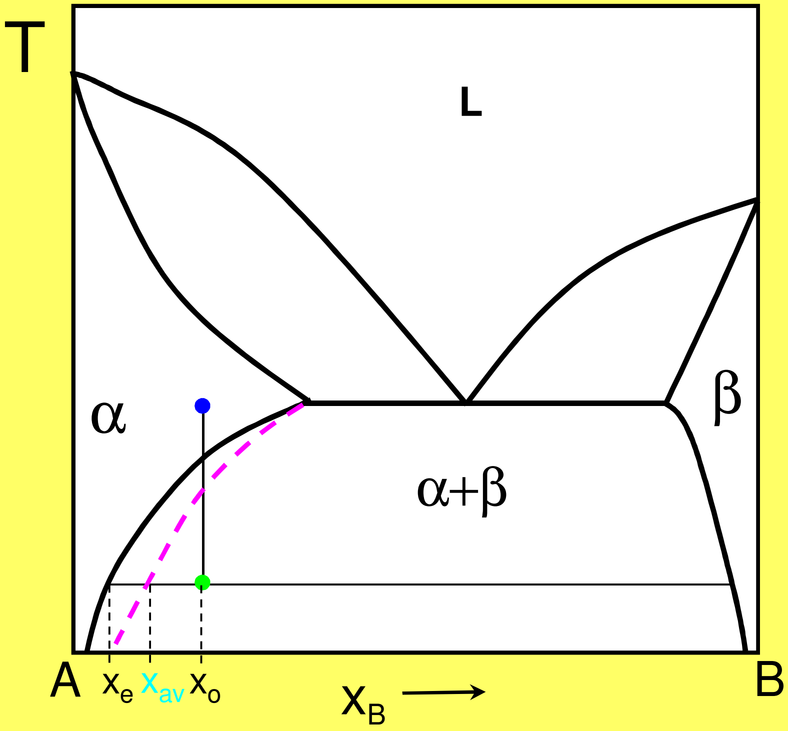
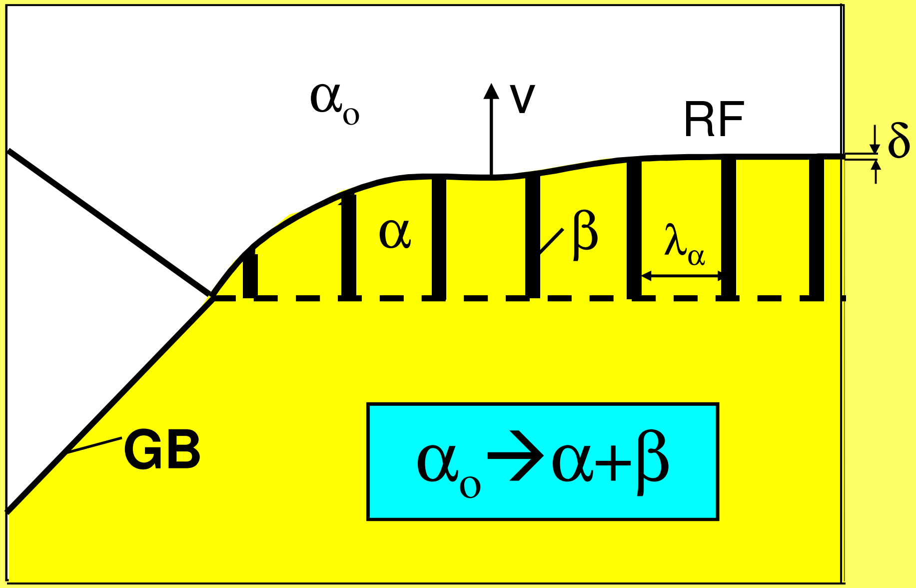
Characterization of the kinetics of diffusion process at migrating interface of discontinuous precipitates

1. **Introduction**
2. **Global characterization of the DP reaction**
3. **Unsolved problems**
4. **Local characterization of the DP reaction via AEM**
5. **Principles of high resolution microchemical analysis of lamellar structures**
6. **Grain boundary diffusivities via AEM**
7. **Concluding remarks**

Discontinuous Precipitation (DP) Reaction





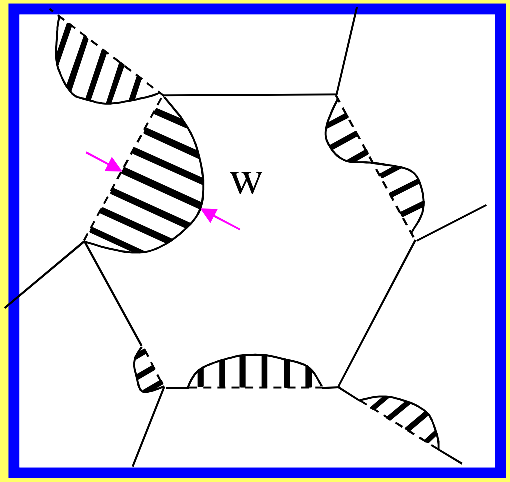
The solute redistribution occurs at the moving RF.

There exists an excess of solute atoms within the α lamella compared to the equilibrium state

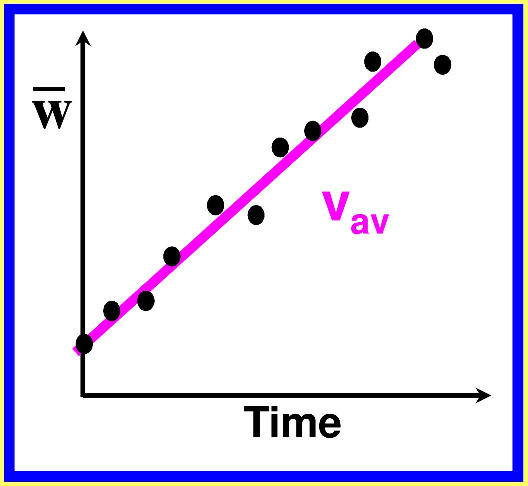
Global Concept of DP Reaction

All the parameters represent the average values for the whole population of the cells in the sample

Quantitative metallography: λ_α, v_{av}



$\overline{w}=\pi w/4$



X-ray diffraction: average solute concentration in the α lamellae: x_{av}

Diffusion Models - Global Concept

Cahn´s model

$$\frac{x_o - x_{av}}{x_o - x_e} = \frac{2}{\sqrt{C}} \tanh \frac{\sqrt{C}}{2}$$

$$s\delta D_b = \frac{v_{av}\lambda_\alpha^2}{C}$$

Petermann- Hornbogen (P-H) model

Z. Metallkde 59 (1968) 814

$$s\delta D_b = \frac{v_{av}\lambda_\alpha^2 RT}{8\Delta G}$$

D_b-grain boundary (GB) chemical diffusion coefficient

s-segregation factor

ΔG-driving force for the DP reaction: $\Delta G = f(x_{av}, x_o, x_e)$

R-gas constant

T-absolute temperature of the DP reaction

x_o, x_e -solute content in the alloy and at the α/β interface

Questions

Why?

(Petermann-Hornbogen model) (Cahn´s model)

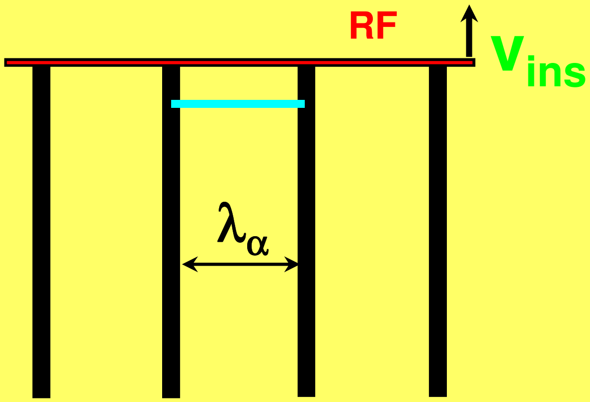
$s\delta D_b \approx 10^2 \ldots 10^4 \times s\delta D_b$

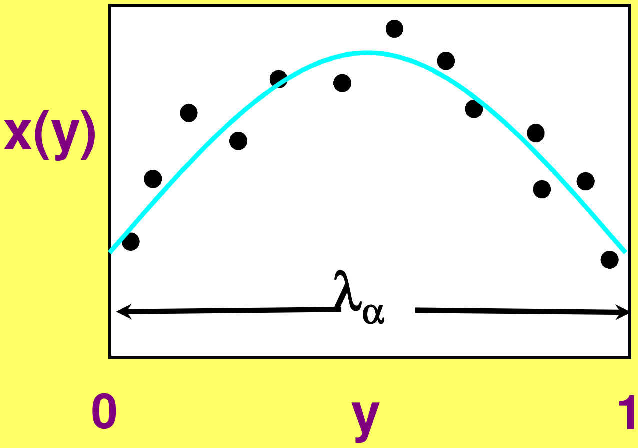
Does diffusivity at the migrating grain boundary (GB) occur at the same speed as for the stationary GB?

Local Concept of DP Reaction

All the parameters are relevant for the individual set of α and β lamellae (single cell)

DP - Solute concentration profile across the α lamella





J.W. Cahn: *Acta Metallurgica* 7 (1959) 18

$$\delta D_b \frac{d^2 x_b}{dx^2} - v\,\left[x(y) - x_o\right] = 0$$

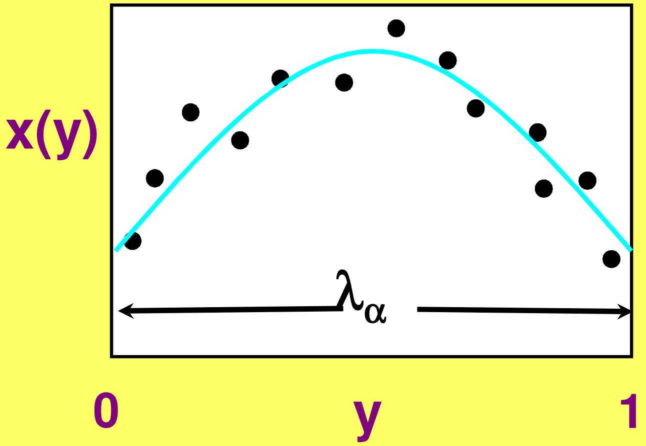
Boundary conditions: For y=0 and y=1 y(x) = x_e

$$x(y) = (x_e - x_o)\frac{\cosh\left[(y-0.5)\sqrt{C}\right]}{\cosh(\sqrt{C}/2)} + x_o$$

