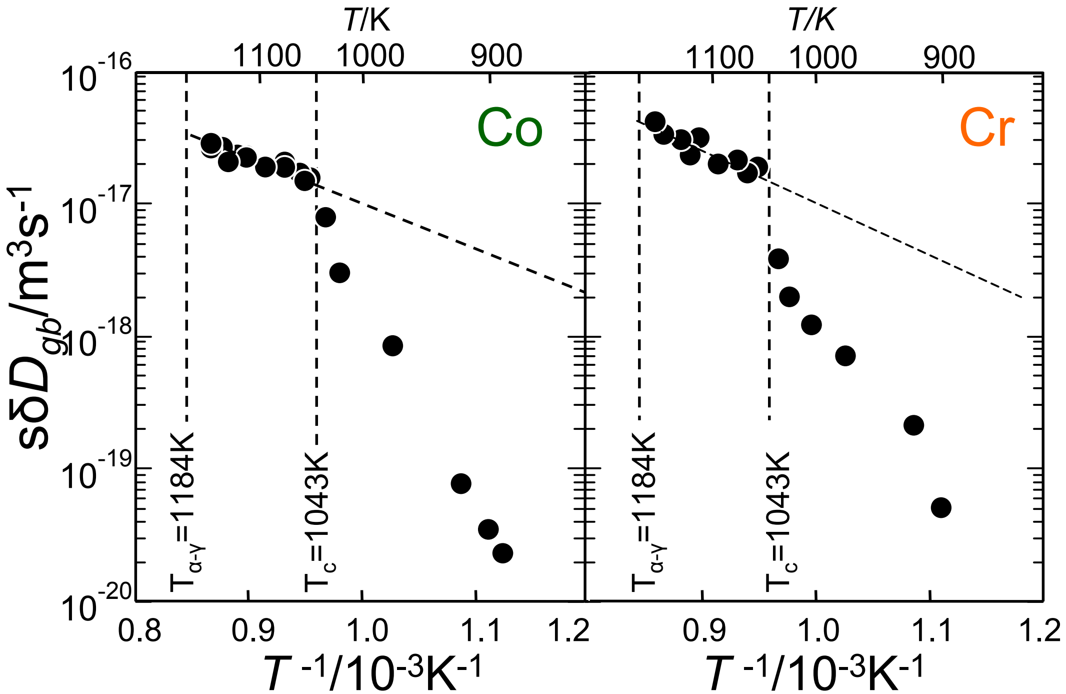
Character of grain boundary

various amouts of impurities

small angle grain boundary

Results

Arrhenius plots of $s\delta D_{gb}$ of ^{57}Co and ^{51}Cr in High Purity iron.



Paramagnetic state
Linear relationship

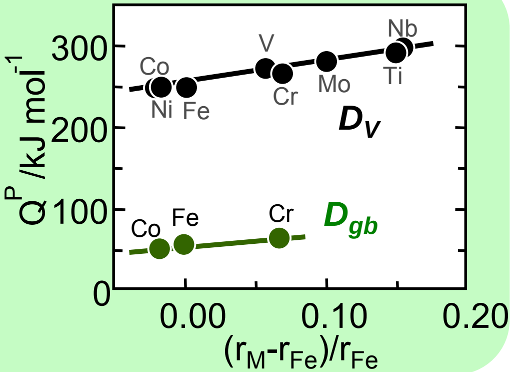
Ferromagnetic state
Downward deviation

Grain boundry diffusion is affected by *magnetic spin ordering*

	Co	Fe	Cr
Q^P/kJ mol^{-1}	50.4	55.7	63.4
$s\delta D_{gb,0}$ /$10^{-15}m^3s^{-1}$	5.0	6.3	28.3

