Mass transport during discontinuous precipitation

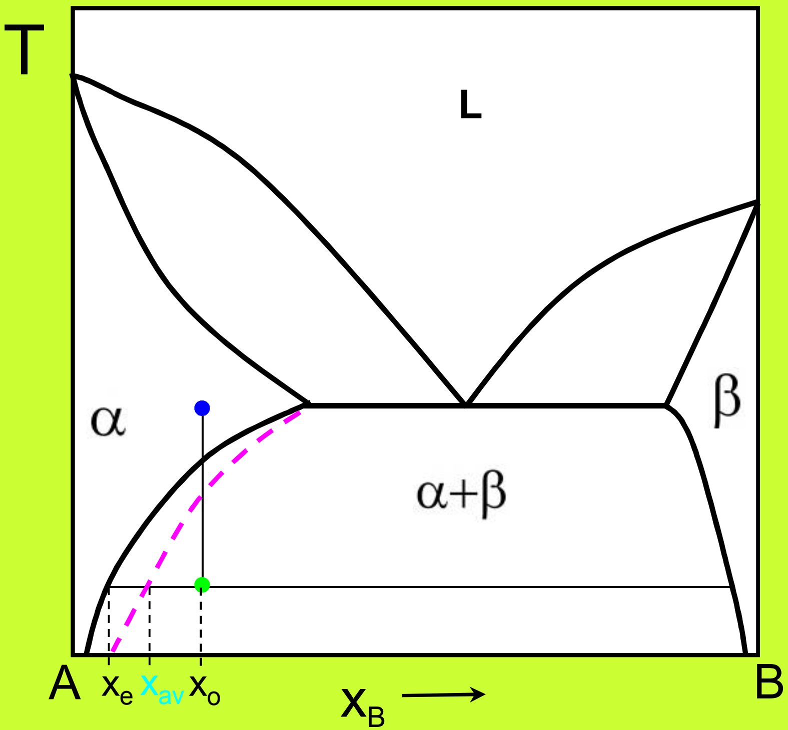
1. Nucleation period
2. Non-steady state period of growth
3. Steady state growth- regular morphology

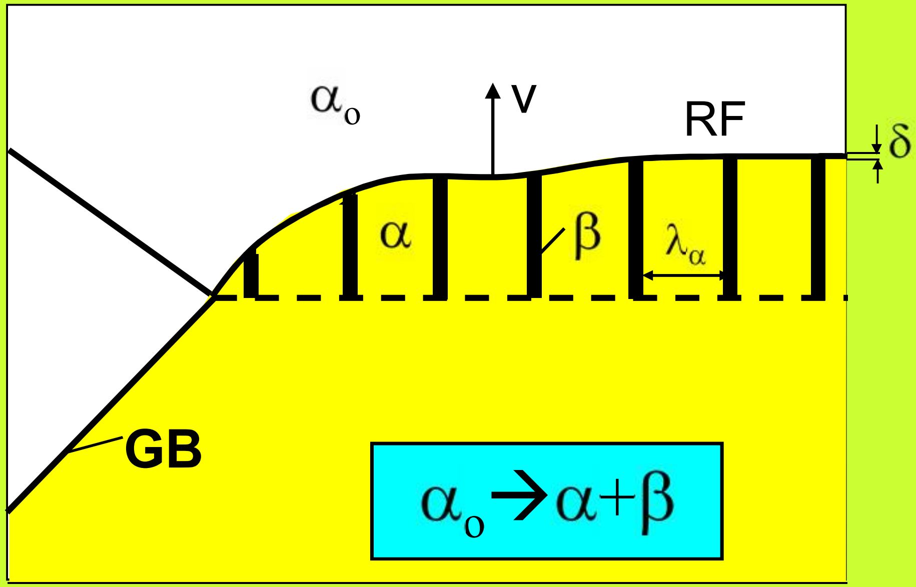
2.3.2. Solute concentration profiles

2.3.2.1. Across the reaction front

2.3.2.2 Across the α lamella

DP reaction





x_o- solute content in alloy

x_e – equilibrium solute content at α/β interface

x_{av}- average solute content in α lamella

δ – width of reaction front (RF)

λ_α– thickness of α lamella

v - growth rate of discontinuous precipitates

GB- grain boundary; RF=GB

The solute redistribution occurs at the moving RF

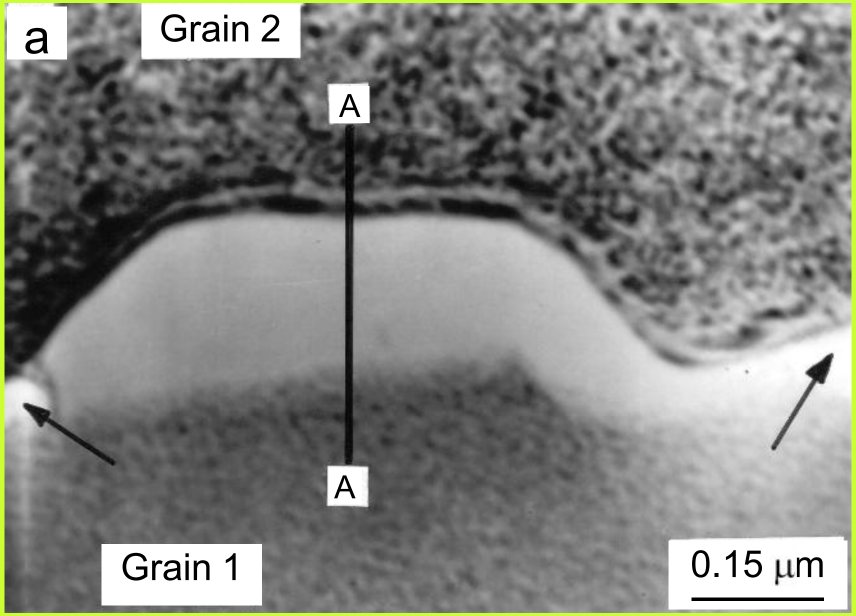
There exists an excess of solute atoms within the α lamella compared to the equilibrium state

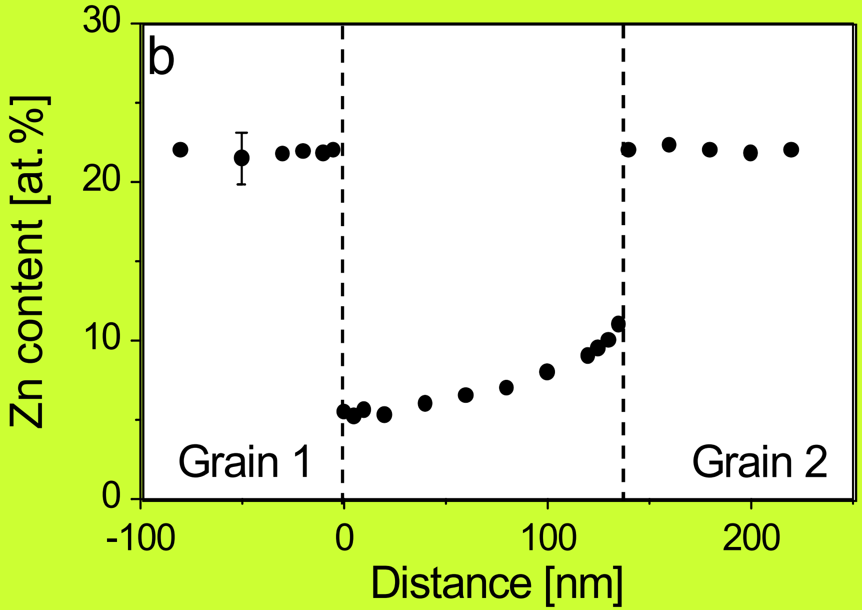
Changes of soute concentration during DP reaction

Solute profiles ⊥ RF (reaction front)

Solute profiles across the α phase lamella (II RF)

DP- nucleation period

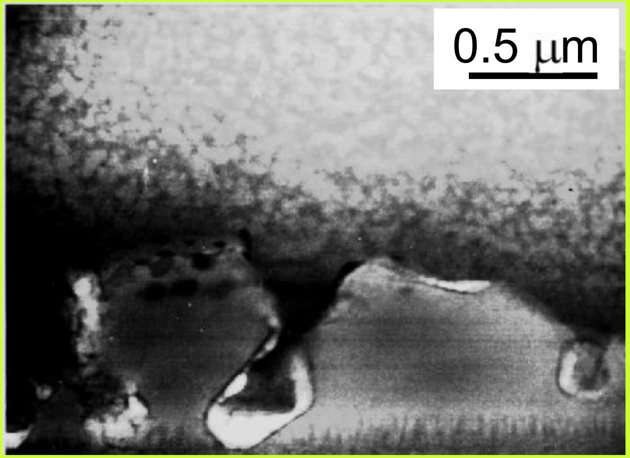


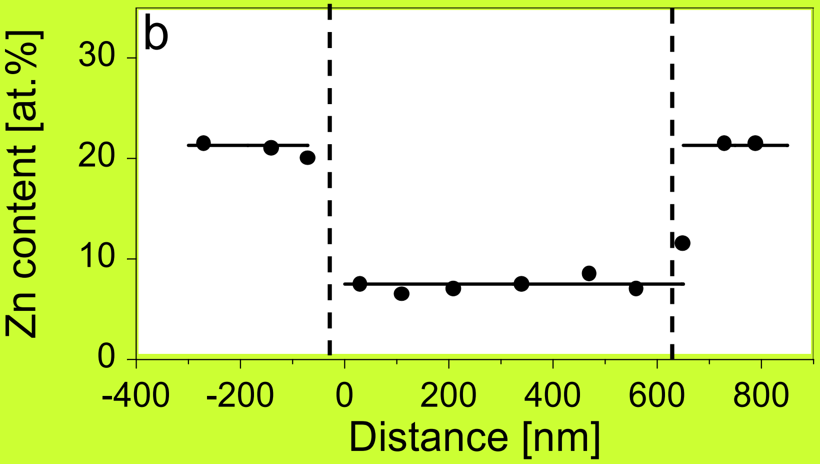


P. Zięba, W. Gust: *Inter. Mater. Rev.* 43 (1998) 70
Al-22 at.% Zn aged at 450 K for 1 min

- Formation at grain boundary of solute-rich precipitates (allotriomorphs)
- Migration of primary grain boundary (bowing between allotriomorphs) accompanied by diffusion along it.
- Transformation of allotriomorphs into solute-rich β phase lamellae while grain boundary becomes the reaction front (RF) of discontinuous precipitation
- Step-like change of solute content across RF