$$C = \frac{v_{ins}\lambda_\alpha^2}{s\,\delta D_b}$$

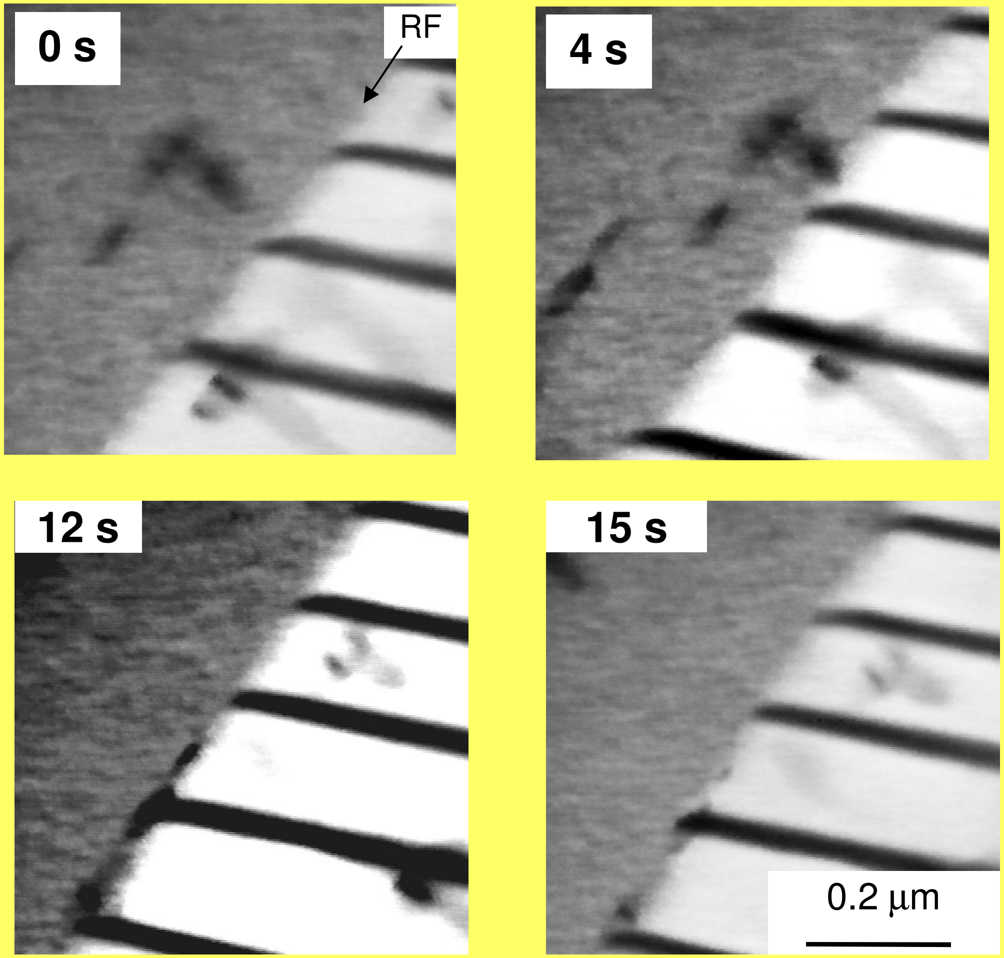
$$s = \frac{x_b}{x_o}$$

v_{ins} – instantaneous growth rate,
λ_α – thickness of α lamella,
x_e – equilibrium concentration at α/β interface,
x_o – solute content in alloy,
δ – width of grain boundary,
s - segregation factor,
$s\delta D_b$ – diffusivity at moving grain boundary

