A STEM study of Mn diffusion and interfacial segregation during the formation of partitioned grain boundary ferrite

H. Guo and G. R. Purdy

University of Science and Technology Beijing

McMaster University

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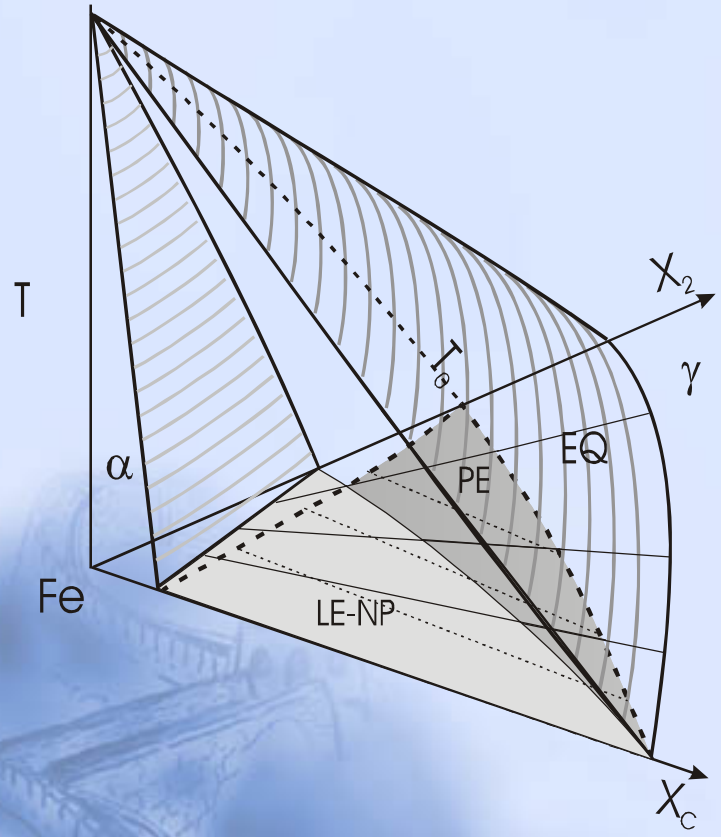
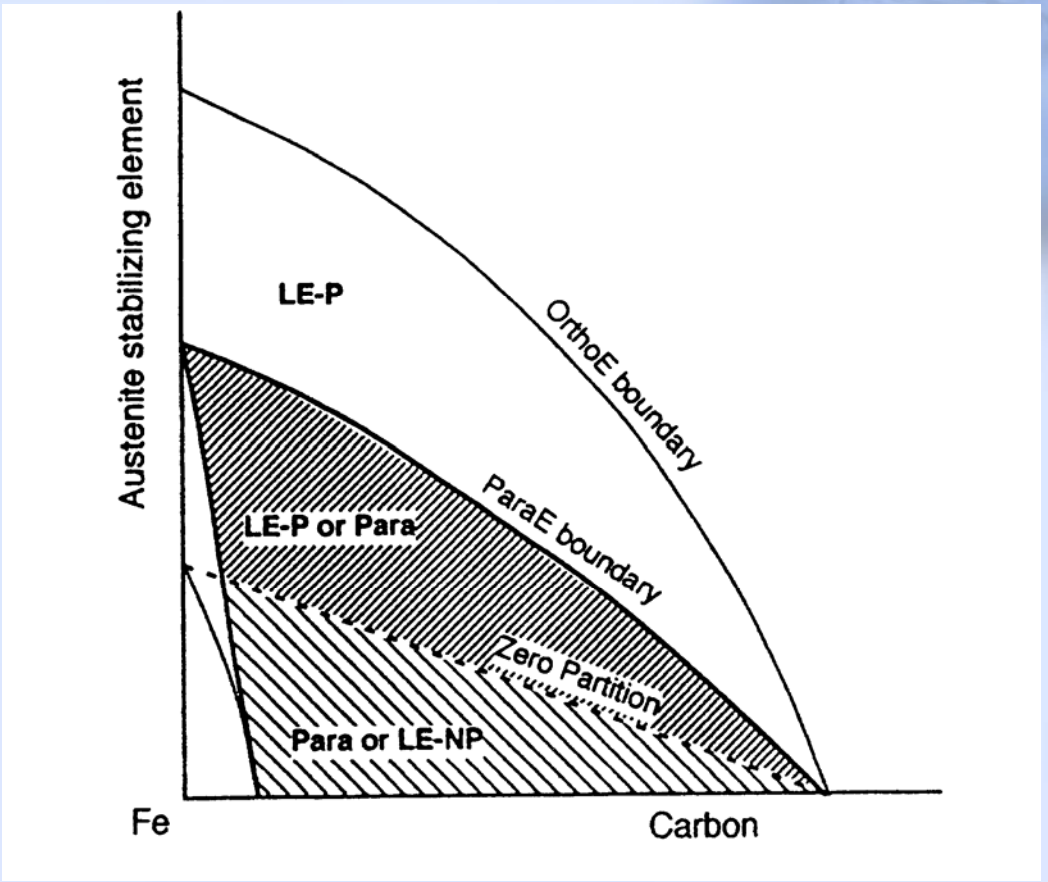
Outline