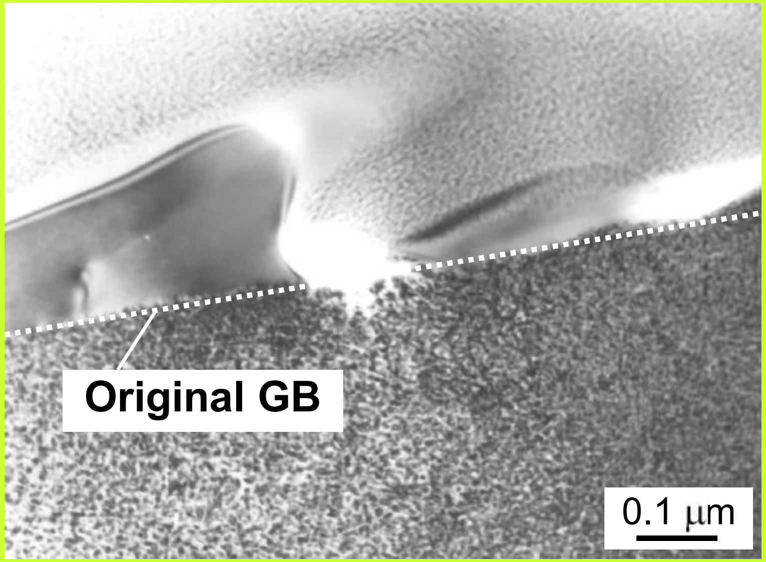
DP- nucleation period

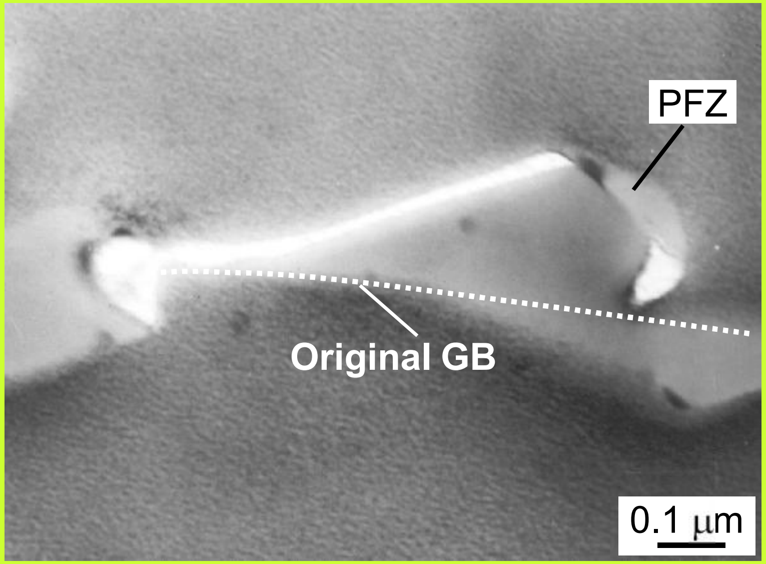




I.G. Solorzano, G.R. Purdy, G.C. Weatherly:
Acta metall. 32 (1984) 1709
Al-22 at.% Zn aged at428 K for 5 min

DP- nucleation period



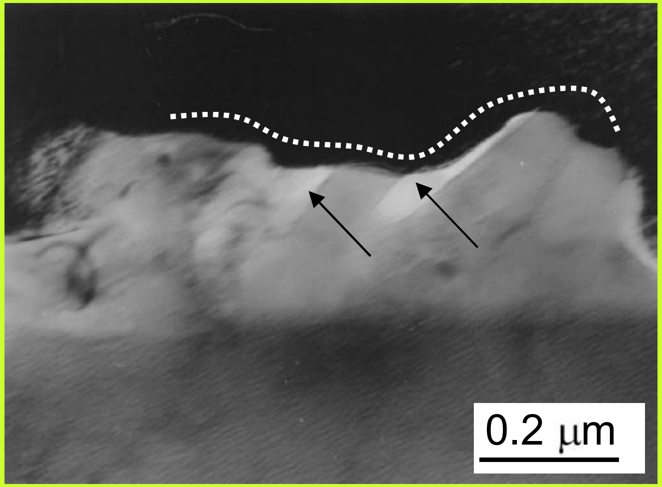


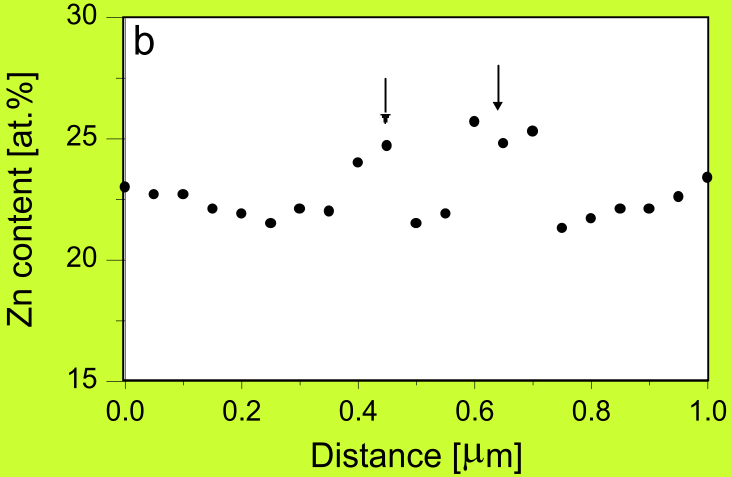
TRANSITION TO β LAMELLAE

If the direction of movement is strongly inclined to the original location of the GB, non-uniform migration of the GB around the pinning enables the β lamella to develop much faster on one side of the shrinking grain.

P. Zięba, D.B. Williams: *Microchim. Acta* 145 (2004) 275, Al-22 at.% Zn aged at 450 K for 1 min

DP- nucleation period



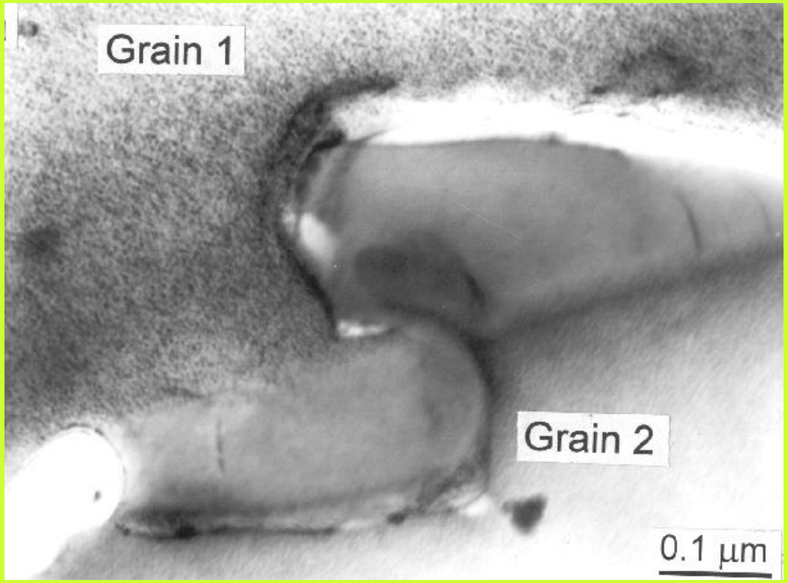


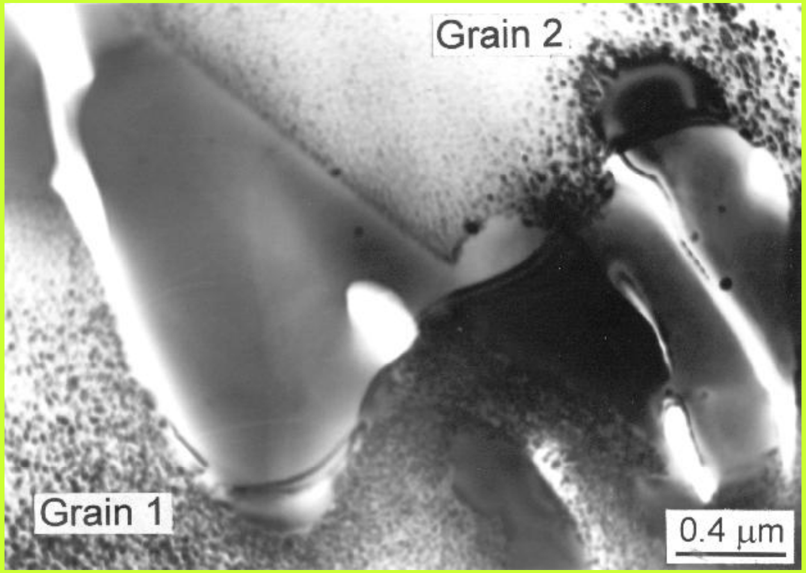
INITIATION WITHOUT PRECURSOR GB PRECIPITATION

Movement of a GB which was not originally occupied by the GB precipitates. The migration distance is relatively short, usually 50-100 nm. Then precipitation of the β lamellae occurs. The EDX line-scan in the matrix just ahead of the reaction front indicated that in such a case the β lamella formation is preceded by accumulation of Zn at certain positions adjacent to the moving GB.

P. Zięba, W. Gust: *Inter. Mater. Rev.* 43 (1998) 70, P. Zięba, D.B. Williams: *Microchim. Acta* 145 (2004) 275
Al-22 at.% Zn aged at 450 K for 1 min