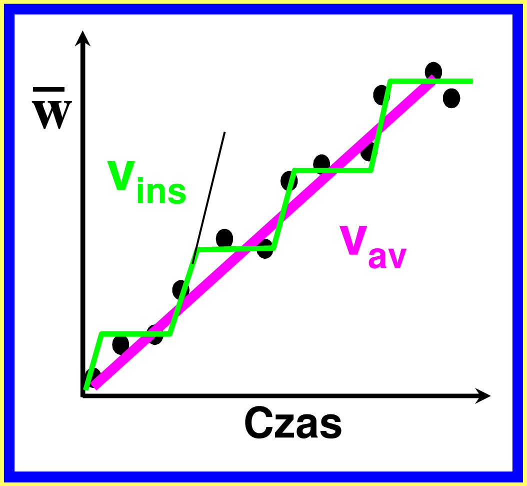


Growth velocity of the DP reaction

In-situ observation in TEM



Al-22 at.% Zn
aged at 450 K

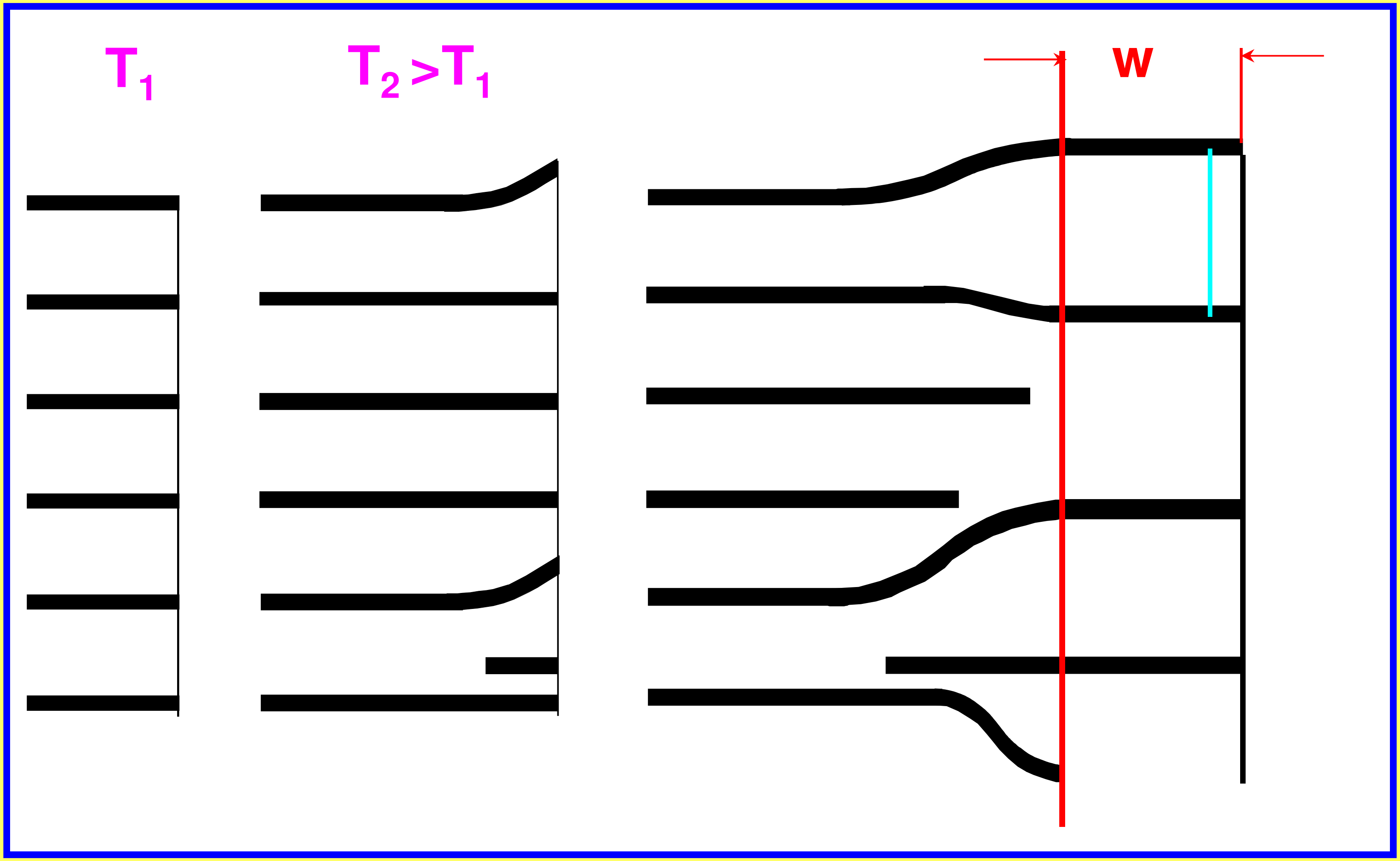


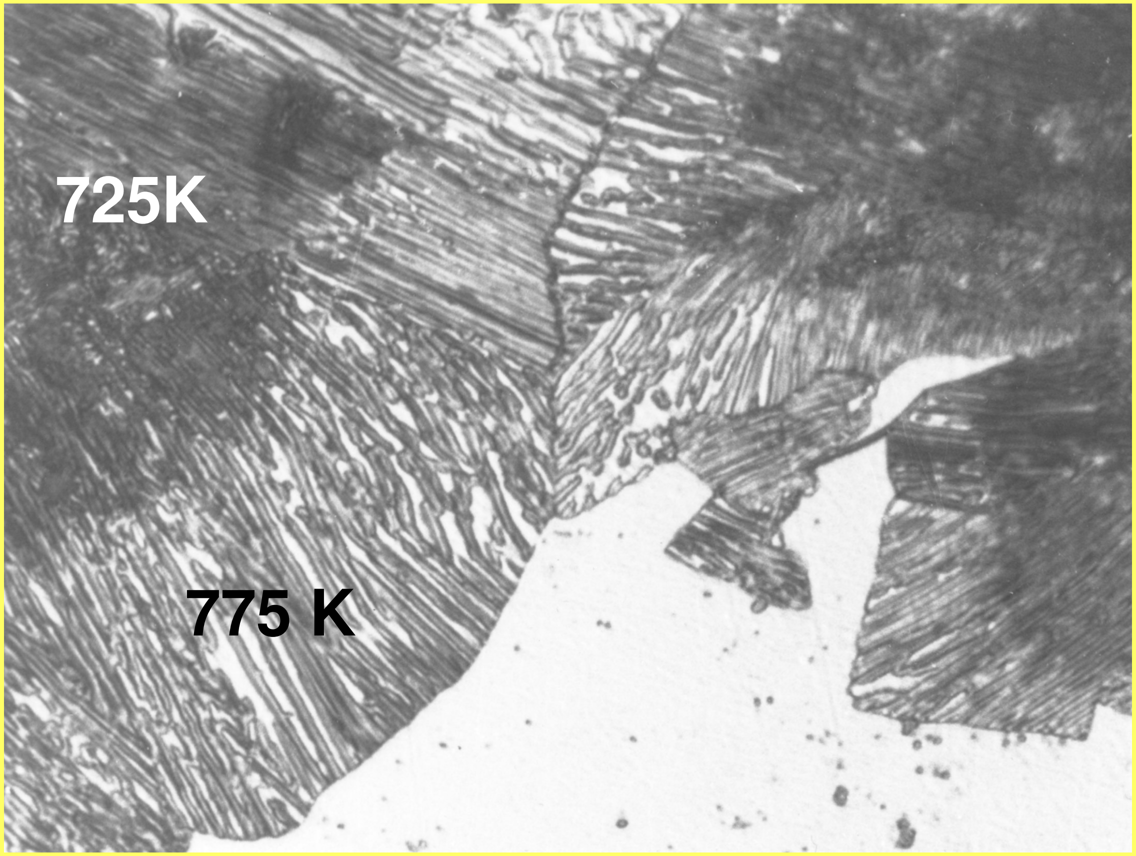
Stop- and –Go ⇨ v_{av}

only Go ⇨ v_{ins}

$v_{ins} >> v_{av}$

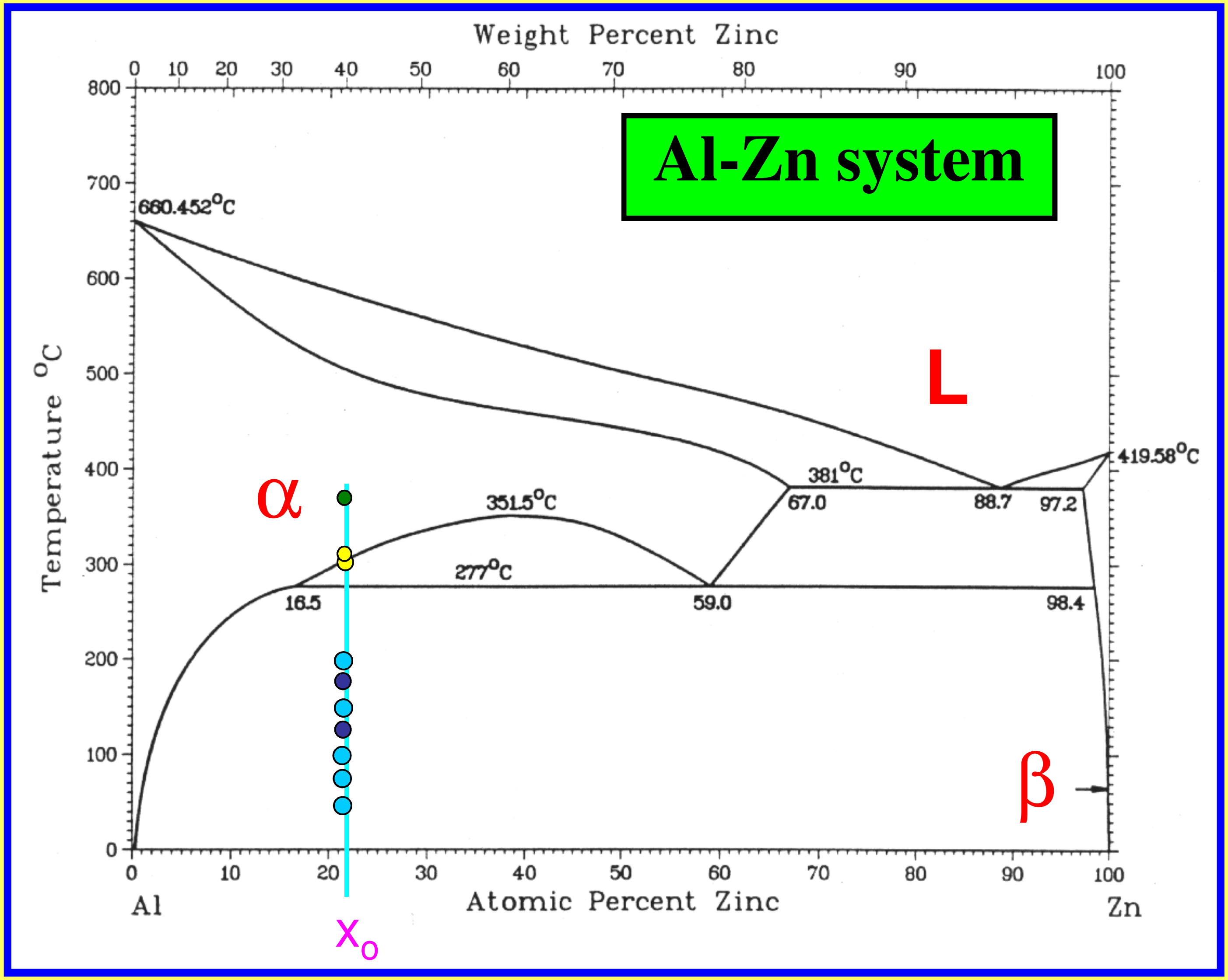
Two-step ageing procedure



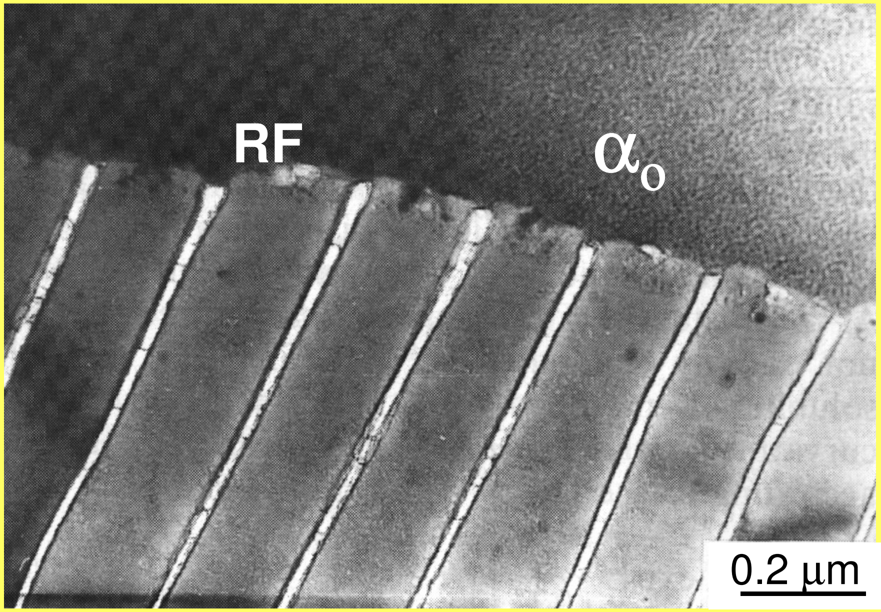


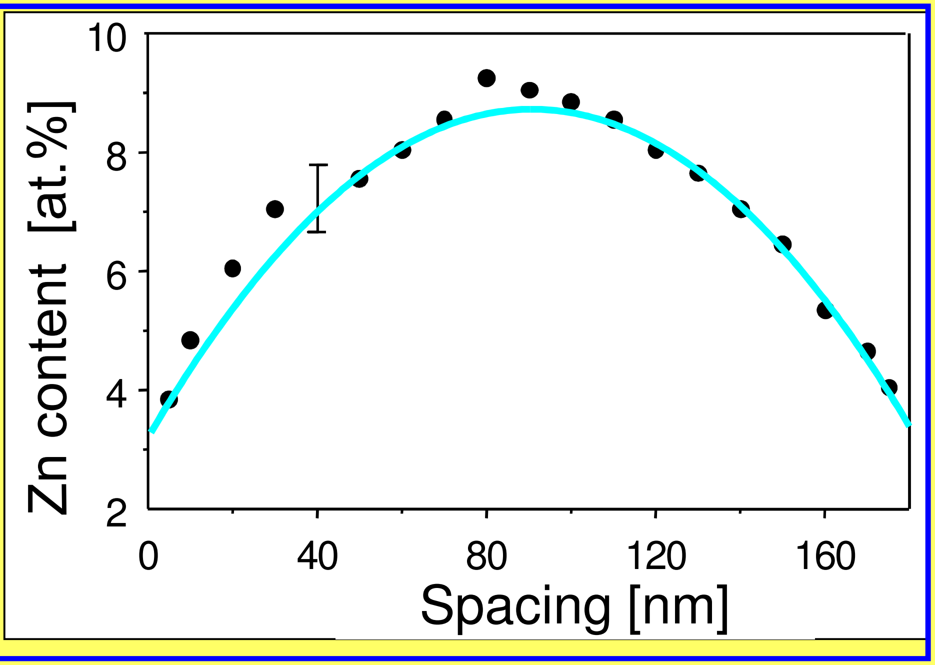
P. Zięba, W. Gust, *Acta mater.* 47, (1999) 2641
Ni-4 at.% Sn alloy aged for 250 h at 725 K
followed by 60 h at 775 K.

- The α lamellae exhibited approximately the same thickness for a sufficiently long distance;
- The thickness of several neighbouring α lamellae within the same colony remained more or less the same;
- No distinct changes of the reaction front velocity within the same colony
- Any case of increasing the α lamella spacing, preceding branching or re-nucleation of the new β lamella, is not taken into account;
- The influence of the stop- and -go fashion of the reaction front movement on the solute concentration profiles is avoided.


Al-Zn system
Weight Percent Zinc
0
10
20
30
40
50
60
70
80
90
100
Temperature °C
800
700
600
500
400
300
200
100
0
660.452°C
L
α
β
419.58°C
381°C
351.5°C
277°C
67.0
88.7
97.2
16.5
59.0
98.4
0
10
20
30
40
50
60
70
80
90
100
Atomic Percent Zinc
Al
Zn
x_o