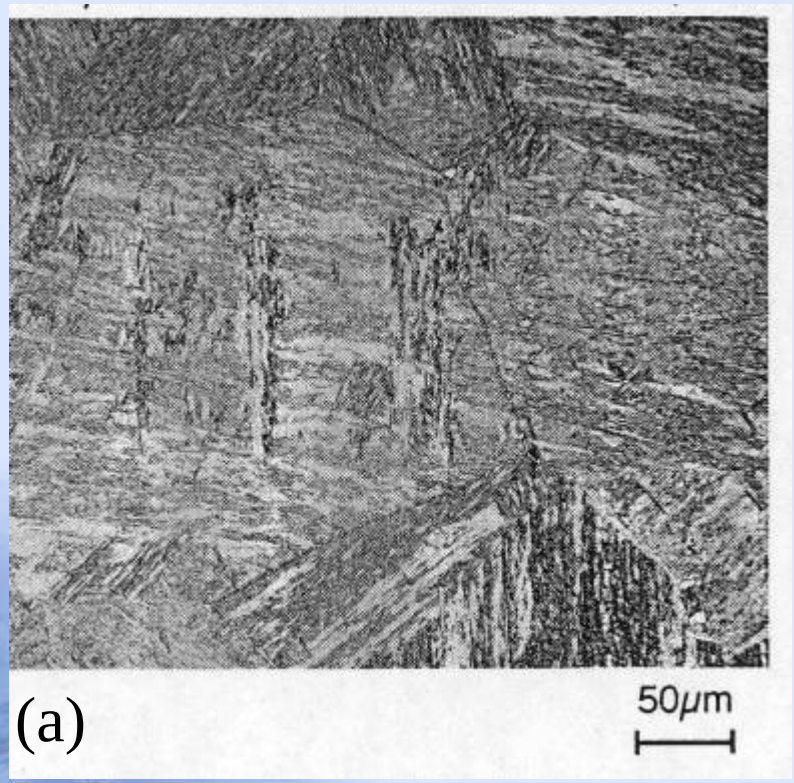
1. A brief review
2. Experimental
3. Some Mn profiles across the grain boundary ferrite
4. A simulation of Mn segregation at α/γ interface
5. Summary