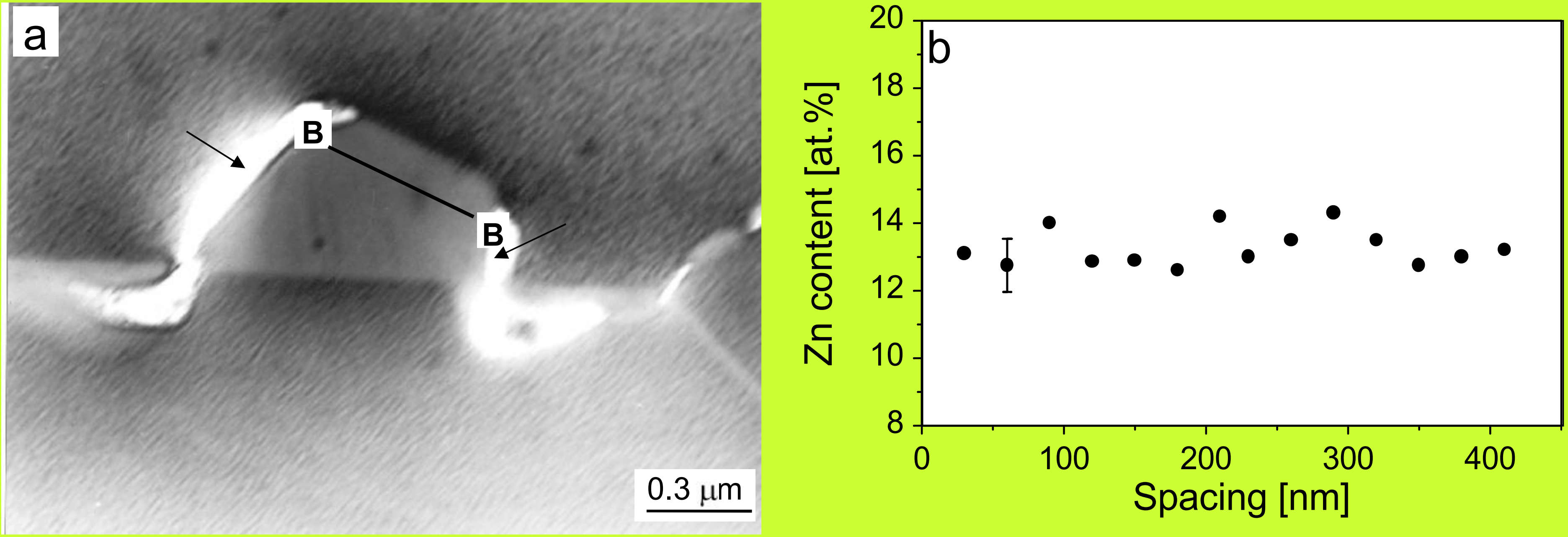
DP- nucleation period





Al-22 at.% Zn aged at 450 K for 2 min

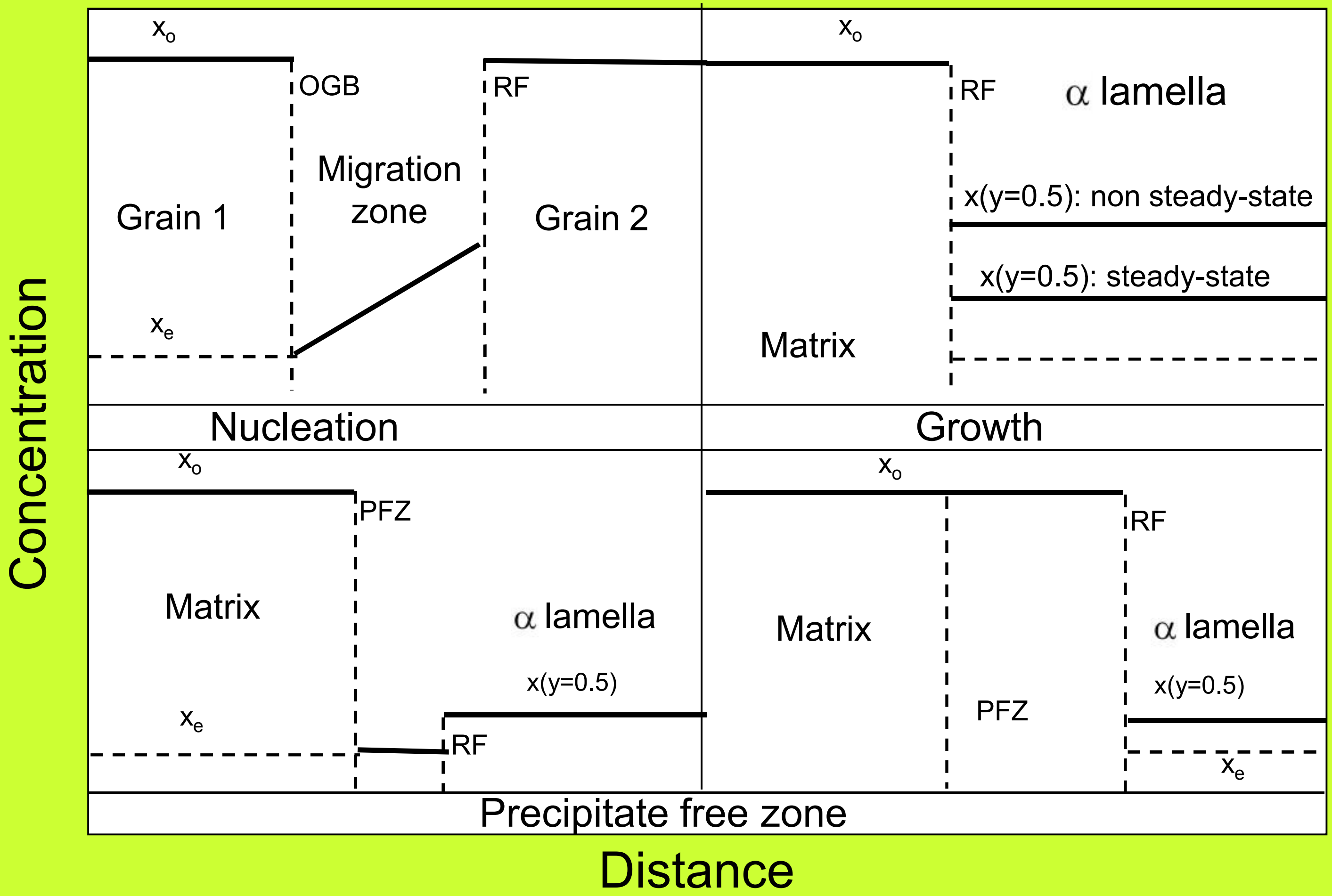
DP- non-steady state period of growth



P. Zięba, W. Gust: *Inter. Mater. Rev.* 43 (1998) 70
Al-22 at.% Zn aged at 450 K for 1 min

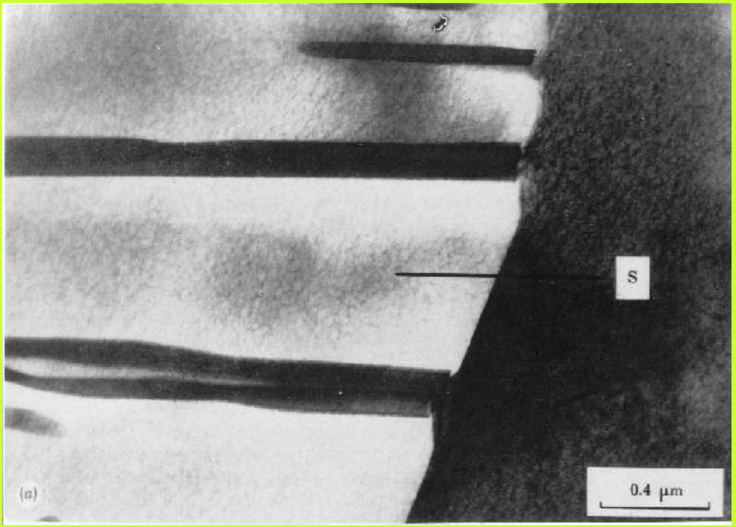
- Frequent changes of α lamellae thickness as well as direction and growth rate
- Thickness of α lamella 2-3 times larger than for steady-state growth
- Almost flat solute concentration profile across the α lamella with average value much larger than during steady-state growth

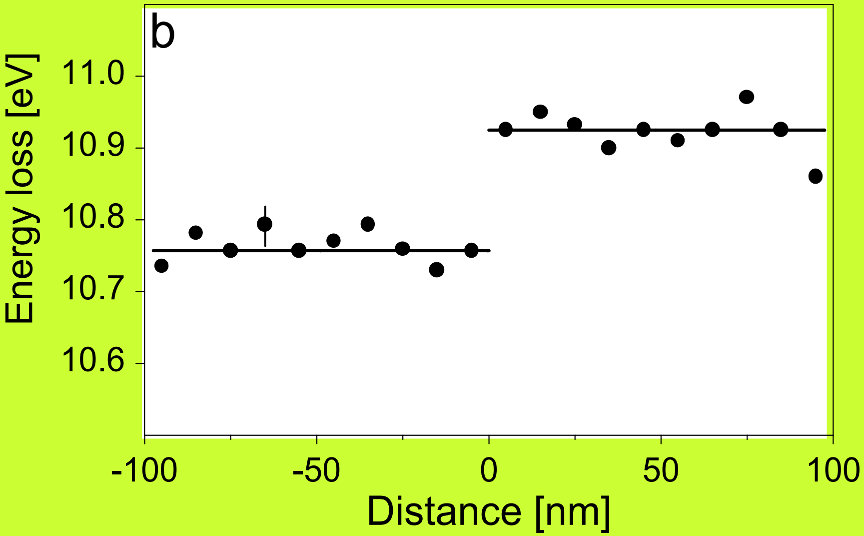
Summary: Solute profiles ⊥ RF (reaction front)



DP- steady state period of growth

Solute concentration profile across RF

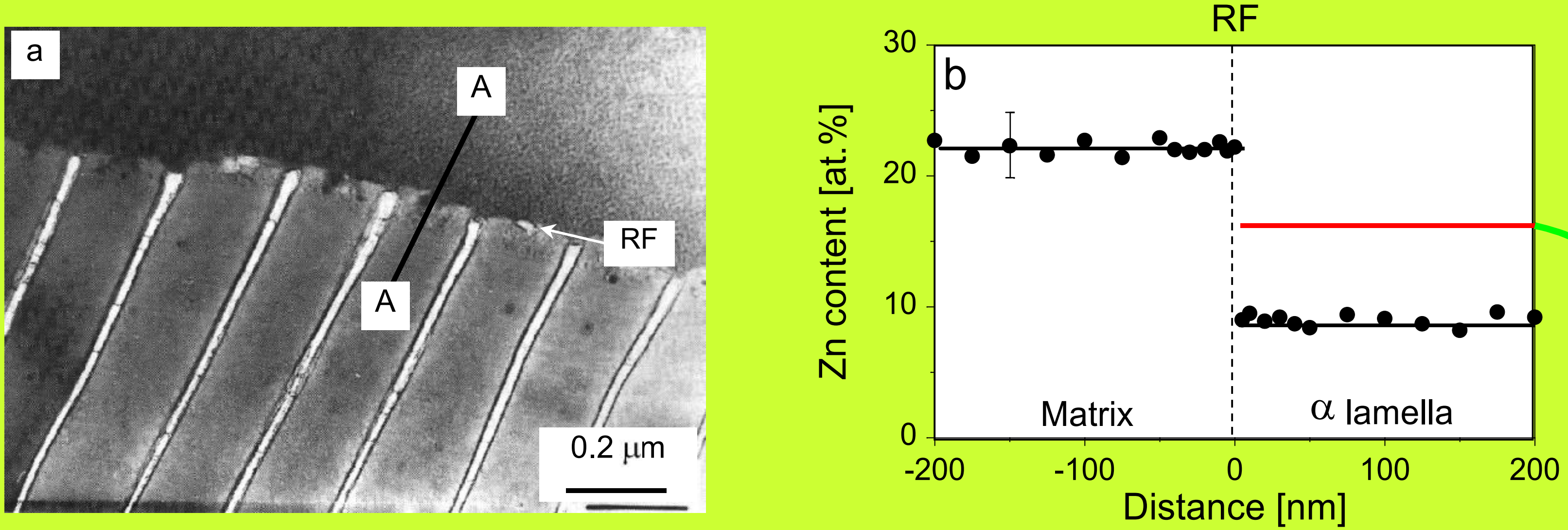




D.A. Porter, D.B. Williams, J.W. Edington:
Proc. Conf. *Electron Microscopy*, Canberra, Australia, 1974,
The Australian Academy of Sciences, str. 656

DP- steady state period of growth

Solute concentration profile across RF

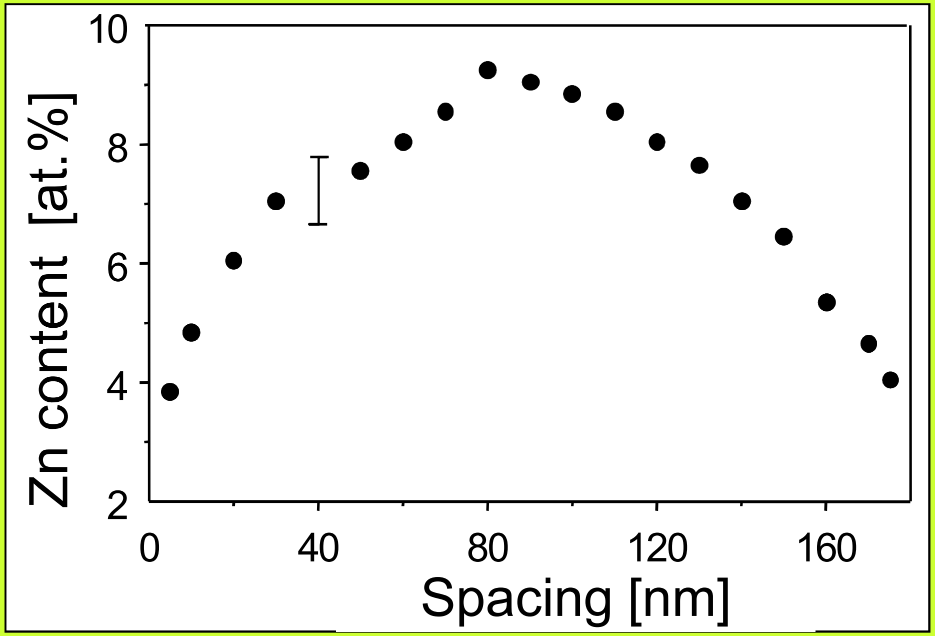


P. Zięba: *Mater. Chem. Phys.* 62 (2000) 183
Al-22 at.% Zn aged at 450 for10 min

For non-steady state growth the shape of solute profile is similar, but the average solute concentration in α phase lamella is much higher