Al-22 At.% Zn

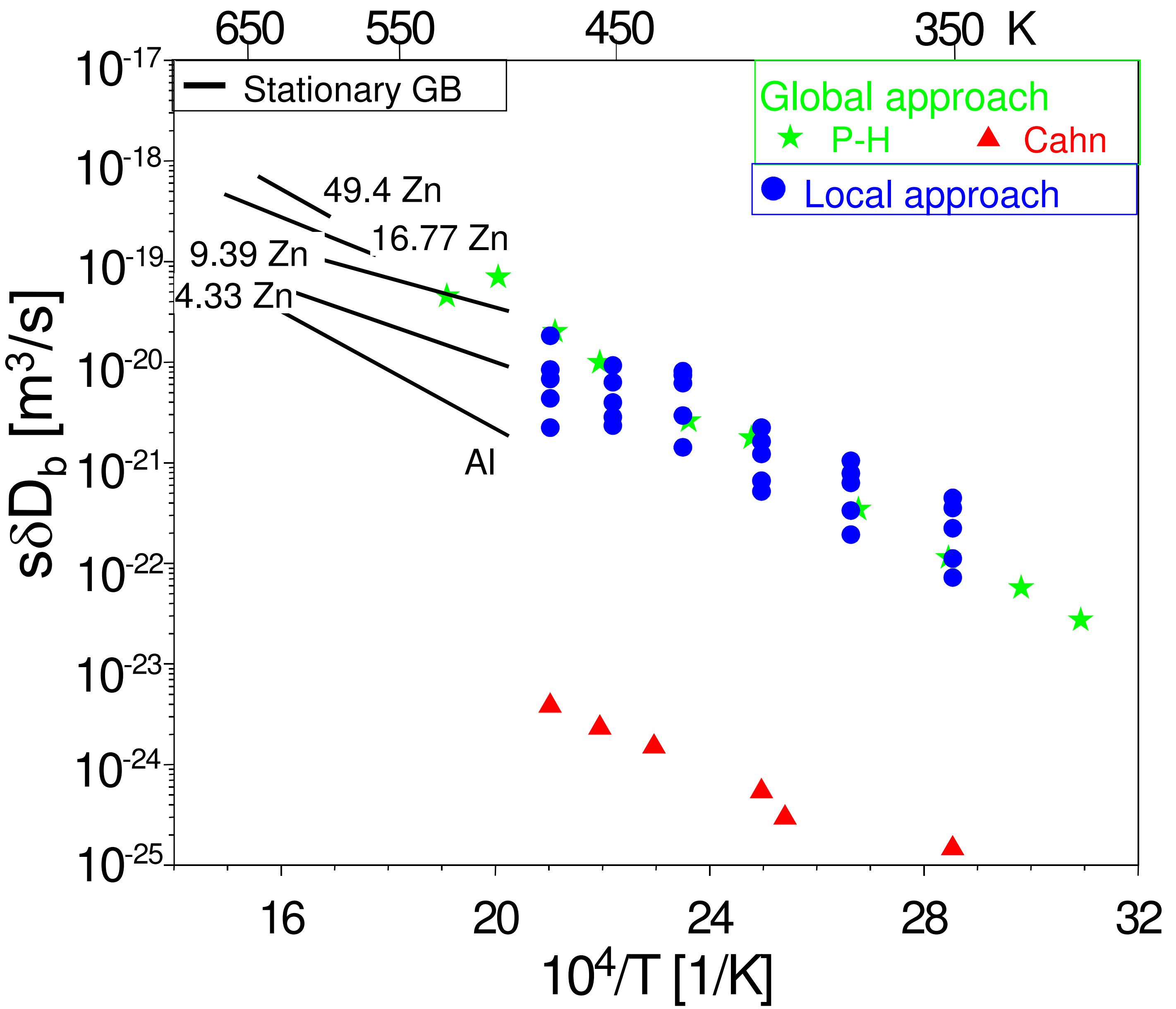




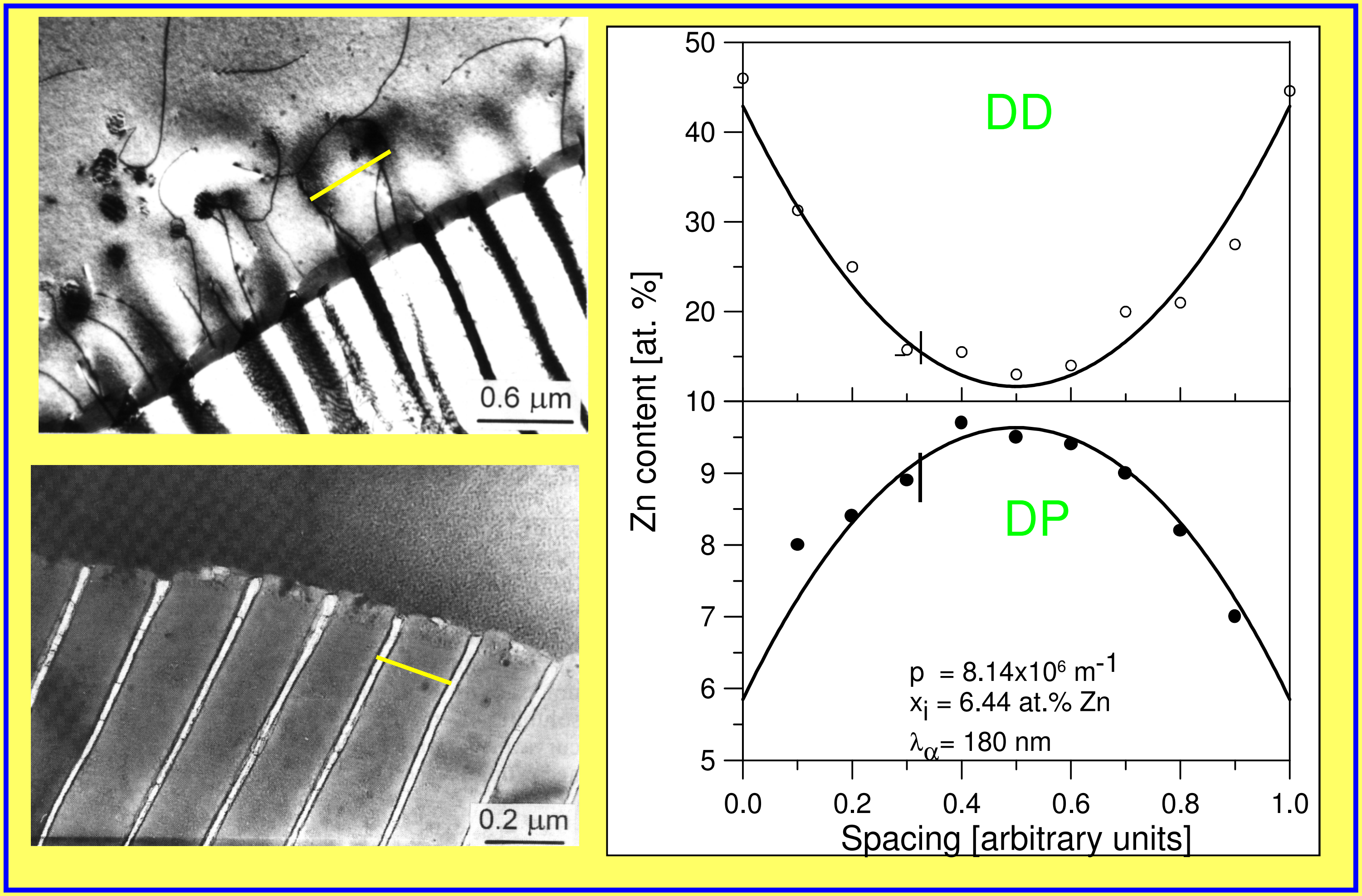
EDX analysis after DP reaction in the temperature range 350-475 K and for 5 different colonies.

Details of the a lamellae examined after ageing at 400 K in Al-22 at.% Zn alloy

Region of cells	Lamella analysed	λ_α (nm)	C	x_i (at.% Zn)	y(x=0.5) (at.% Zn)	v (nm/s)	$s\delta D_b$ (m^3/s)
1	1	210	2.14	3.28	7.38	86	1.8×10^{-21}
	2	225	1.66	4.32	7.44		2.6×10^{-21}
	3	205	2.51	3.74	8.27		1.4×10^{-21}
	4	195	1.95	3.51	7.29		1.7×10^{-21}
	5	240	2.21	4.07	8.08		2.2×10^{-21}
2	1	308	2.74	4.02	8.80	121	4.2×10^{-21}
	2	289	2.92	3.84	8.91		3.5×10^{-21}
	3	280	3.11	3.87	9.18		3.1×10^{-21}
	4	295	3.01	3.69	8.93		3.5×10^{-21}
	5	300	2.87	4.11	9.04		3.8×10^{-21}
3	1	154	1.84	3.54	7.10	57	0.7×10^{-21}
	2	167	1.75	3.76	7.13		0.9×10^{-21}
	3	143	1.71	3.91	7.19		0.7×10^{-21}
	4	148	1.68	3.62	6.90		0.7×10^{-21}
	5	159	1.62	3.82	6.97		0.9×10^{-21}

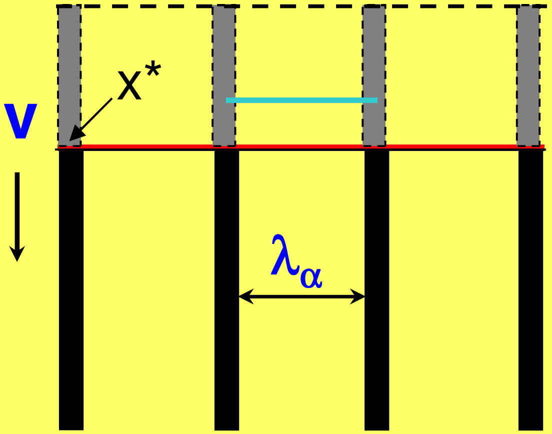

650
550
450
350 K
Stationary GB
Global approach
★ P-H
▲ Cahn
● Local approach
49.4 Zn
16.77 Zn
9.39 Zn
4.33 Zn
Al
10^{-17}
10^{-18}
10^{-19}
10^{-20}
10^{-21}
10^{-22}
10^{-23}
10^{-24}
10^{-25}
$s\delta D_b$ [m^3/s]
16
20
24
28
32
$10^4/T$ [1/K]

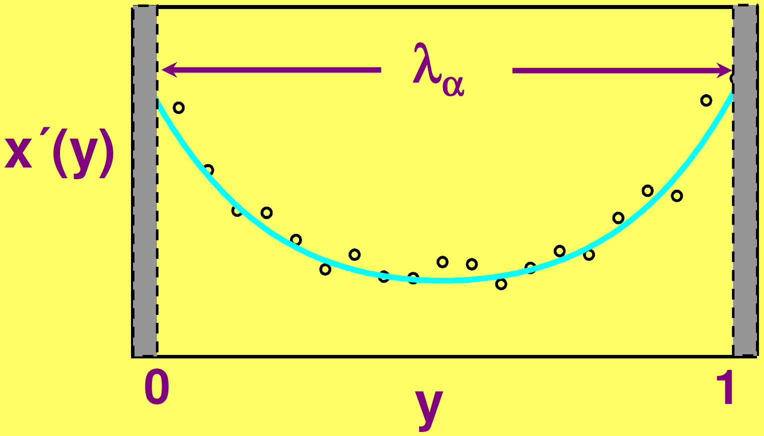
Al-22 at.% Zn



EDX analysis after DP reaction at 400 and 450 K and then after DD reaction at 560 K and 570 K, for 3 single cells of different colonies

DD-diffusion model





K.N.Tu, D.B. Turnbull: *Metall. Trans.* A2 (1971) 2509

Assumption: p=z (small difference between DP and DD temperatures)

P. Zięba, A. Pawłowski: *Scripta Metall.* 20 (1986) 1653

Separate description of p and z parameters (p≠z)

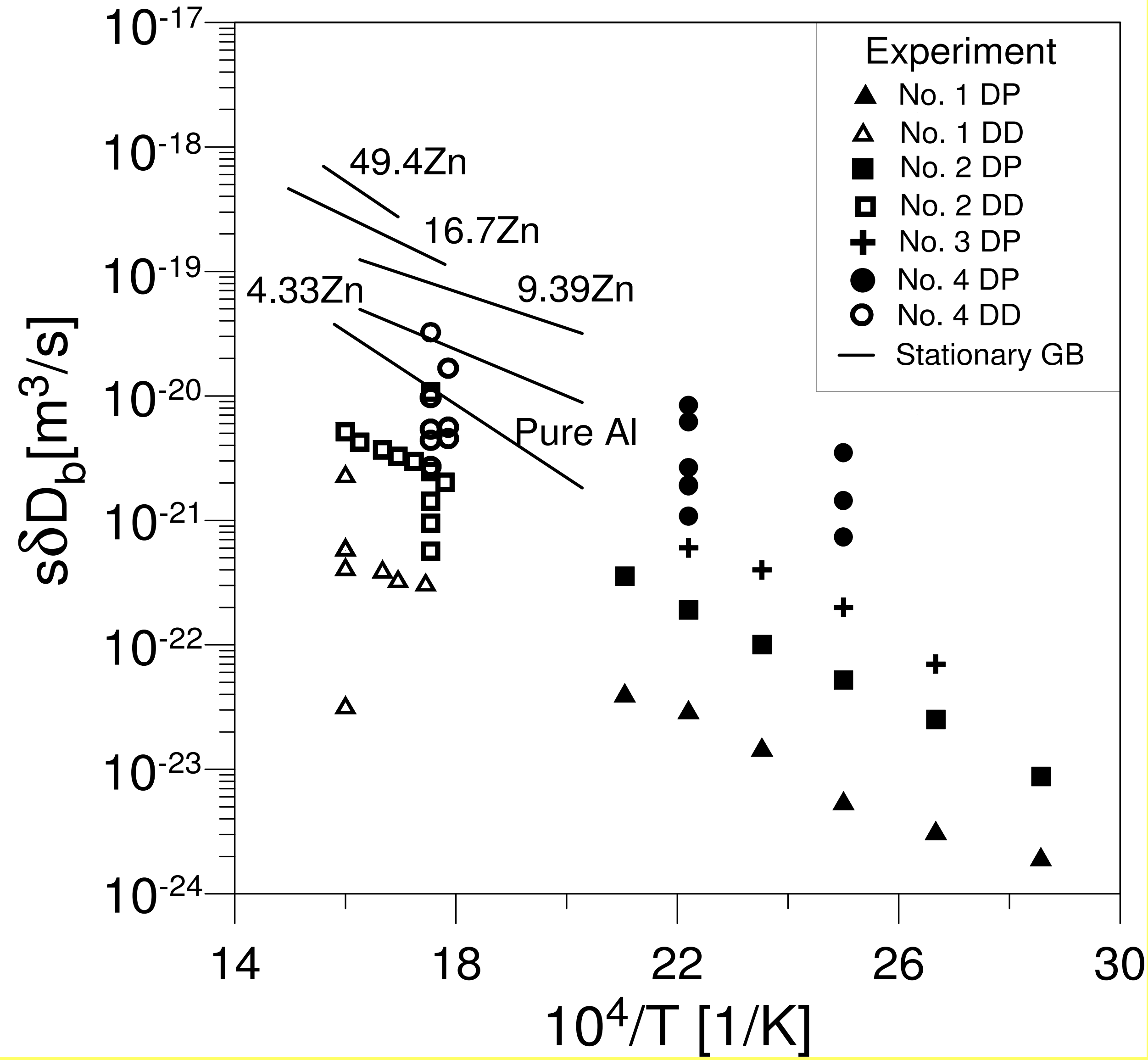
$$x'(y)=A\cdot\sinh(zy\lambda_\alpha)+B\cdot\cosh(zy\lambda_\alpha)+\frac{a}{p^2-z^2}\cosh(py\lambda_\alpha)-\frac{b}{p^2-z^2}\sinh(py\lambda_\alpha)+x_o$$

$$p=\left(\frac{v_{inst}}{s\delta D_b}\right)^{\frac{1}{2}},\ z=\left(\frac{v_{inst}}{s\delta D_b}\right)^{\frac{1}{2}}$$