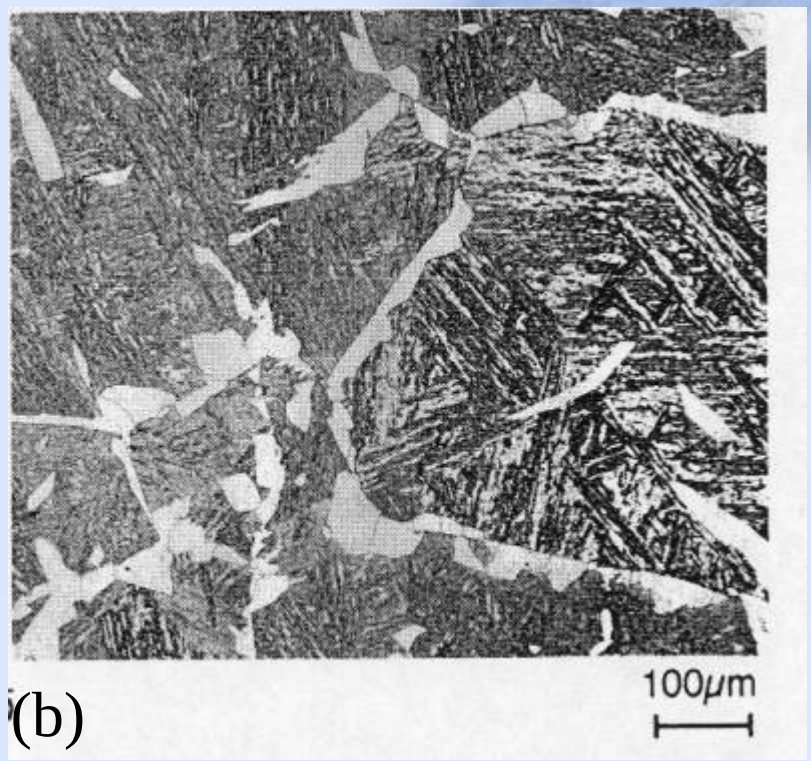




Schematic relation among the local equilibrium with or without M-partitioning and paraequilibrium for the system Fe-C-M.

(Oi *et al*, 2000)