DP- steady state period of growth

Solute concentration profile across α phase lamella

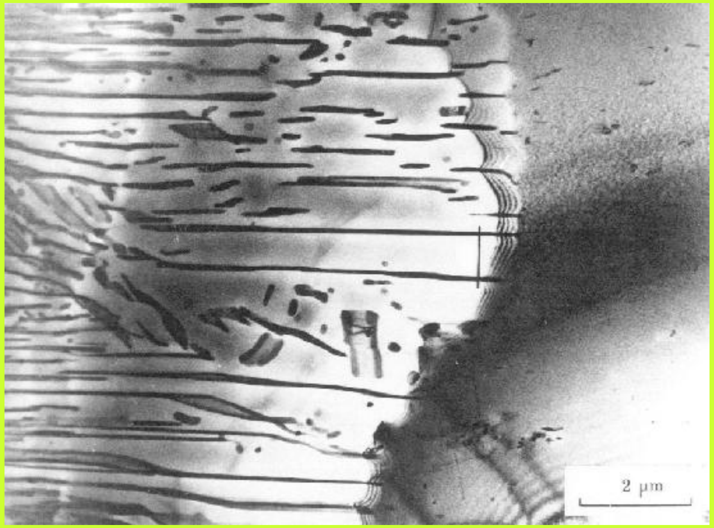


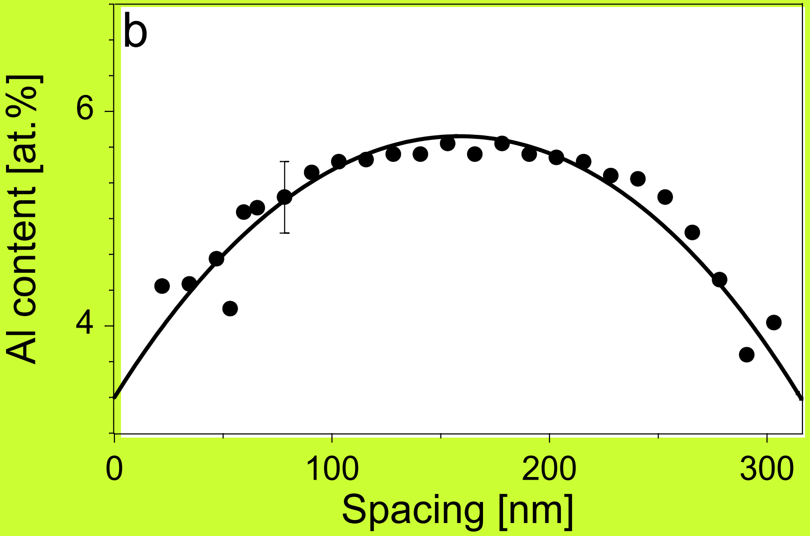
Al-22 at.% Zn aged at 450 K for 10 min

Regular morphology-concentration profile is symmetrical

DP- steady state period of growth

Solute concentration profile across α phase lamella





D.A. Porter, J.W. Edington: Proc. Royal Soc. A 358 (1977) 335
Mg-9 at.%Al aged at 450 K for 3 min

Valid for regular morphology-concentration profile is symmetrical

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

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

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,

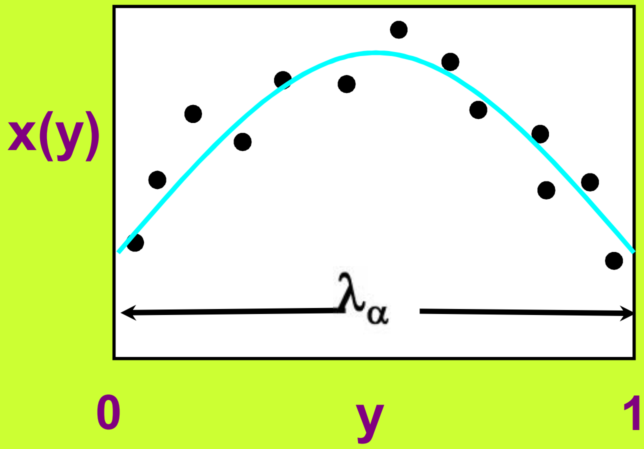
x_e – equilibrium concentration at α/β interface,

x_o – solute content in alloy,

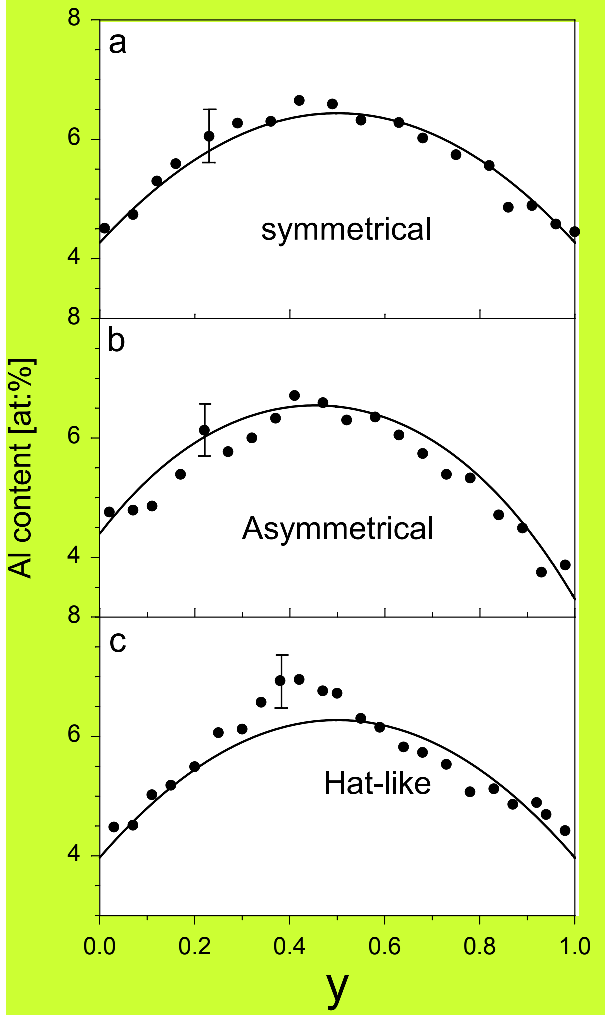
δ – width of grain boundary,

s - segregation factor,

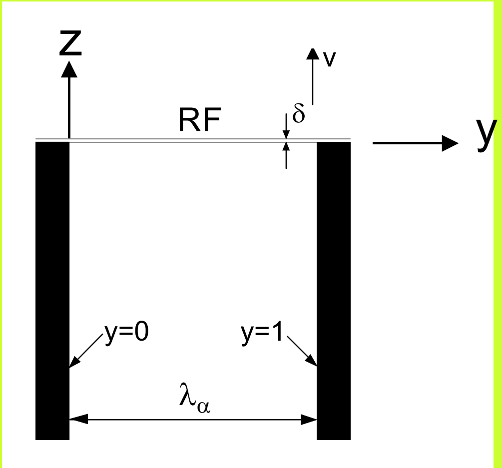
$s\delta D_b$ – diffusivity at moving grain boundary



Steady-state growth-irregular morphology asymmetrical solute concentration profile



D. Duly, M.G. Cheynet, Y. Brechet:
Acta metall. mater. 42 (1994) 3843
Mg-10 at.% Al aged at 493 K



D. Duly, M.G. Cheynet, Y. Brechet, *Acta Metall. & Mater.* 42 (1994) 3843

Boundary conditions:

Various solute content at y=+0.5 and y=-0.5

Origin of the co-ordinate system in the middle of the α phase lamella (y=0.5)

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

P. Zięba, *Acta Materialia* 46 (1998) 369

Boundary conditions:

(i) for y=0 y(x)=x_e,

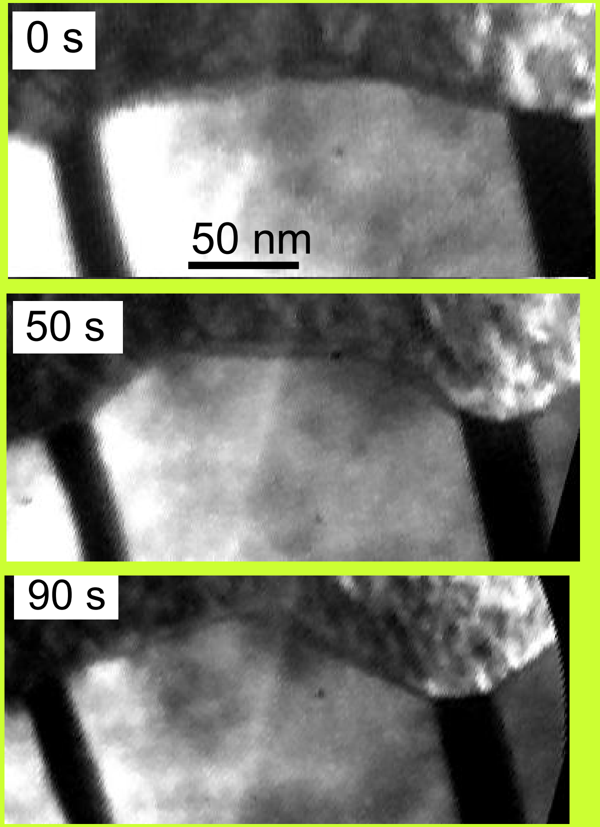
(ii) for x=k dy/dx=0,

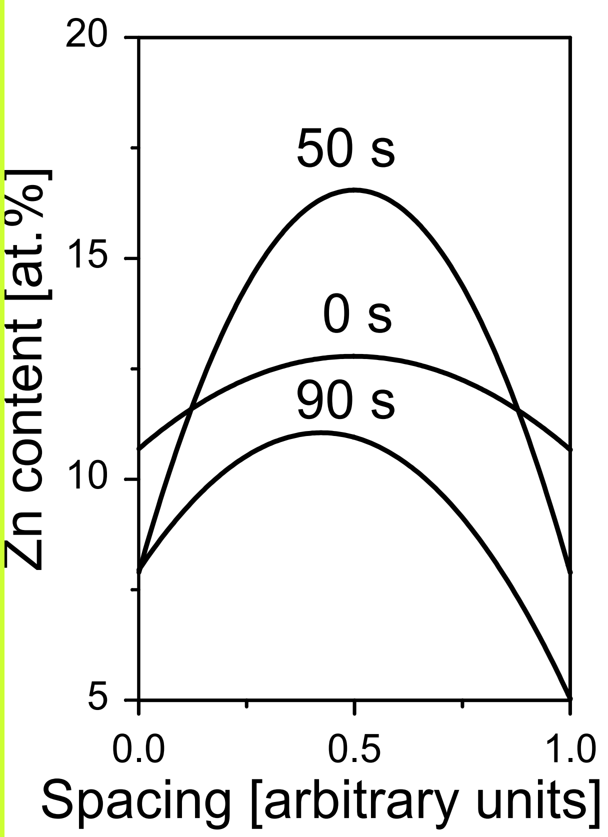
k distance, for which *x(y)* attains maximum