$$A,B,a,b = f(x_o,\ x_e,\ \lambda_\alpha,\ p,\ x^*,\ z)$$

Growth velocity of the DD reaction

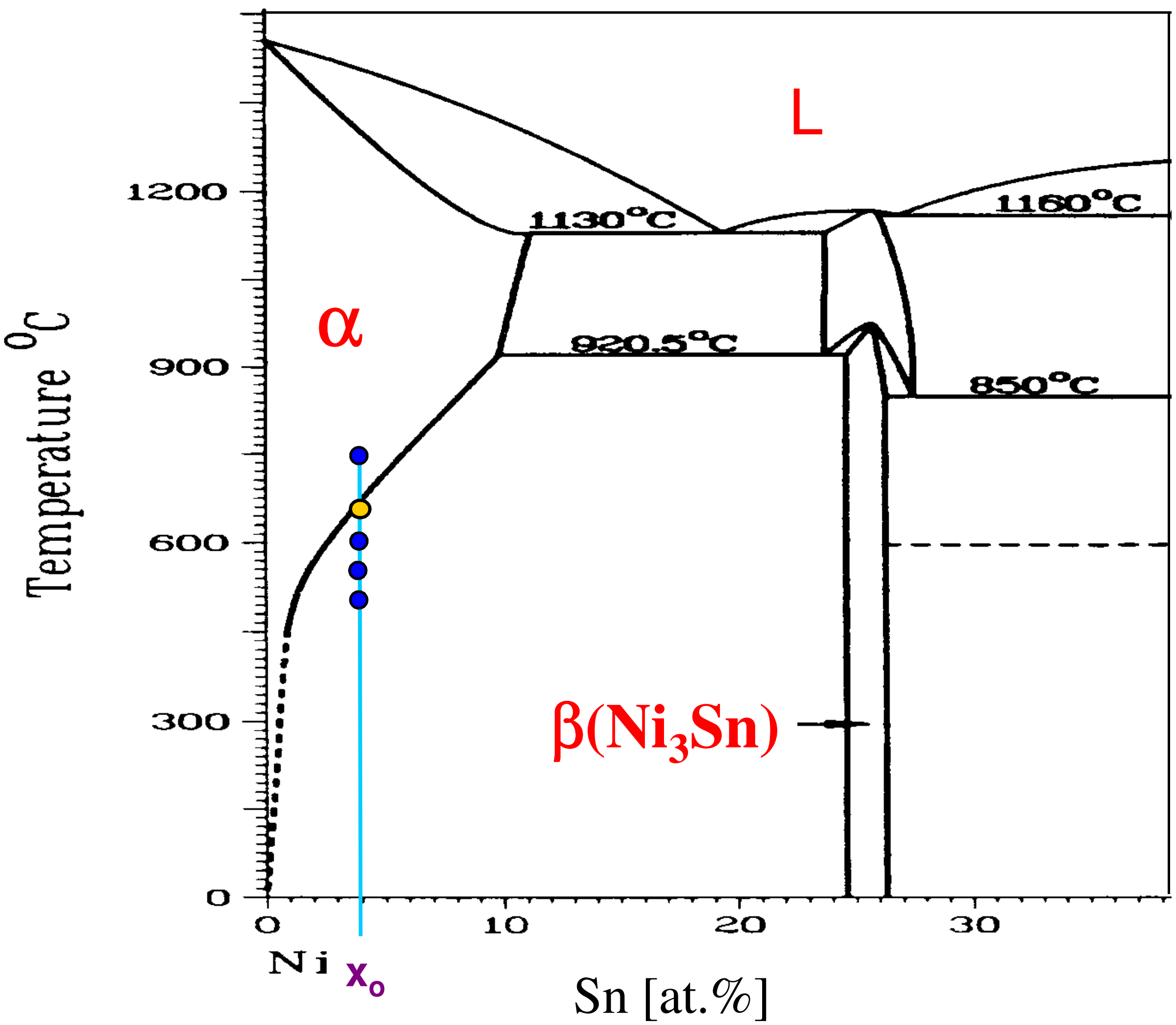
- *In-situ* observation in the TEM
- Directly from TEM micrographs (receding distance)



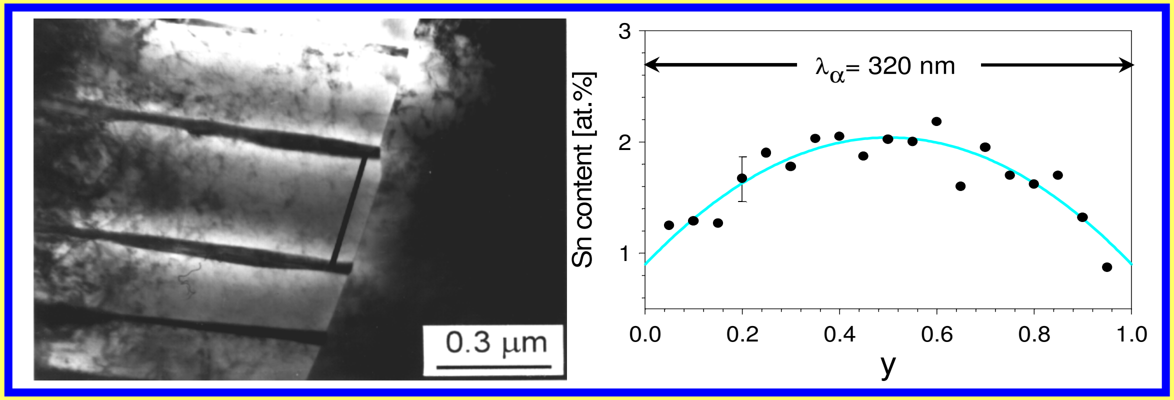
10^{-17}
10^{-18}
10^{-19}
10^{-20}
10^{-21}
10^{-22}
10^{-23}
10^{-24}
$s\delta D_b[m^3/s]$
14
18
22
26
30
$10^4/T$ [1/K]
49.4Zn
16.7Zn
9.39Zn
4.33Zn
Pure Al
Experiment
▲ No. 1 DP
△ No. 1 DD
■ No. 2 DP
□ No. 2 DD
+ No. 3 DP
● No. 4 DP
○ No. 4 DD
— Stationary GB

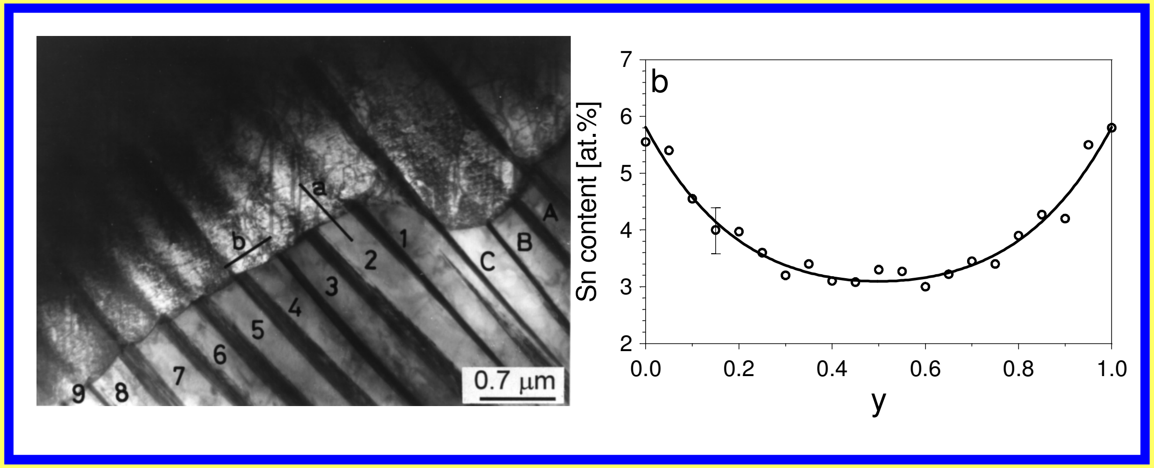
Parameter	Investigation			
	No. 1	No. 2	No. 3	No. 4 (This study)
v_{DP}	Average by quantitative metallography	Average by quantitative metallography	Average by quantitative metallography	Directly from *in situ* observation
l_{α}	Average by quantitative metallography	Directly from TEM micrographs	Directly from TEM micrographs	Directly from TEM micrographs
x_{av}	X-ray analysis for 30% volume occupied by DP	X-ray analysis for 60% volume occupied by DP	-	-
p	Indirectly from x_{av}	-	Directly from EDX analysis	Directly from EDX analysis
x^*	Average by X-ray analysis	Directly from EDX analysis but as average for the whole sample	-	Directly from EDX analysis
v_{DD}	Average by quantitative metallography	Average by quantitative metallography	-	Directly from *in situ* observation
z	Indirectly from x* and the formula	Indirectly from x*	-	Directly from EDX analysis

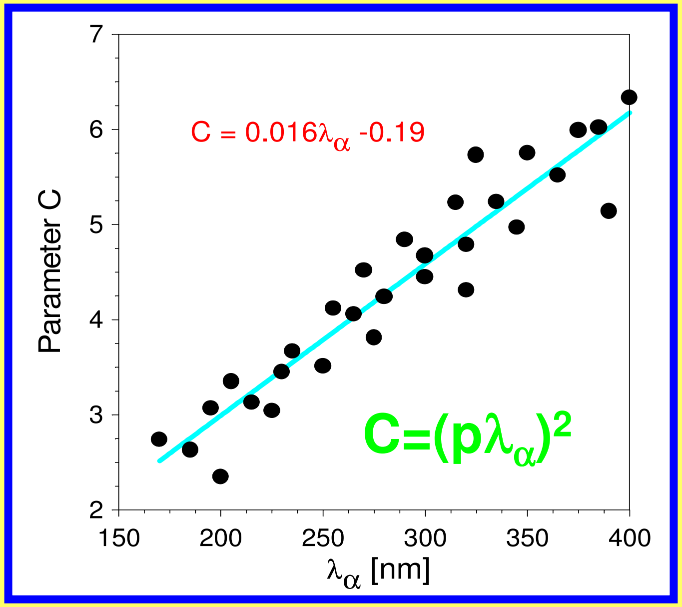
Ni-Sn System


L
α
1130°C
1160°C
920.5°C
850°C
β(Ni₃Sn)
Temperature °C
1200
900
600
300
0
0
10
20
30
Ni
x₀
Sn [at.%]