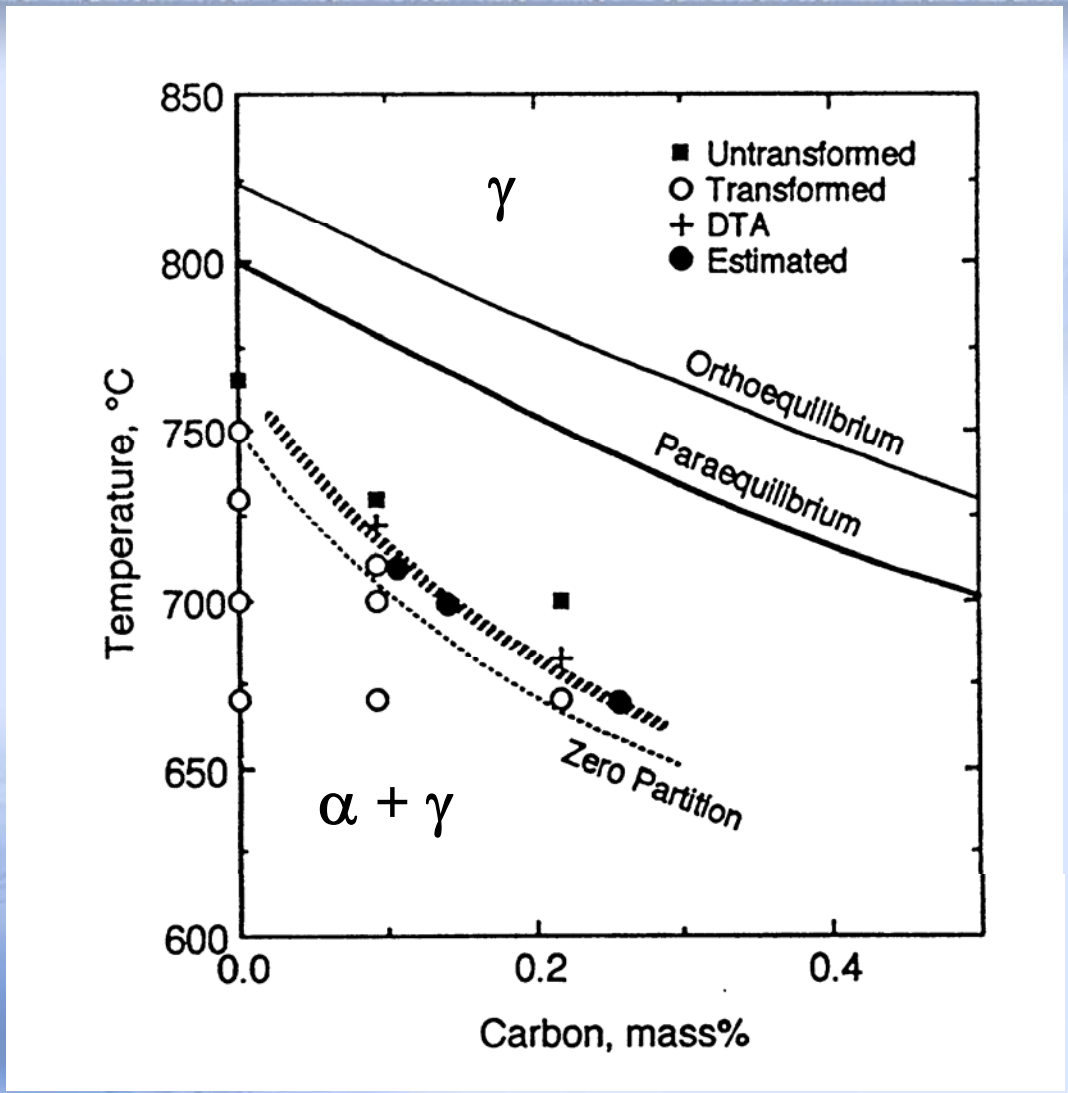




Slow growing ferrite

Fast growing ferrite

Microstructures of a Fe-0.2C-2.2Mn formed during the isothermal holding at (a) 700°C and (b) 670°C for 60 min.