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

DP- steady state period of growth

Irregular morpholy- changes of RF shape



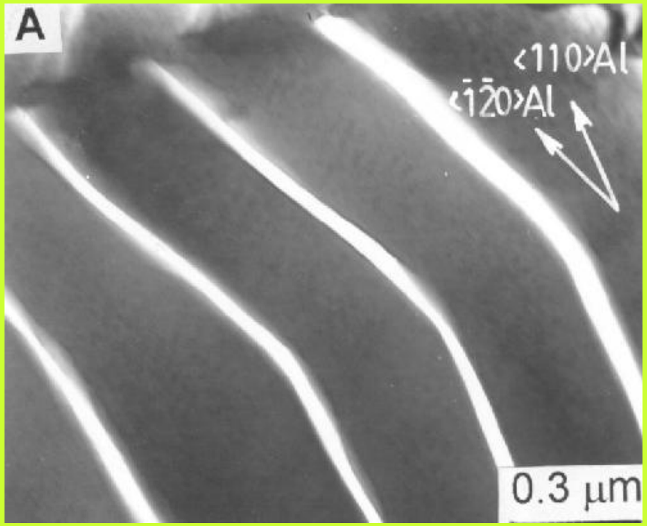


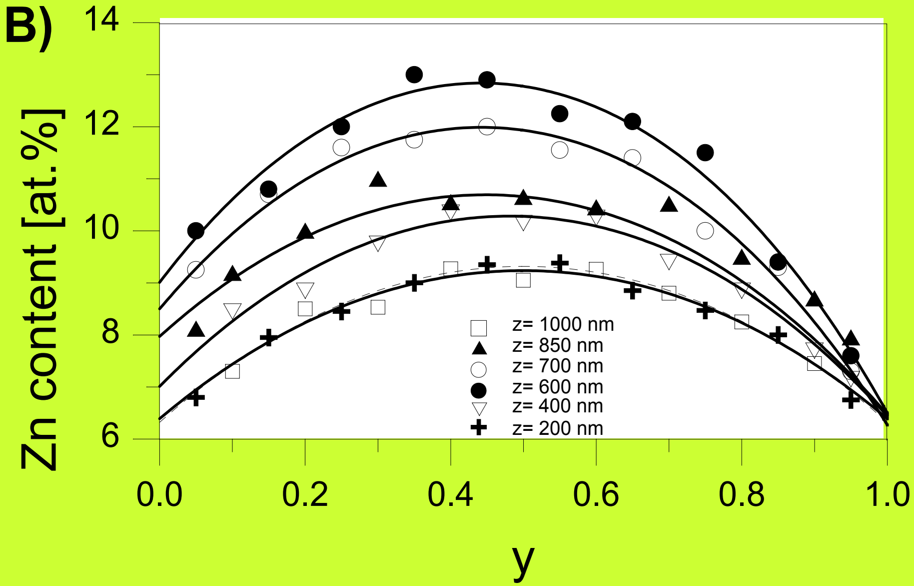
Time [s]	C
0	1.76
50	9.4
90	3.0

P. Zięba: *Z. Metallkunde* 90 (1999) 9

DP- steady state period of growth

Irregular morphology-growth direction change



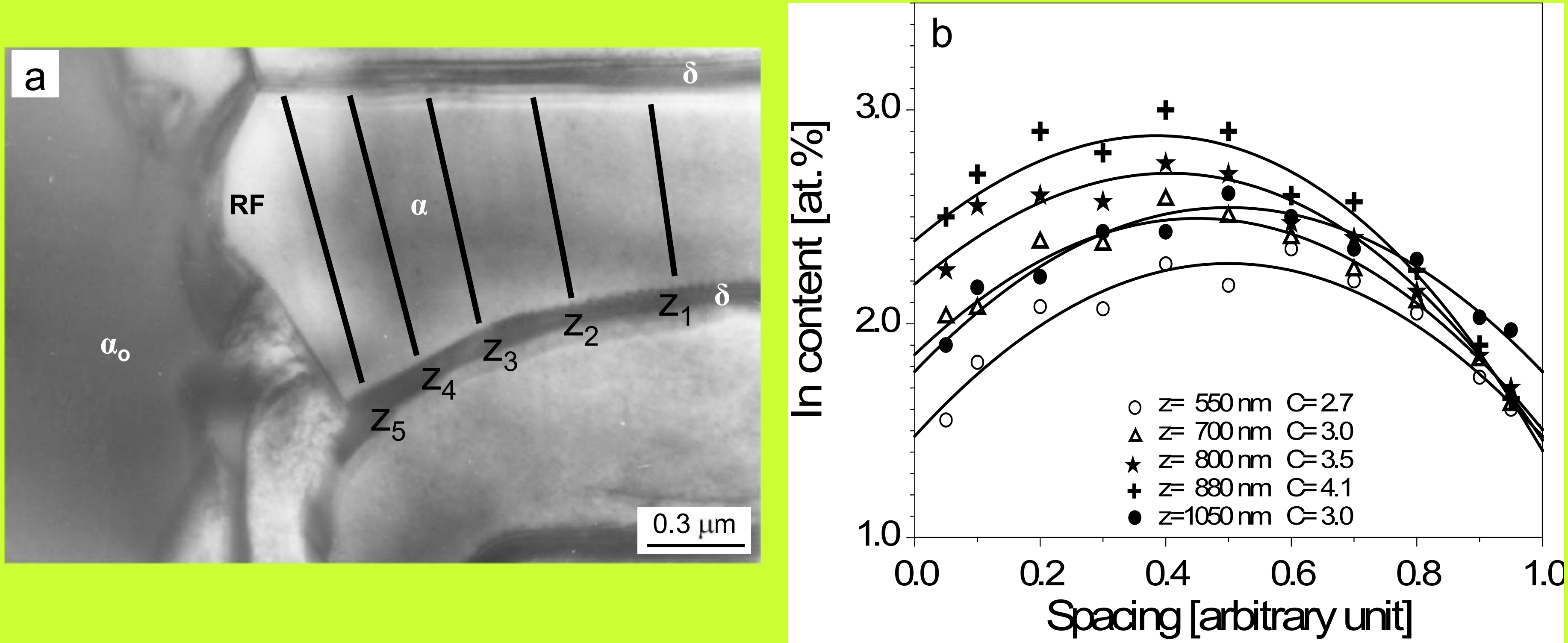


z [nm]	y(x=0)	y(x=1)	y_{max}	$x(y_{max})$	C
1000	6.39	6.39	9.23	0.5	1.72
850	7.39	6.47	10.67	0.447	2.29
700	8.5	6.27	11.99	0.442	3.37
600	9.0	6.5	12.84	0.442	4.01
400	7.0	6.44	10.28	0.481	2.31
200	6.32	6.32	9.3	0.5	1.81

Al-22 at.% Zn
aged at 450 K for 10 min

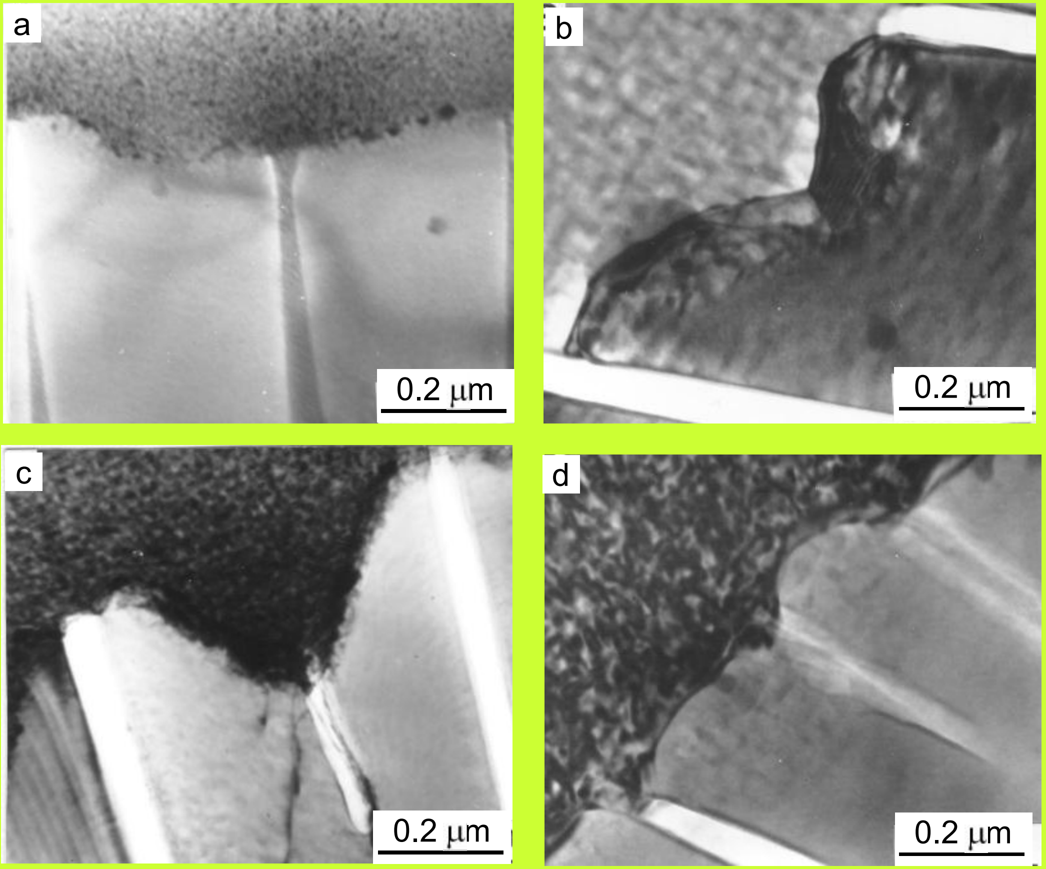
DP- steady state period of growth

Irregular morphology-growth direction change



G.A. Lopez, P. Zięba, W. Gust, E.J. Mittemeijer: *Mater. Sci. Technol.* 19 (2003)
Cu-4.5 at.% In aged for 10 h at 600 K, followed by 10 h at 550 K

Perturbation of solute concentration ahead of RF



Al-22 at.% Zn aged at 450 K: Images taken at total time 10 sec showing re-nucleation of β phase lamella

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

$$g(y) = h \cdot \sum_{n=0}^{N} b_n \cos(\pi n y)$$

$$y(x) = A \cdot \exp\left(y\sqrt{C}\right) + B \cdot \exp\left(-y\sqrt{C}\right) + x_o + h \cdot k(y, C)$$

$$k(y, C) = C \sum_{n=0}^{N} \frac{b_n \cos(n\pi y)}{C + (n\pi)^2}$$

$$A = \frac{\exp\left(-\sqrt{C}\right)\left(x_o - x_i + h \cdot k(0, C)\right) + x_R - x_o - h \cdot k(1, C)}{\exp\left(\sqrt{C}\right) - \exp\left(-\sqrt{C}\right)}$$

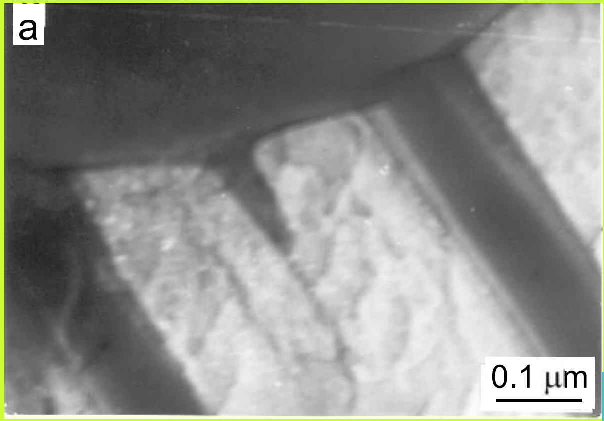
$$B = \frac{\exp\left(\sqrt{C}\right)\left(x_o - x_i + h \cdot k(0, C)\right) + x_o - x_R - h \cdot k(1, C)}{\exp\left(\sqrt{C}\right) - \exp\left(-\sqrt{C}\right)}$$

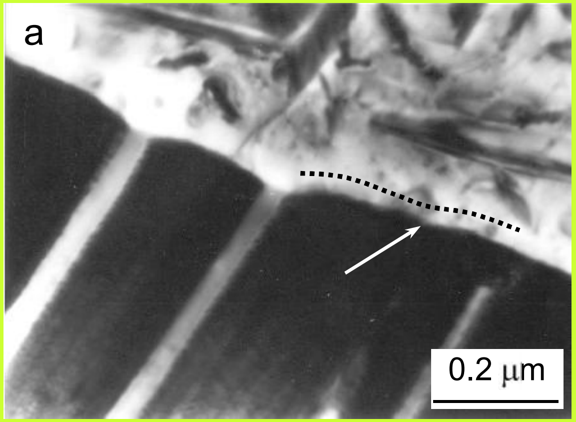
The *g(y)* describes the local perturbation in the solute distribution in the matrix just ahead of the reaction front The shape and the quantity of the perturbation are described by Fourier´s series, *N* is the upper limit of summation of *n* in Fourier´s series, *h* - parameter defining the height of the perturbation.