Microstructure and EDX Analysis - Ni-4 at.% Sn

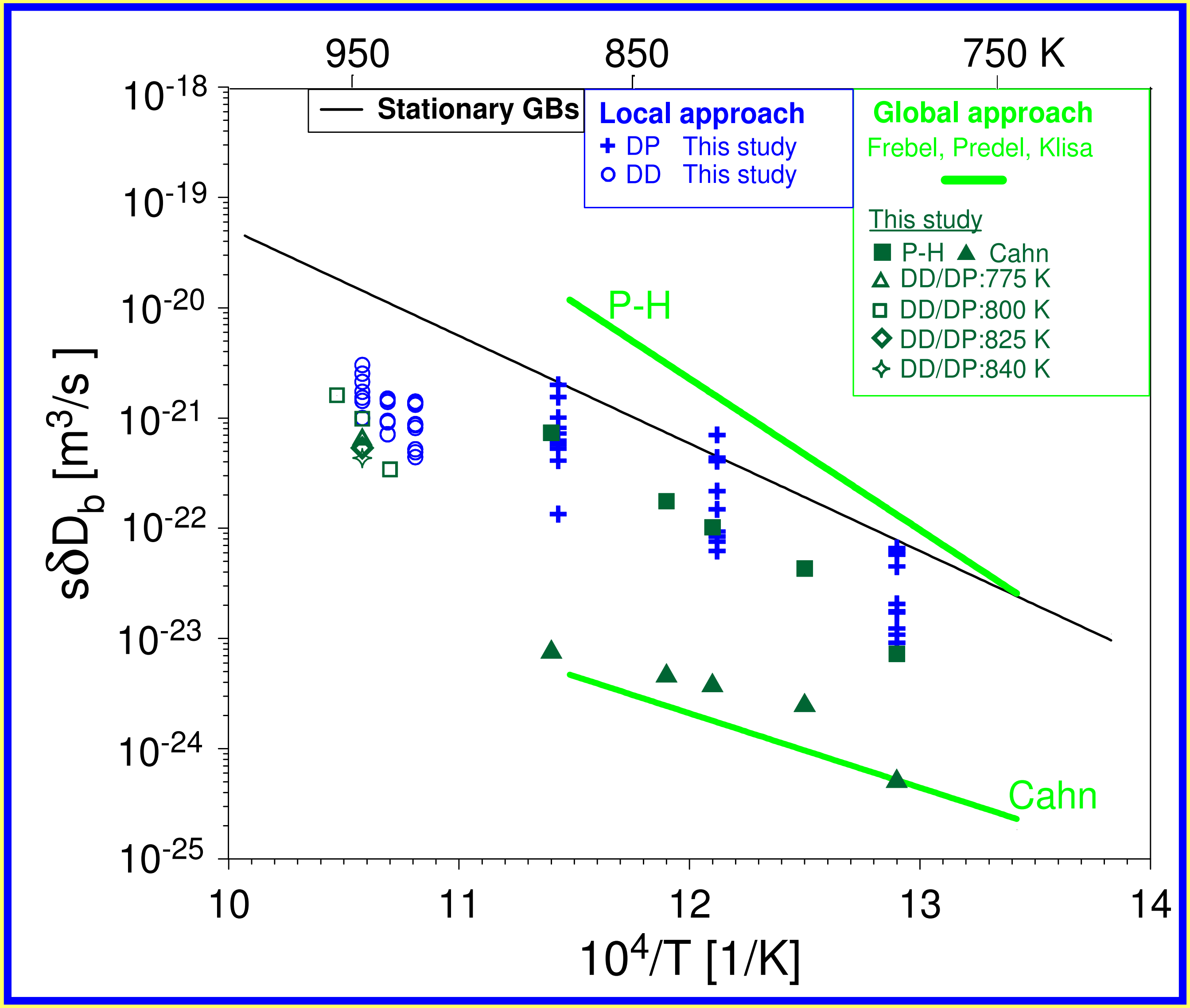


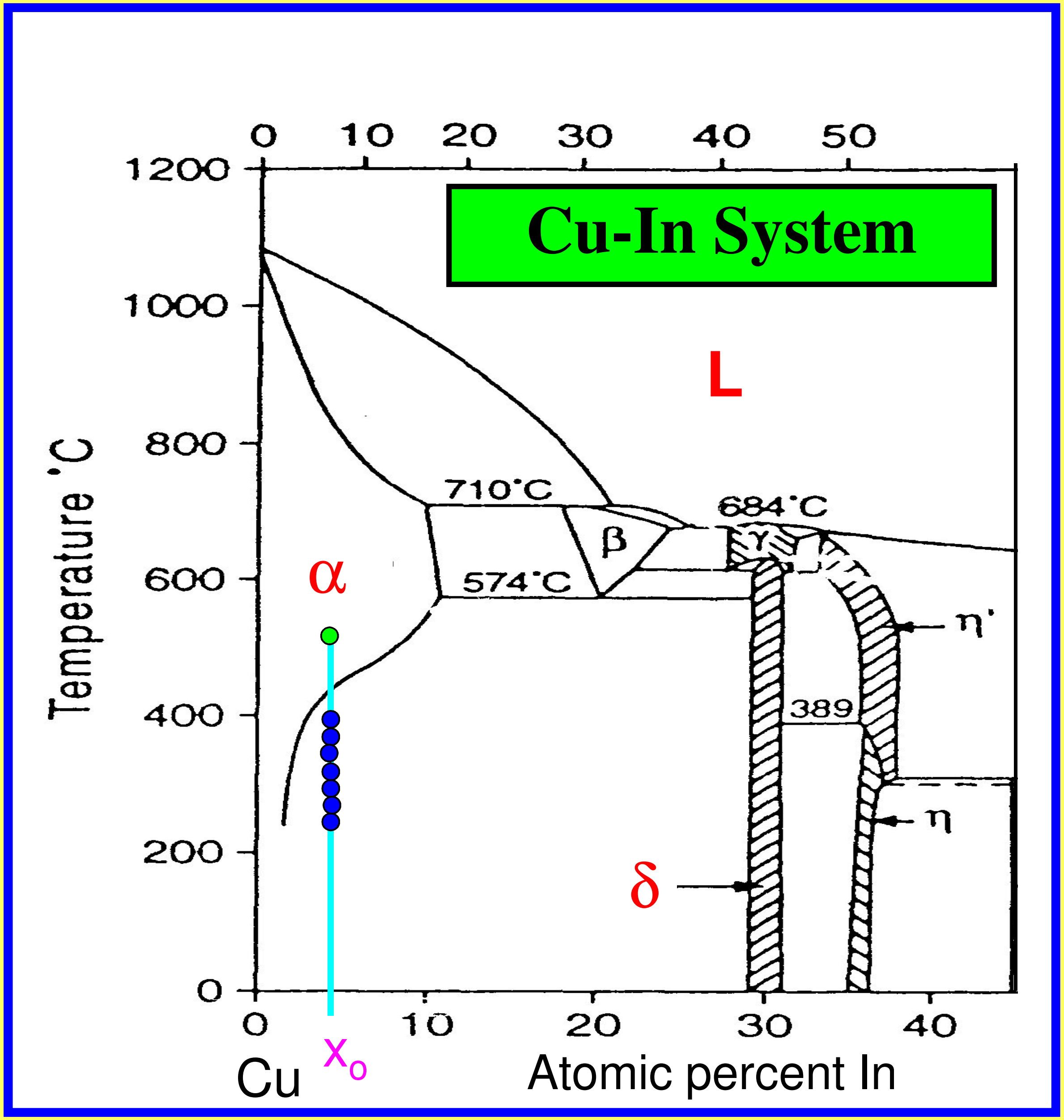




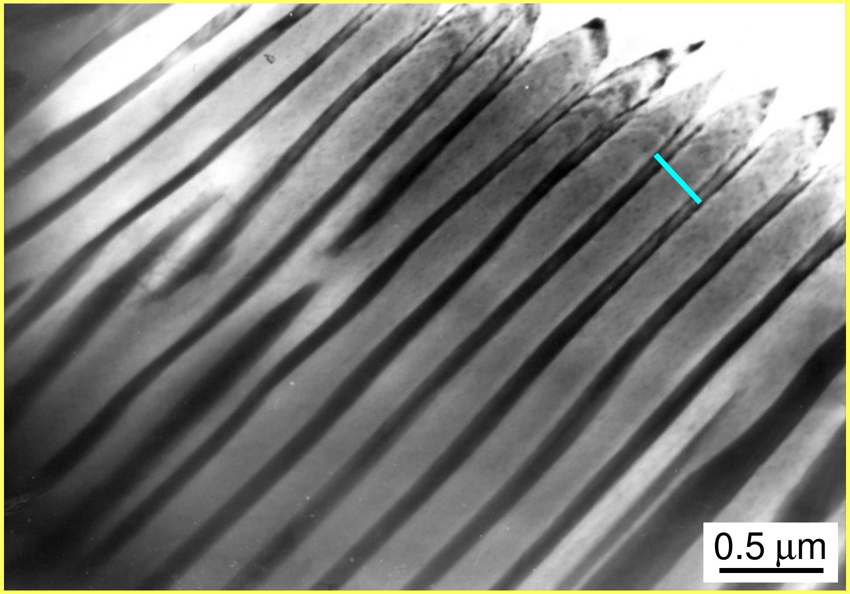
EDX analysis for the 10 lamellae randomly chosen from 10 different colonies after ageing at 775, 825 and 875 K

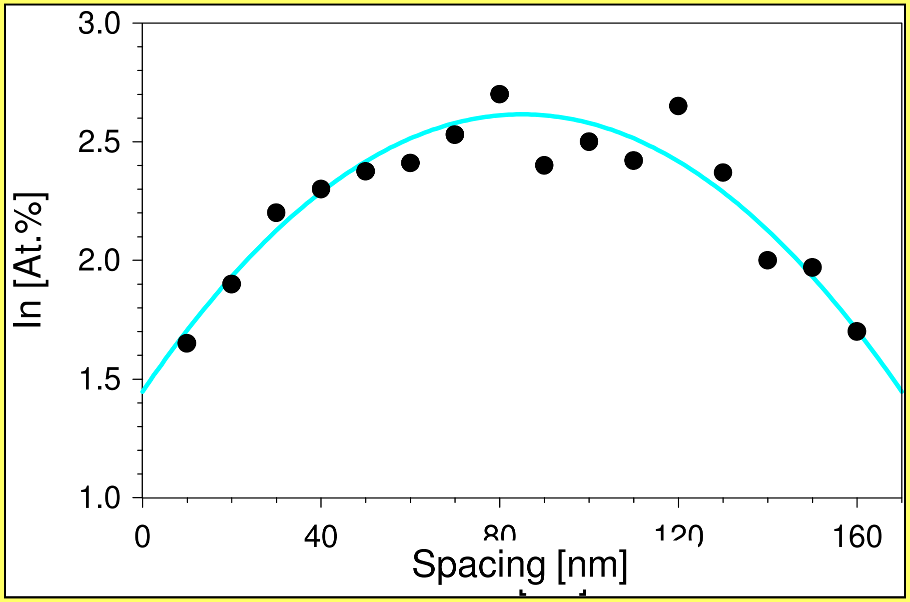
Arrhenius Graph – Ni-4 at.% Sn



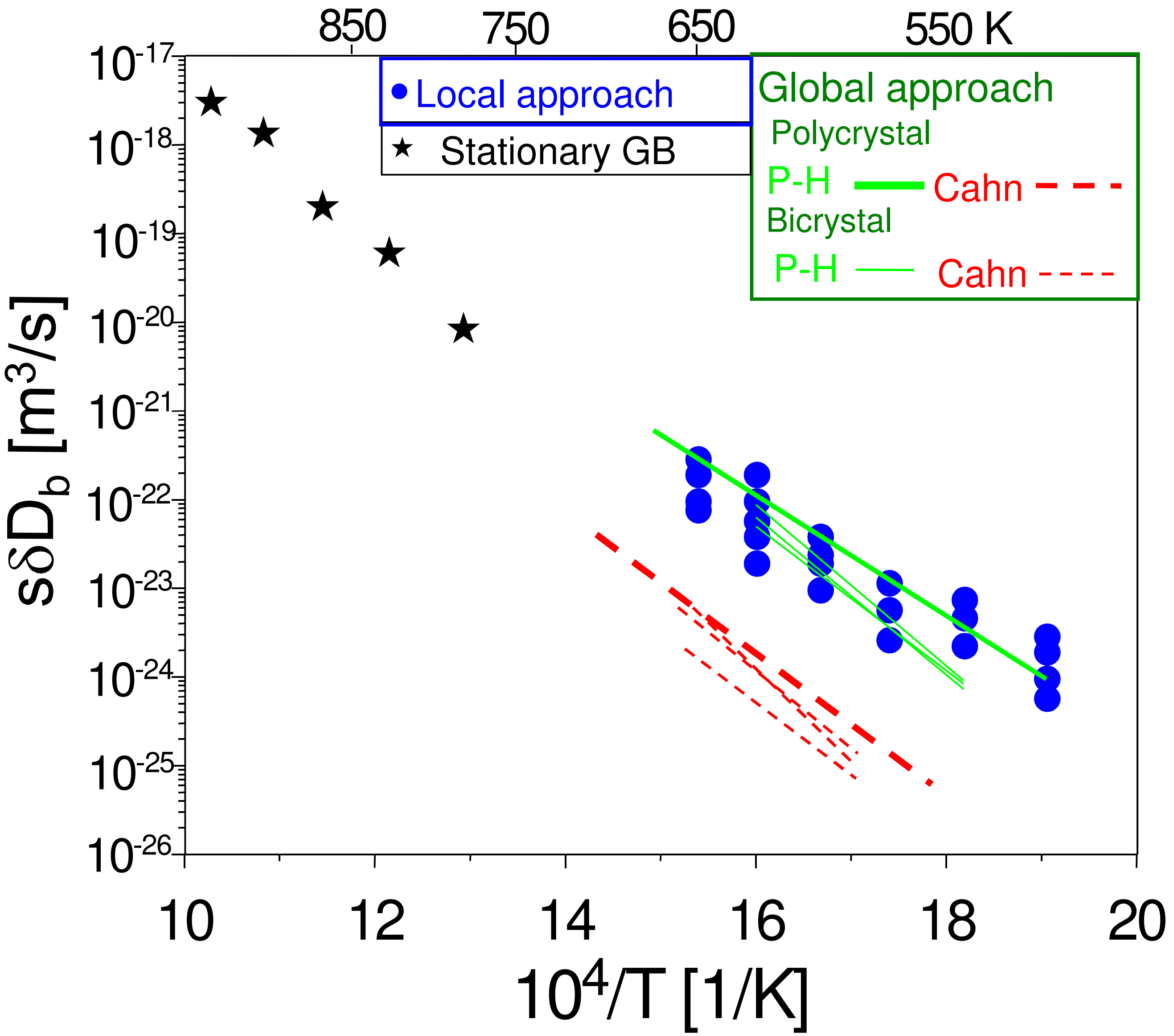

0
10
20
30
40
50
1200
1000
800
600
400
200
0
Temperature °C
Cu-In System
L
710°C
684°C
β
γ
574°C
α
η'
389
η
δ
0
10
20
30
40
Cu
x_o
Atomic percent In