$Q^P_{Cr} > Q^P_{Fe} > Q^P_{Co}$

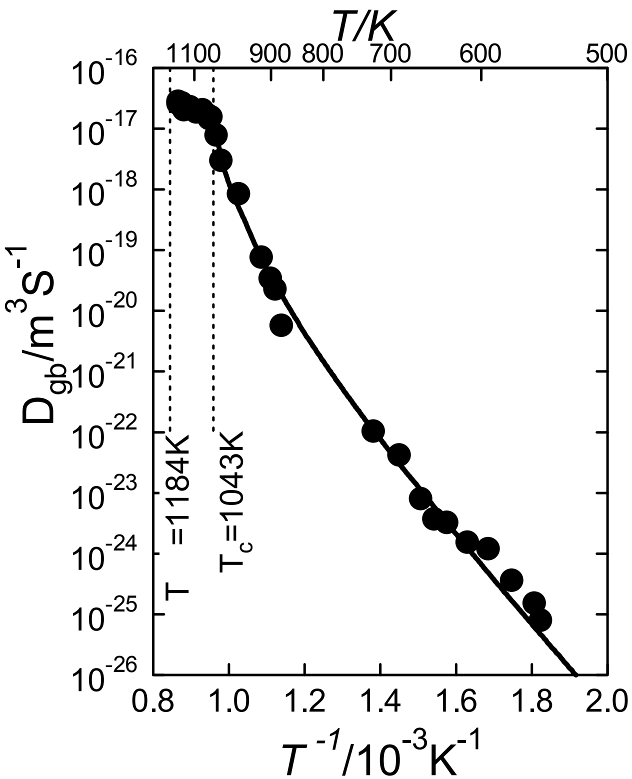
in proportion to the atomic radius



Results

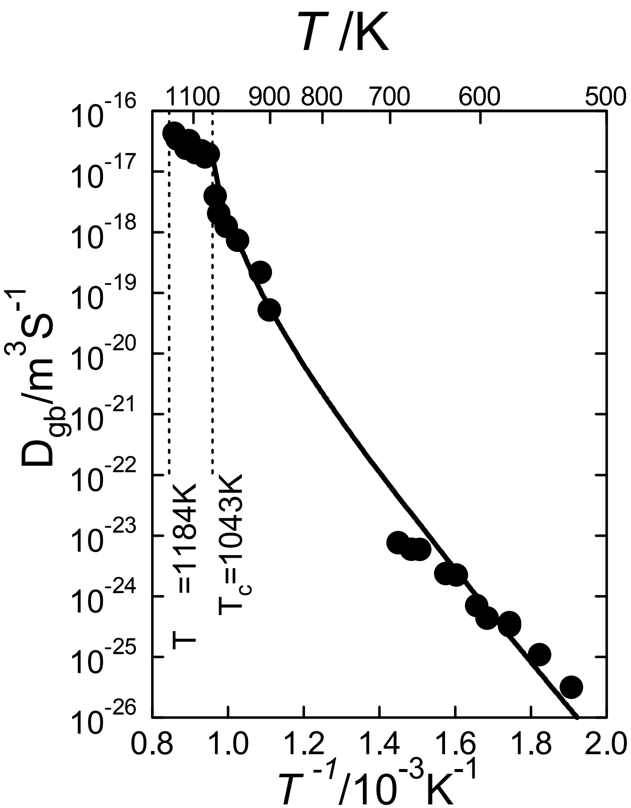
Arrhenius plots of sδD_{gb} of ^{57}Co and ^{51}Cr in High Purity iron.

Arrhenius Plot of sδD_{gb}, Co



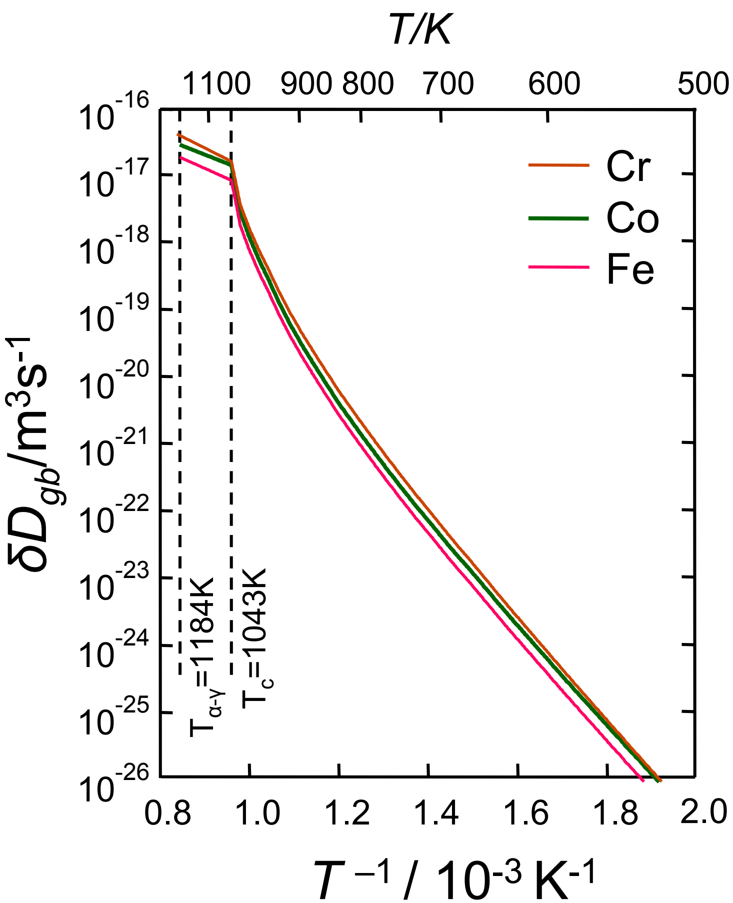
$$s\delta D_{gb}/m^3s^{-1} = 5.0\times10^{-15} \times \exp[-\frac{50.4_{[kJ/mol]}(1+1.49M^2)}{RT}]$$