Boundary conditions: For $x(y=0)=x_i$ and $x(y=1)=x_R$

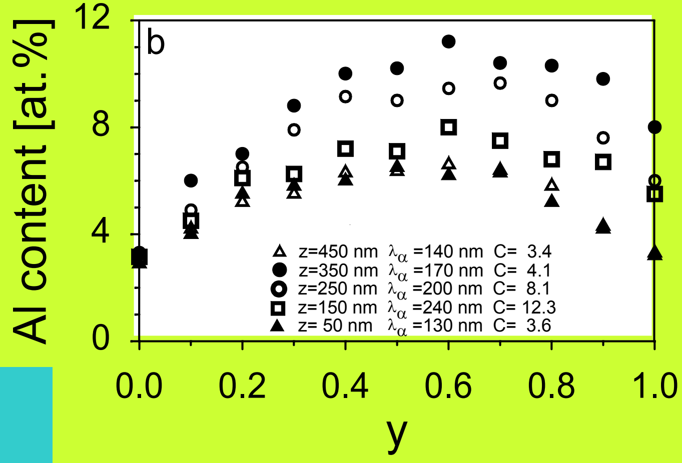
DP- steady state period of growth

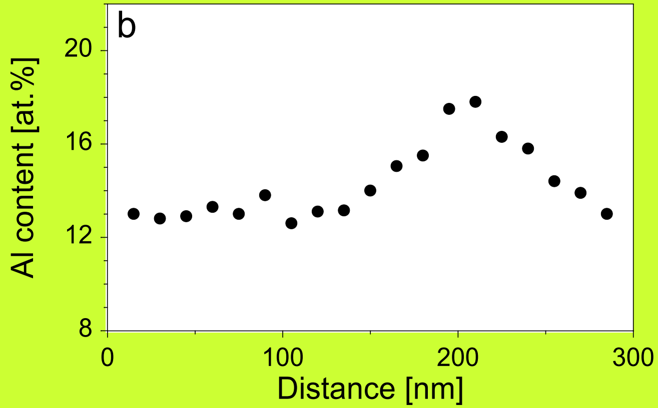
Irregular morphology- β phase lamella re-nucleation





P. Zięba: *Acta Mater.* 46 (1998) 369
Co-13 at.% Al aged for 2 h at 800 K, followed by 20 min at 950 K



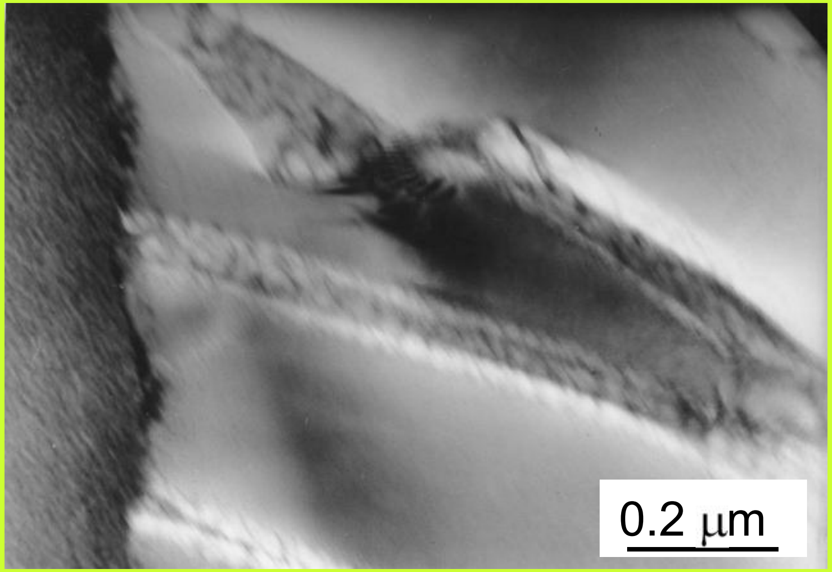


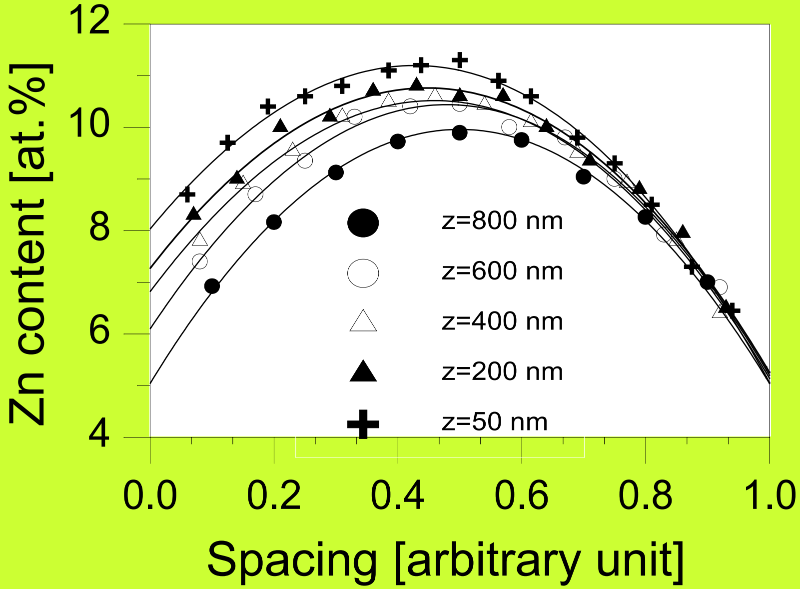
Irregular growth- β phase lamella re-nucleation

z [nm]	h	y(x=0)	y(x=1)	y_{max}	$x(y_{max})$	C
450	0	3.13	3.13	6.45	0.5	3.76
350	0.33	3.21	5.2	7.68	0.587	4.15
250	0.67	3.15	6.1	9.49	0.609	6.7
150	1	3.25	7.5	10.95	0.641	8.3
50	0	3.1	3.1	6.31	0.5	3.58

DP- steady state period of growth

Irregular growth-branching of β lamella





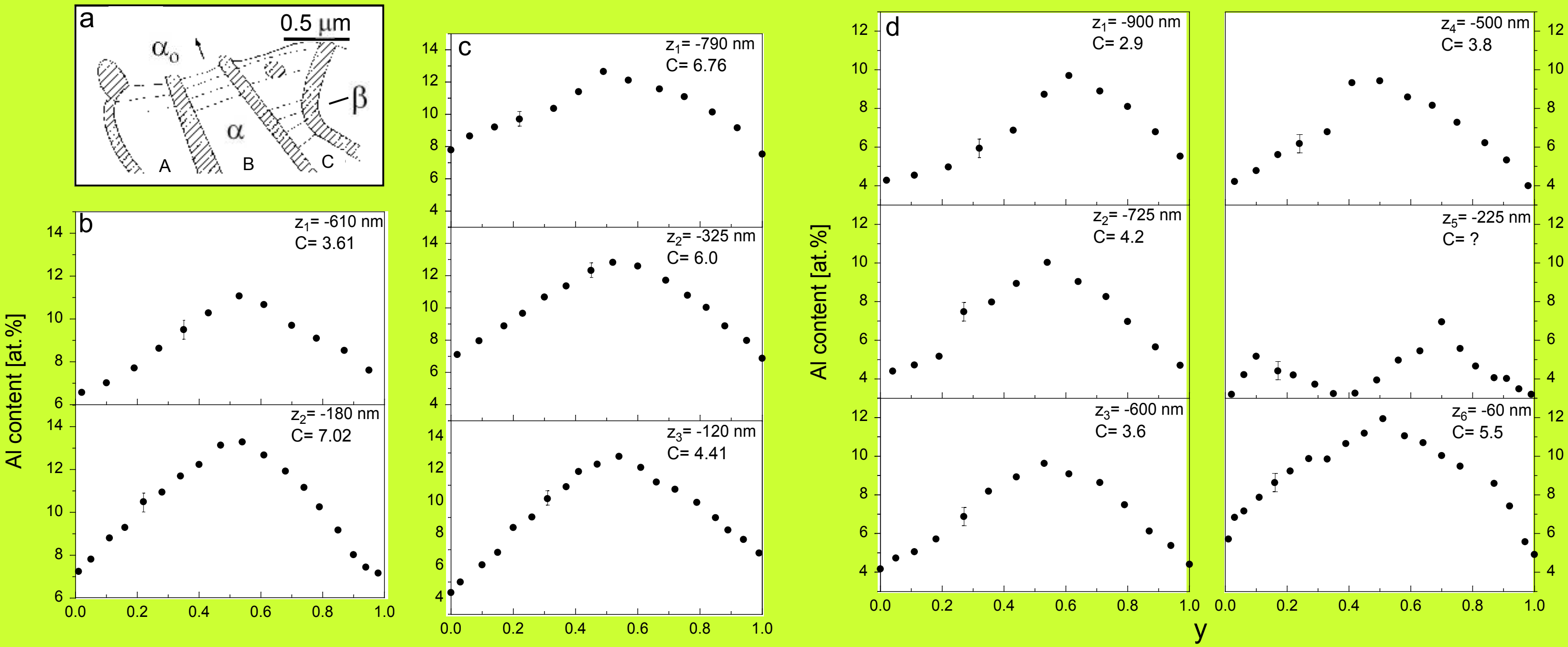
Al-22 at.% Zn aged for 5 min at450 K

Irregular morphology- β phase lamella re-nucleation

z [nm]	λ [nm]	y(x=0)	y(x=1)	y_{max}	$x(y_{max})$	C
800	237	5.0	7.98	11.17	0.412	3.14
600	192	5.18	7.21	10.75	0.445	3.01
400	167	5.11	6.78	10.51	0.456	2.94
200	148	5.15	6.05	10.41	0.578	3.11
50	127	5.0	5.0	9.89	0.5	3.05

DP- steady state period of growth

Irregular growth-symphathetic nucleation,
direction change, precipitation



Mg-18 at.% Al., D. Duly, M.G. Cheynet, Y. Brechet:
Acta Metall. & Mater. 42 (1994) 3855.