Cu-4.5 At.% In

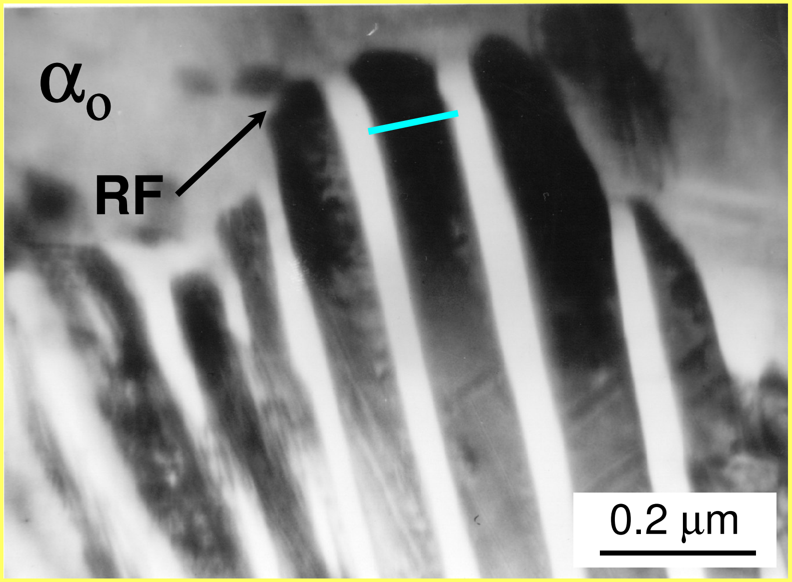


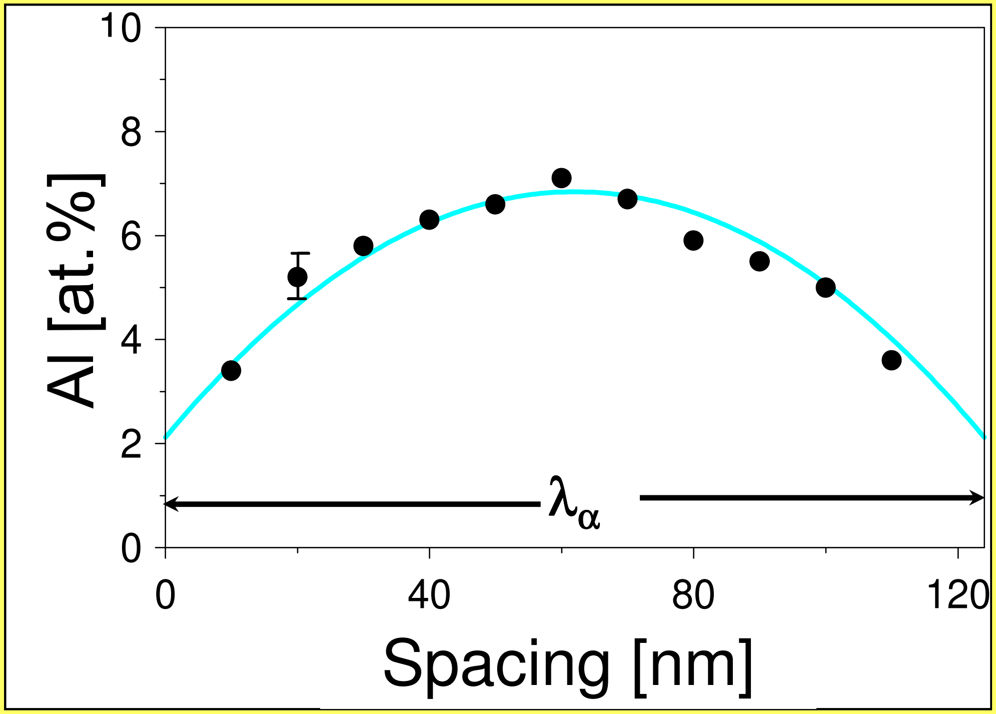


5 EDX line-scans in various colonies after ageing at 525, 550, 575, 600, 625, 650 K.


850
750
650
550 K
● Local approach
★ Stationary GB
Global approach
Polycrystal
P-H
Cahn
Bicrystal
P-H
Cahn
10^{-17}
10^{-18}
10^{-19}
10^{-20}
10^{-21}
10^{-22}
10^{-23}
10^{-24}
10^{-25}
10^{-26}
$s\delta D_b$ [m^3/s]
10
12
14
16
18
20
$10^4/T$ [1/K]

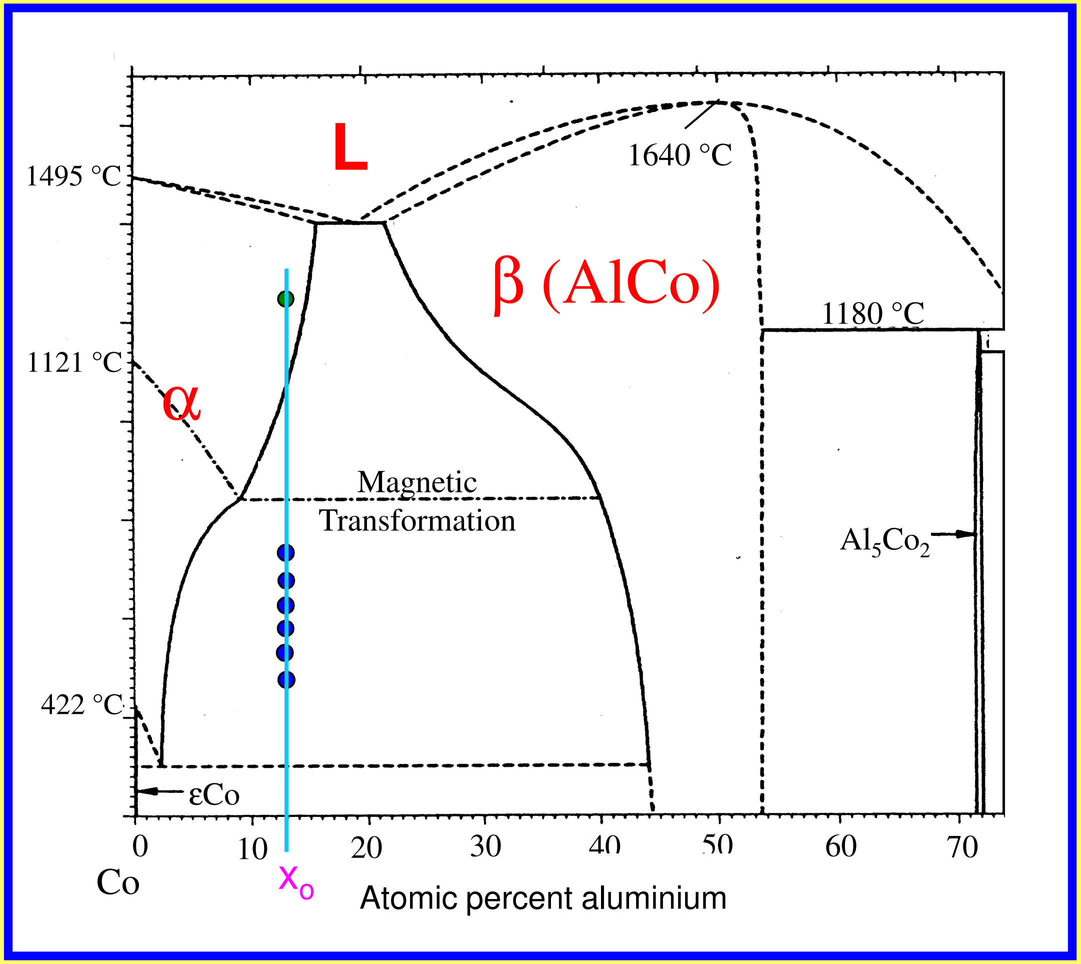
Co-13 At.% Al

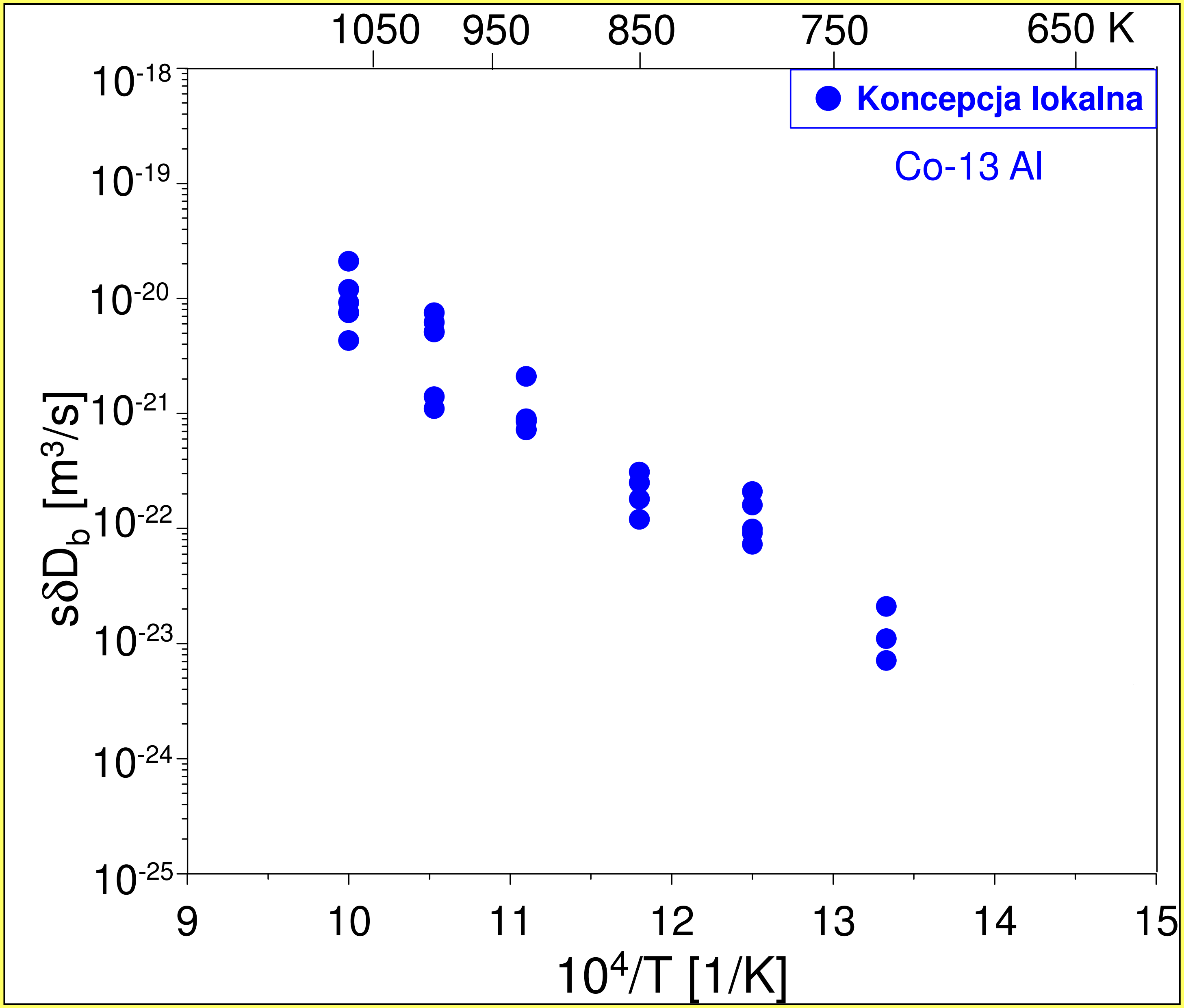




Five EDX analysis taken in various colonies after DP reaction at 750, 800, 850, 900, 950, 1000 K.