Arrhenius Plot of sδD_{gb}, Cr



$$s\delta D_{gb}/m^3s^{-1} = 2.8\times10^{-14} \times \exp[-\frac{63.4_{[kJ/mol]}(1+1.05M^2)}{RT}]$$

Results *The Arrhenius plots of Fe, Co and Cr in High Purity Iron*



	Co	Fe	Cr
Q^P/kJ mol^{-1}	50.4	55.7	63.4
$s\delta D_{gb,0}$ /$10^{-15}m^3s^{-1}$	5.0	6.3	28.3
α	**1.49**	**1.28**	**1.05**

Ferromagnetic state

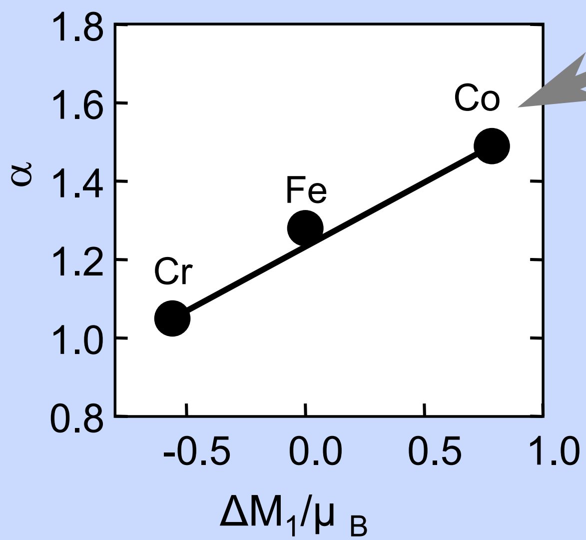
Degree of magnetic influence

$$\alpha_{Co} > \alpha_{Fe} > \alpha_{Cr}$$

α : Extent of the influence of magnetic spin ordering on grain boundary diffusion

Discussion The influence of magnetic spin ordering on Grain Boundary Diffusion in iron

Magnetic influence on grain boundary diffusion



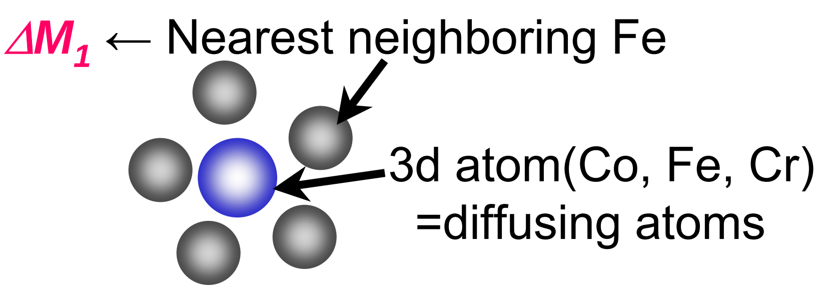
Drittler et al. (1988)

ΔM_1: the change of **local magnetic moment**

α : the extent of the influence of magnetic spin ordering on **diffusion**

ΔM_1-α : Linear relationship

The magnetic influence on grain boundary diffusion is caused by **the *magnetic field* of the *nearest neighboring* iron atoms**



Conclusion

1. The influence of magnetic spin ordering on grain boundary diffusion in iron was observed.

2. The degree of influence of magnetic spin ordering on grain boundary diffusion was larger than that on the volume diffusion.

3. The influence of magnetic spin ordering changes in the following order:

4. The temperature dependence of the Grain Boundary diffusivities of Fe, Co and Cr in high purity α-iron was expressed as follows,

Fe: $$s\delta D_{gb}/\mathrm{m^3s^{-1}} = 6.35^{+6.21}_{-3.19} \times 10^{-15} \exp\left\{-\frac{(55.7 \pm 6.1\,\mathrm{kJ\,mol^{-1}})[1+(1.28 \pm 0.03)M^2]}{RT}\right\}$$

Co: $$s\delta D_{gb}/\mathrm{m^3s^{-1}} = 5.00^{+4.17}_{-2.27} \times 10^{-15} \exp\left\{-\frac{(50.4 \pm 5.5\,\mathrm{kJ\,mol^{-1}})[1+(1.49 \pm 0.03)M^2]}{RT}\right\}$$

Cr: $$s\delta D_{gb}/\mathrm{m^3s^{-1}} = 2.82^{+21.0}_{-2.94} \times 10^{-14} \exp\left\{-\frac{(64.3 \pm 18.5\,\mathrm{kJ\,mol^{-1}})[1+(1.05 \pm 0.03)M^2]}{RT}\right\}$$