Solute concentration profiles across α lamella

Shape → **Symmetrical:** Regular morphology; **Asymetrical:** Irregular morphology

Solute content at the α/β interphase boundary → **Equilibrium value:** Co-Al, Co-W, Ni-Sn, Cu-In; **Non-equilibrium value:** Al-Zn, Co-Mo, Ni-In; **Mixed type:** Mg-Al

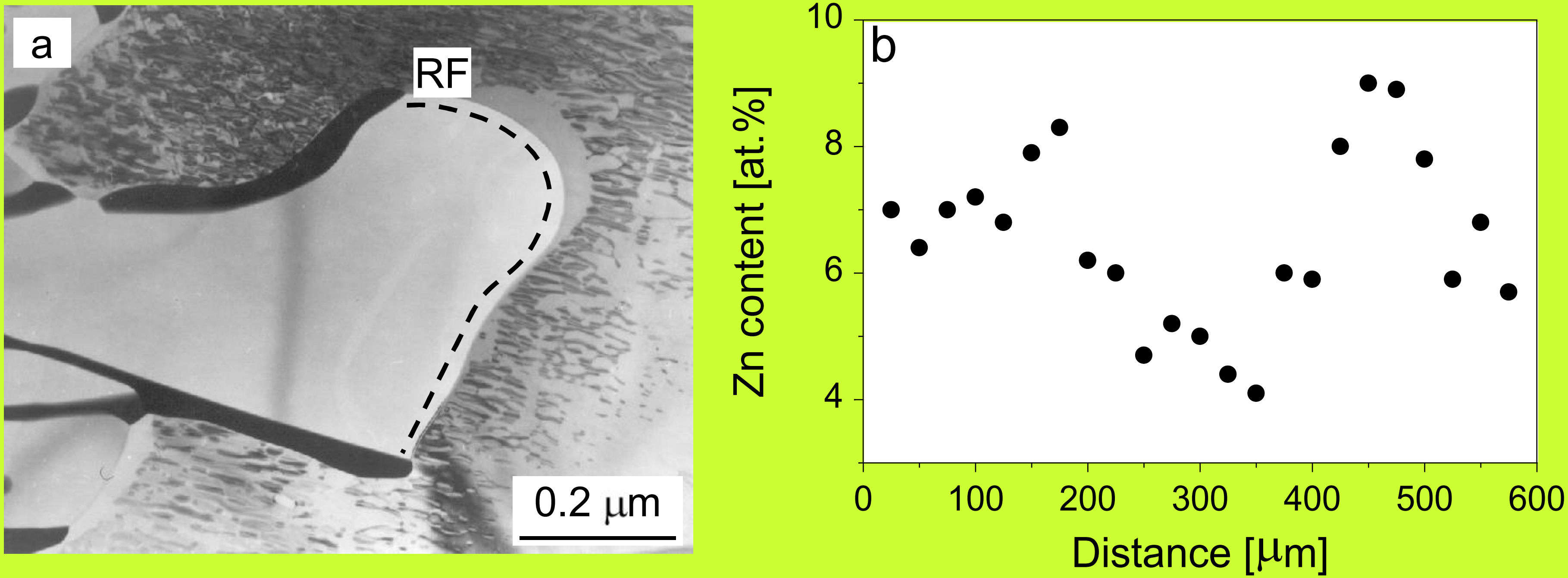
Height → **C parameter**

Modifications of Cahn equation

Cahn equation 1959

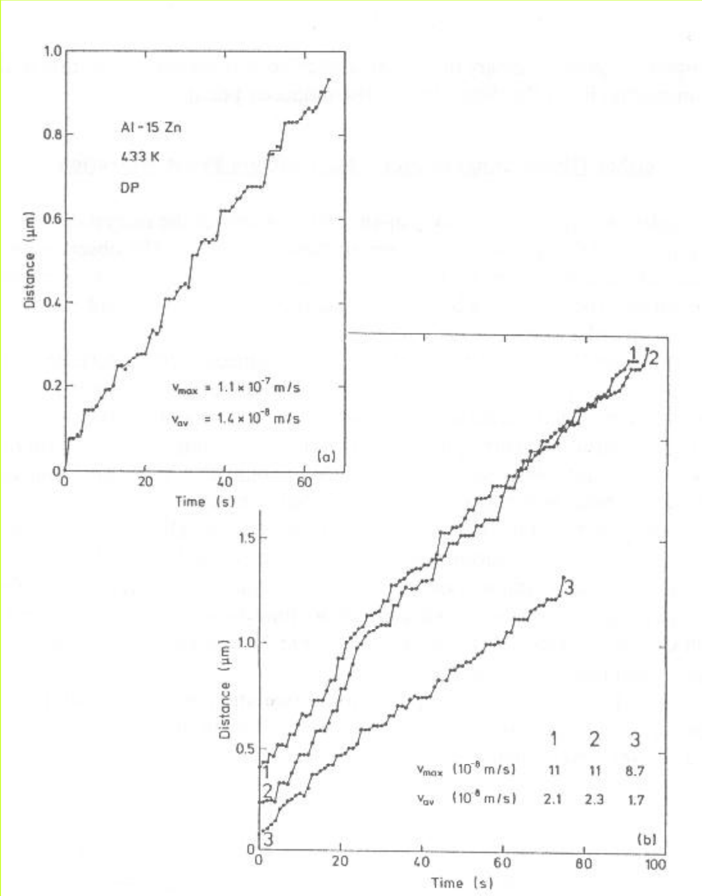
DP- steady state period of growth

Irregular morphology-shape changing – return to non-steady growth



P. Zięba, W. Gust, *Z. Metallkunde* 91 (2000) 532
Al-22 at.% Zn alloy aged at 450 K for 450 s

DP- steady state period of growth



Irregular morphology: stop- and go motion

The differences between the maximum and the average velocities were found as large as one order of magnitude.

The maximum value is true for a very short time of 0.7 s, whereas the largest stop interval amounts to 4 s.

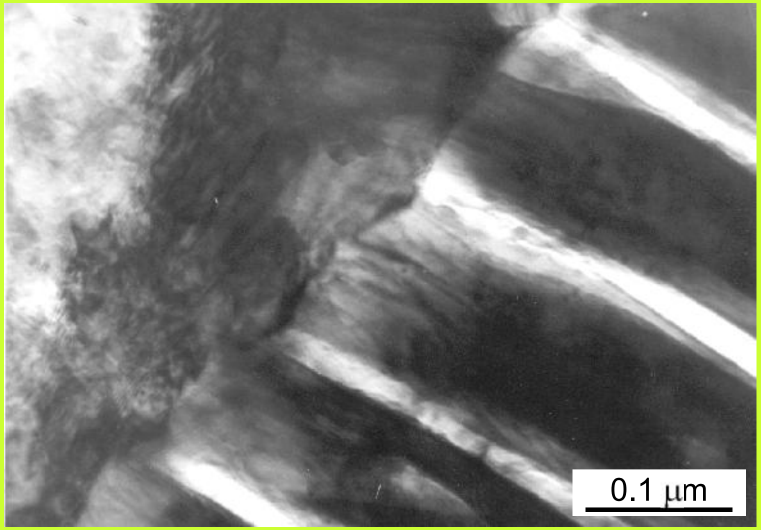
The individual migration distance between two stop intervals were 0.03-0.09 μm, and therefore they were not visible on optical microscope.

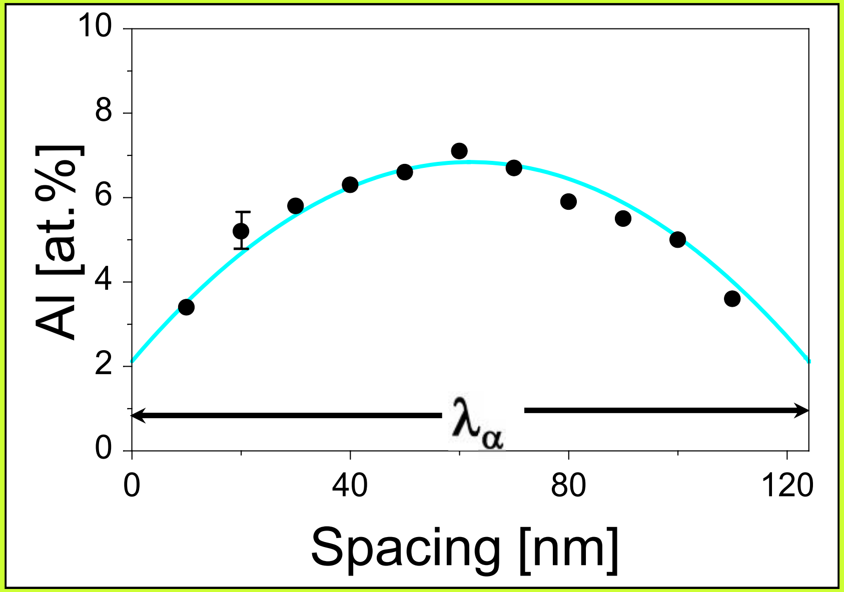
S. Abdou, G.I. Solorzano, M. El-Boragy, W. Gust, B. Predel,
Scripta Mater. 34 (1995) 1431

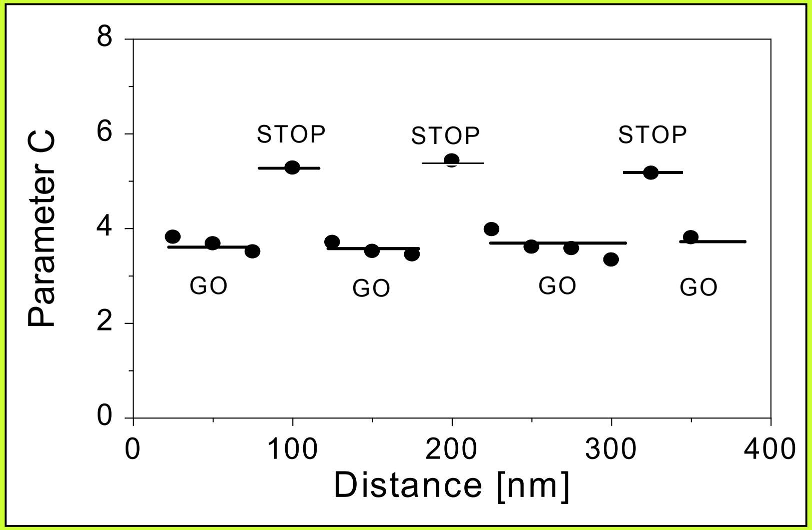
Al-15 at.% Zn alloy: DP: 433 K

DP- steady state period of growth

Irregular morphology: stop- and go motion



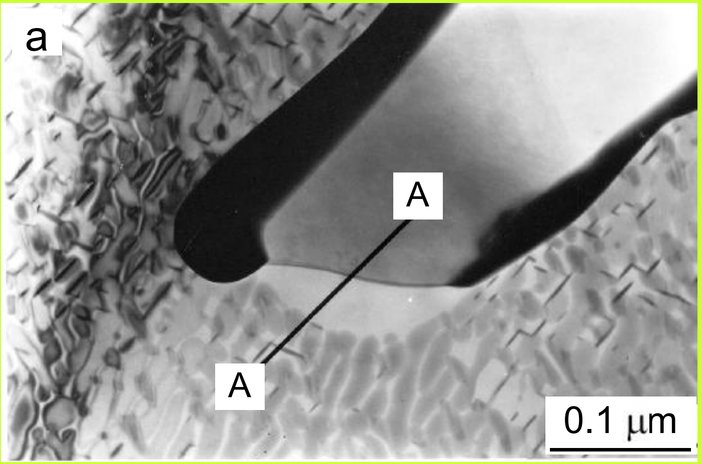


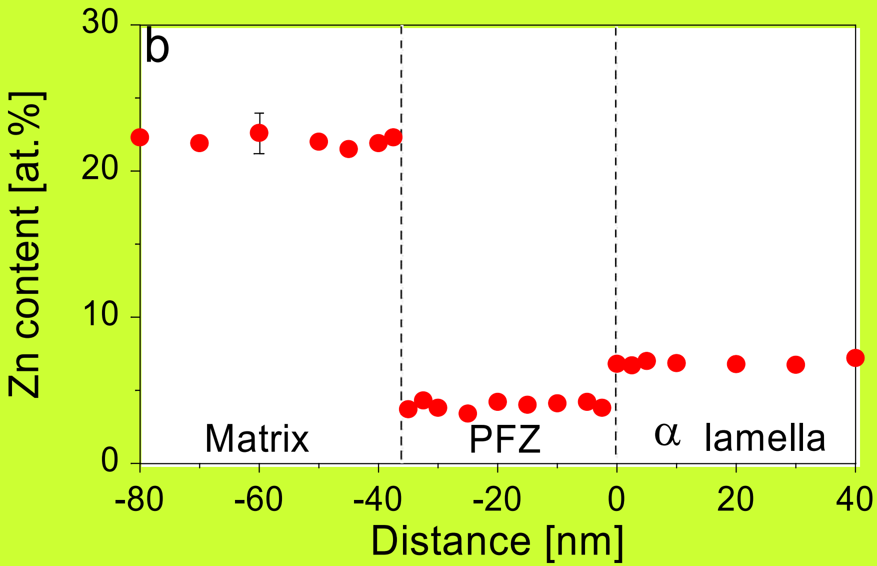


P. Zięba: *Mater. Chem. Phys.* 62 (2000) 183
Co-13 at.%Al aged at 800 K for 2 hours followed by 20 min at 950 K.

DP- steady state growth- growth termination

Precipitate free zone (PFZ)