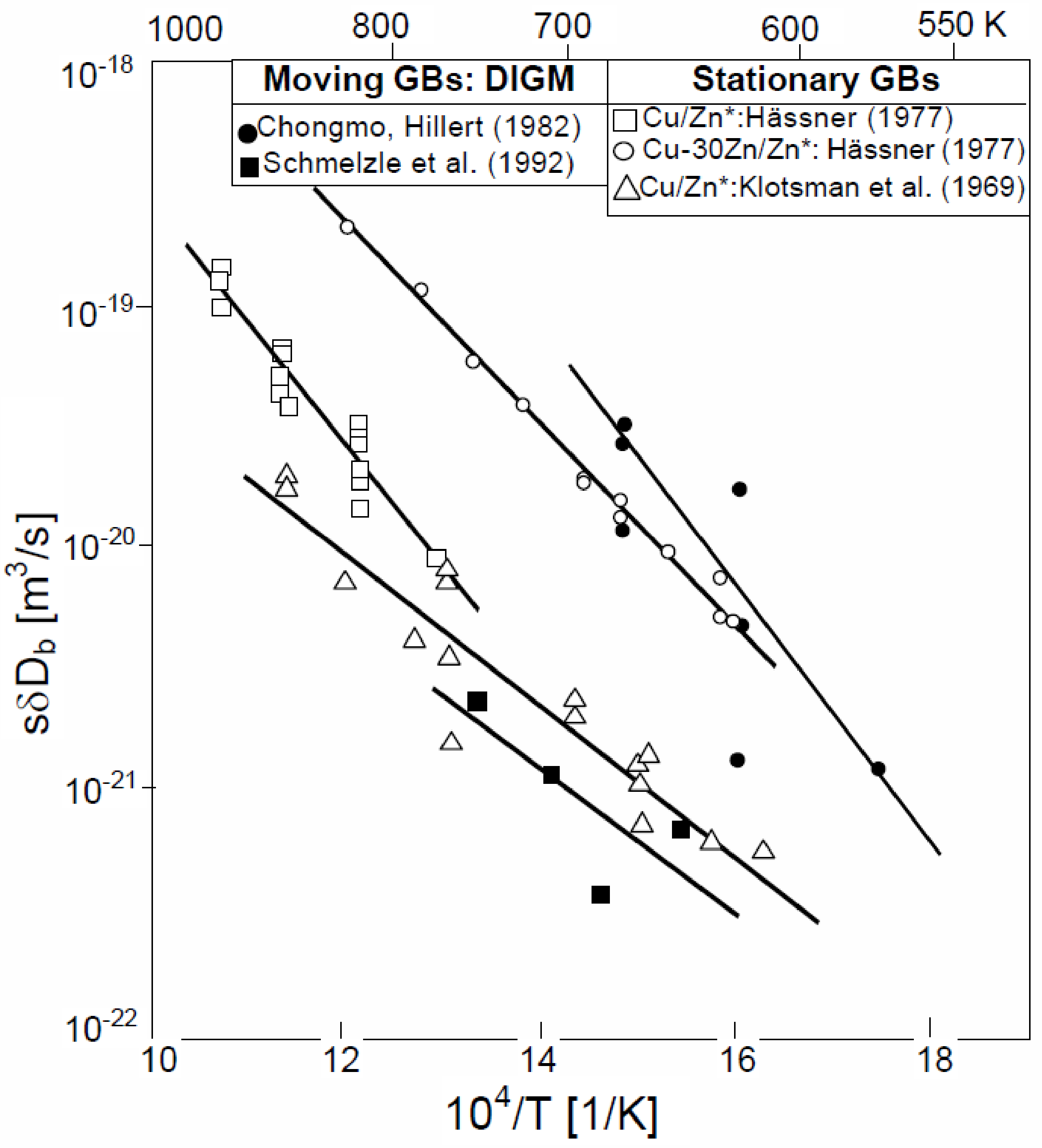
Co-Al System


L
1640 °C
1495 °C
β (AlCo)
1180 °C
1121 °C
α
Magnetic
Transformation
Al_5Co_2
422 °C
εCo
0
10
20
30
40
50
60
70
Co
x_o
Atomic percent aluminium

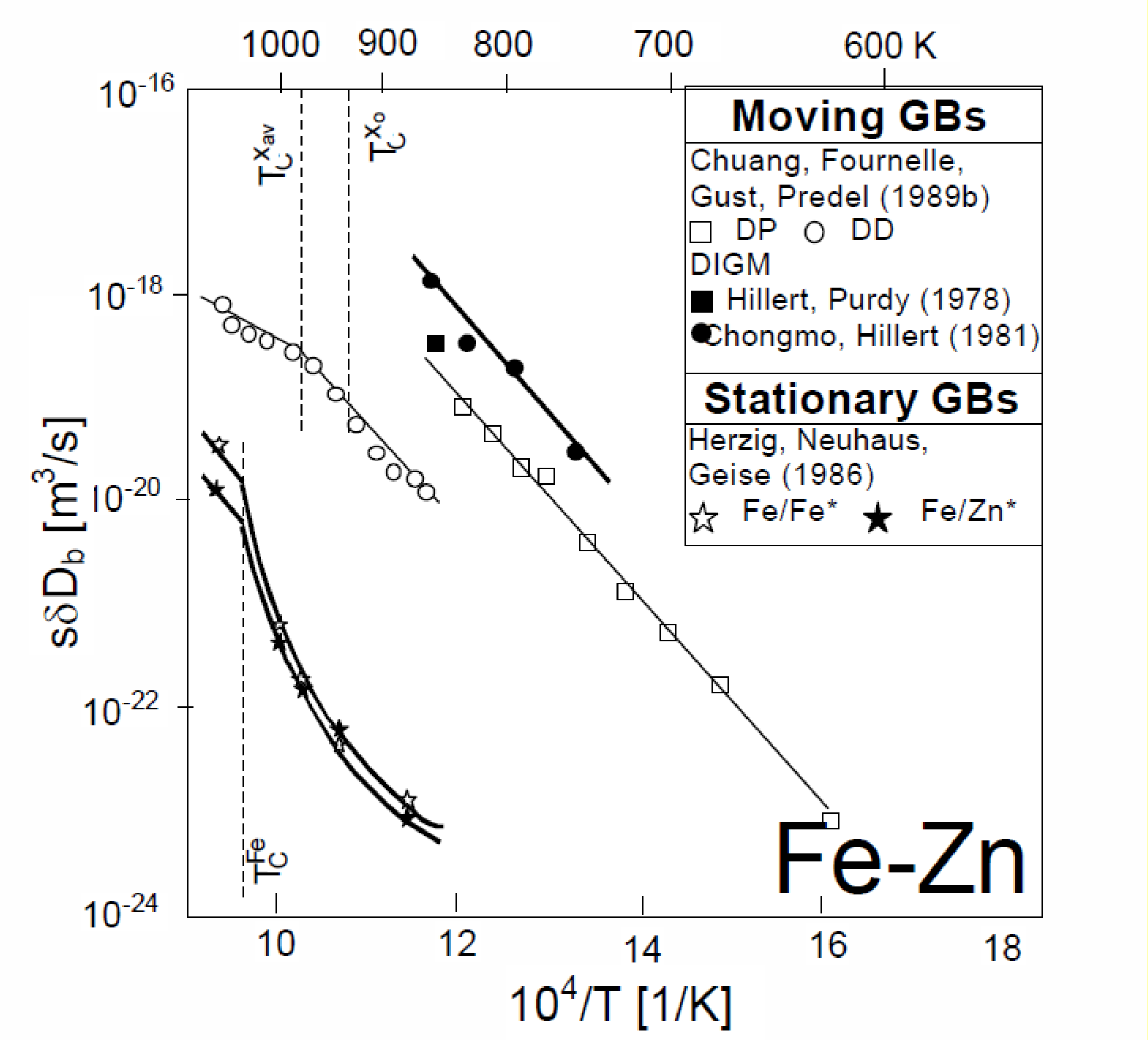

1050
950
850
750
650 K
● Koncepcja lokalna
Co-13 Al
10^{-18}
10^{-19}
10^{-20}
10^{-21}
10^{-22}
10^{-23}
10^{-24}
10^{-25}
$s\delta D_b$ [m^3/s]
9
10
11
12
13
14
15
$10^4/T$ [1/K]

Cu-Zn System

Chongmo-Hillert
Fe-Fe18.8 at.%Zn source



Chongmo, Hillert
DIGM:Fe-Fe18.8 at.%Zn
source
Chuang et. al.: DP: Fe-13.5
at.%Zn



Stationary GB		Migrating GB
$s\delta D_b^{A/B^*}$	$\approx$	$s\delta D_b$
$s\delta D_b^{AB/B^*}$	$\approx$	$s\delta D_b$
$s\delta D_b^{AB/B^*}$	$\approx$	$s\delta D_b^{AB/B^*}$
$s\delta D_b^{AB/A^*}$	$\approx$	$s\delta D_b^{AB/A^*}$
$s\delta D_b^{A/B^*}$	$\approx$	$s\delta D_b^{A/B^*}$

A and B- solvent and solute atom, respectively

$D_b^{A/B*}$, $D_b^{AB/B*}$ and $D_b^{AB/A*}$- tracer diffusion coefficients of B* in A, B in the alloy A-B, and A* in the alloy A-B

Conclusions

Technique of analytical electron microscopy was shown as a valuable tool in characterisation of diffusion process along migrating grain boundaries of discontinuous precipitates

With careful assessment of experimental conditions, it seems likely that quantitative microanalyses of relatively high quality can be performed with an good spatial resolution approaching a few nanometers. This allows to determine the solute concentration profiles across the α lamellae (DP reaction) or left behind receding reaction front of DD and to compare them with the predictions of relevant theories

Consequently, the reaction is no longer considered as mesoscopic phenomenon averaged over the whole volume of the sample but rather local event occurring in single cells

The use of the local concept of the DP reaction for Cahn´s model diminishes existing discrepancies in the diffusivity values in comparison with Petermann-Hornbogen model

The diffusion along migrating and stationary GBs in Al-Zn, Cu-In, Ni-Sn and Ni-In systems occurs equaly fast

It is believed that the diffusivity values of the moving reaction front of the discontinuous precipitation and dissolution can be a source of reliable information about the diffusion rate, especially in systems and/or at temperatures where the radio-tracer data are not available