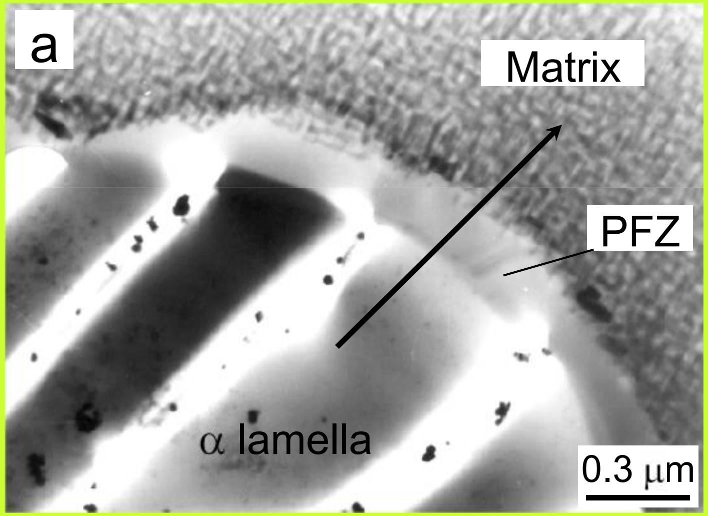


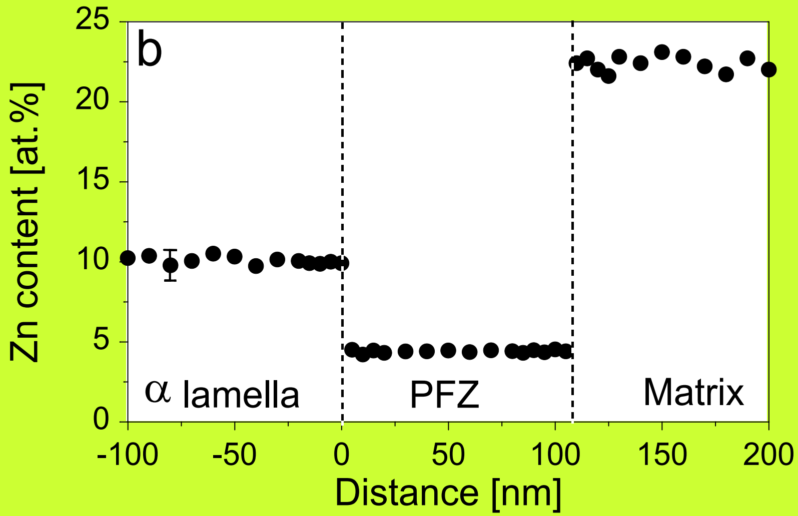


P. Zięba: *Z. Metallkunde* 90 (1999) 9
Al-22 at.% aged at 450 K for 15 min

DP- steady state growth- growth termination

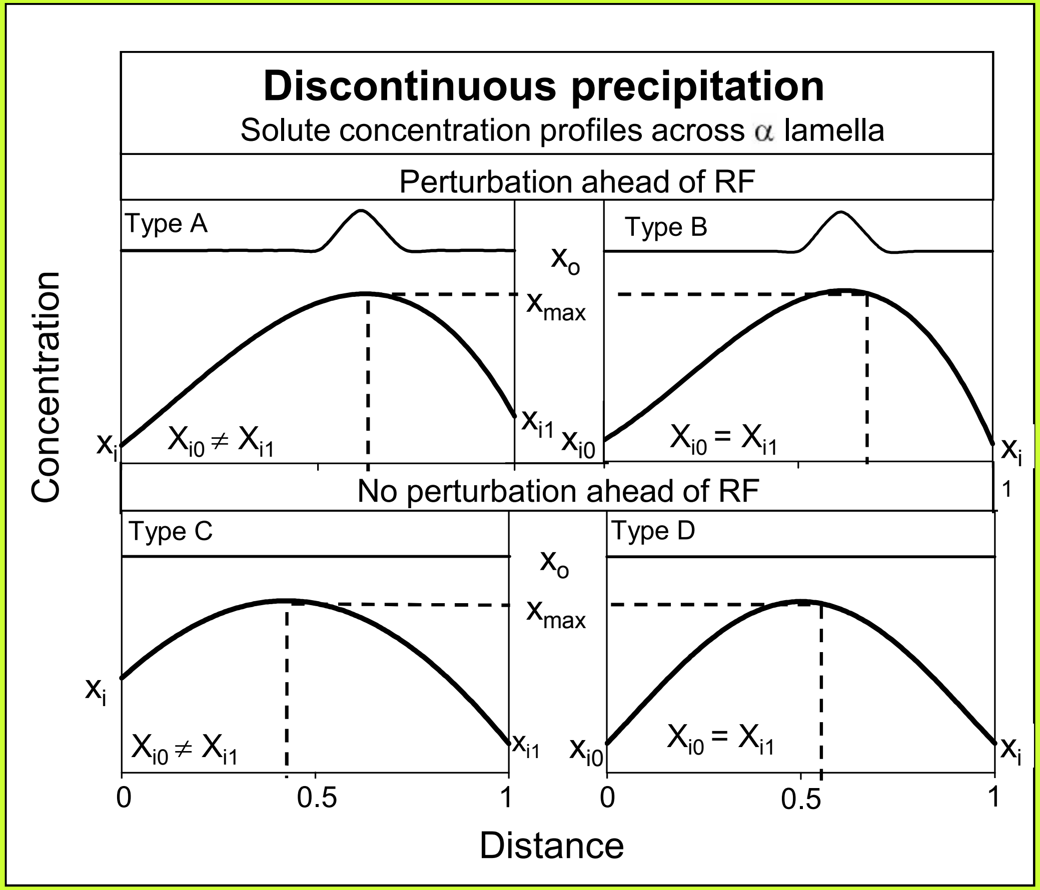
Precipitate free zone (PFZ)





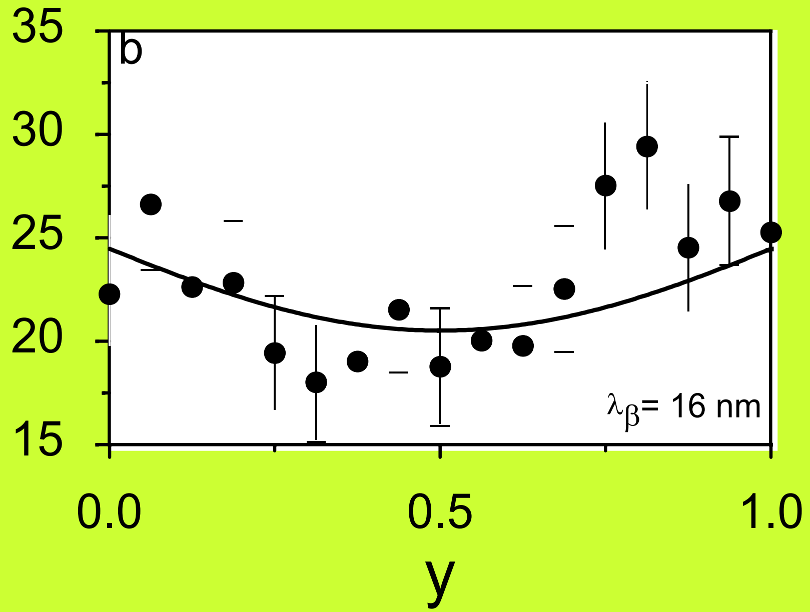
P. Zięba, D.B. Williams: *Mikrochim. Acta* 2004
Al-15 at.% aged at 450 K for 300 sec

DP- steady state period of growth



DP- steady state period of growth

Solute concentration profile across β lamella

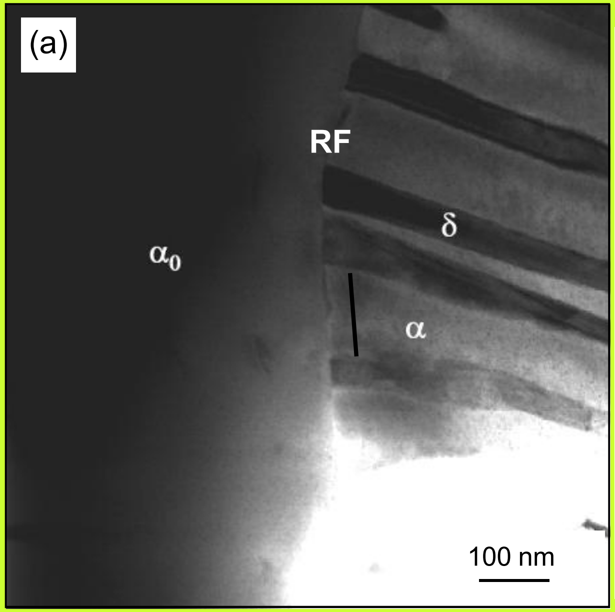


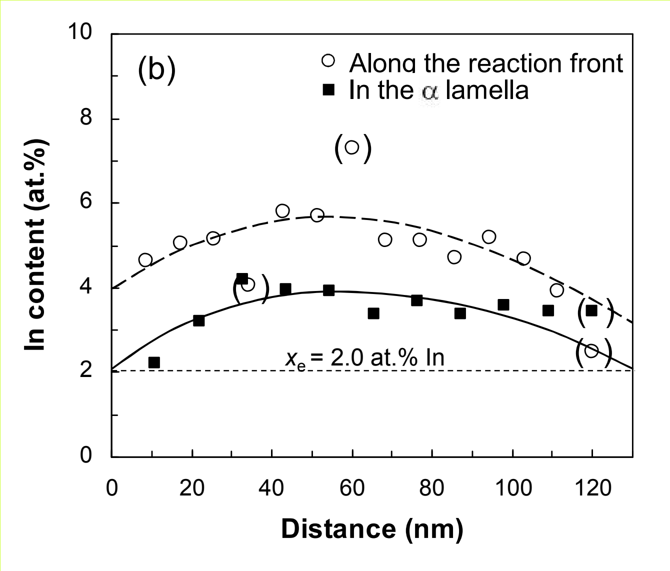
Ni-7.5 at.% aged at 723 K for 72 hours.

G.P. Geber, R. Kirchheim: *Acta Mater.* 45 (1997) 2167

DP- steady state period of growth

First ever high spatial resolution EDX microanalysis within the RF of DP





Cu - 7.5 at.% In annealed at 330 °C for 48 h

A further step in the study of diffusion along migrating grain boundaries

G.A. López, P. Zieba, W. Sigle and E.J. Mittemeijer

DP reaction is associated with a rearrangement of the solute atoms at the moving reaction front, as confirmed by the results of analytical scans across the reaction front.

The DP reaction occurs in two basic steps. After the nucleation period a non-steady state growth is observed.

The creation of parallel arrays of the alternating α and β lamellae initiates the steady-state growth. Steady-state period of growth of DP reaction is influenced by various instabilities.

The system possesses some intrinsic capability to correct local RF shape to balance the forces acting on it if the perturbation is not larger than a certain critical value.

This sensitivity of the system may result in some asymmetry of the solute concentration profile.

If the critical value is exceeded or simply perturbation imposed is too large, re-nucleation and branching phenomena occur.

In some cases system becomes to be unstable: non-steady state growth.

Termination of the DP reaction is due to impingement of colonies or PFZ formation (backward migration of the RF).

The DP reaction does not result in the equilibrium concentration within the α lamellae. A characteristic reverse "U" shape of the solute content shows at most the equilibrium value at the α/β interface.