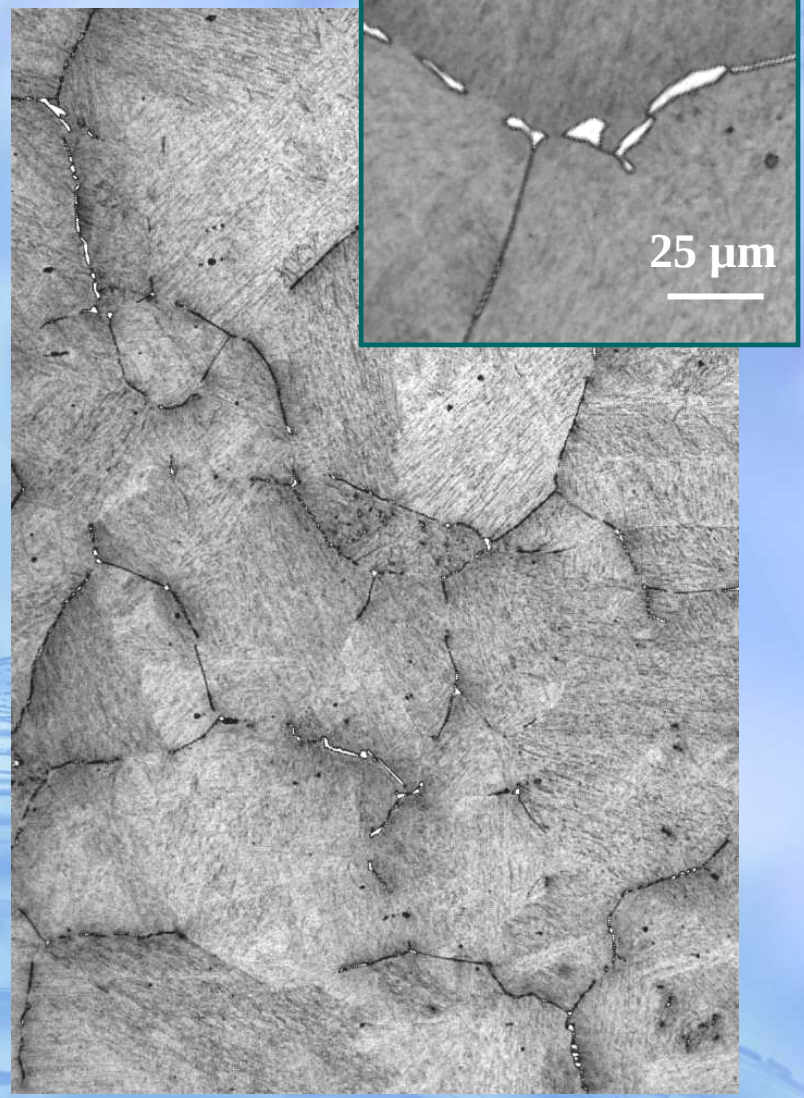


(Oi *et al*, 2000)

The experimental boundary between partitioned and unpartitioned growth (shaded), superimposed on a computed isopleth for 2wt% Mn.

Fe-0.04C-3.00Mn-1.85Si

751°C-1hr



766°C-1hr

250µm

Mn Segregation at α/γ interface in Fe-0.04C-3.00Mn-1.85Si, isothermally held at 751°C.

Reaction time	Ferrite precipitate ID	Segregation, (monolayer)
600s	1 (S4B-F1)	0.00±0.02
	2 (S4D-F1-i1)	0.42±0.14
	3 (S4D-F1-i2)	0.47±0.17
	4 (S4B-F2)	0.57±0.19
	5 (S4D-F2-i1)	0.57±0.21
50000s	1 (S3E-F1)	0.17±0.09
	2 (S3E-F6)	0.36±0.14
	3 (S3C-F7)	0.64±0.24
	4 (S3C-F8)	0.70±0.25

Experimental

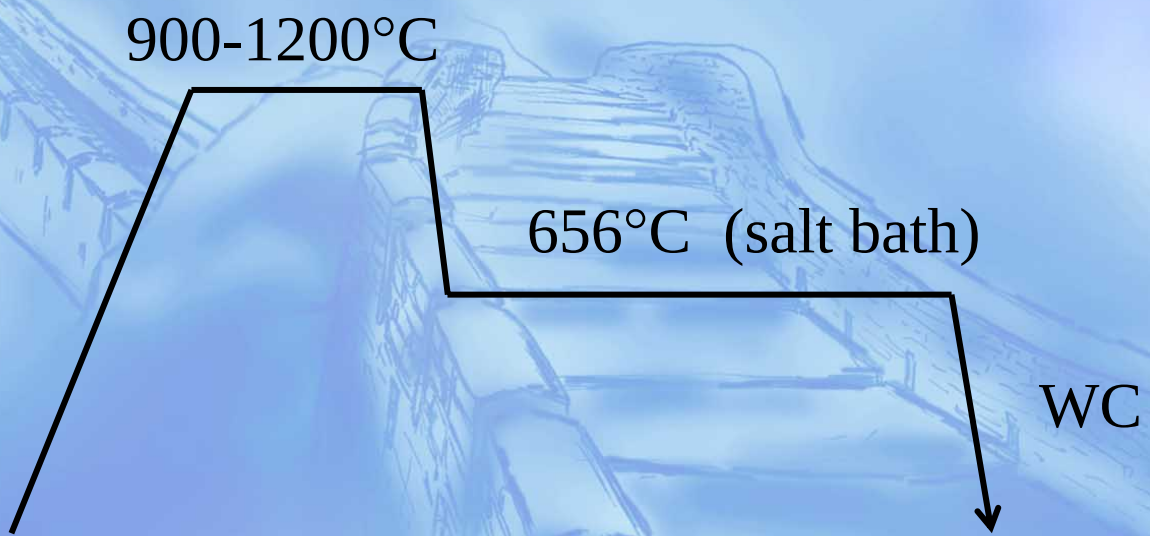
Composition of the alloy:

Fe-**0.37C**-3.00Mn-1.85Si (wt%)

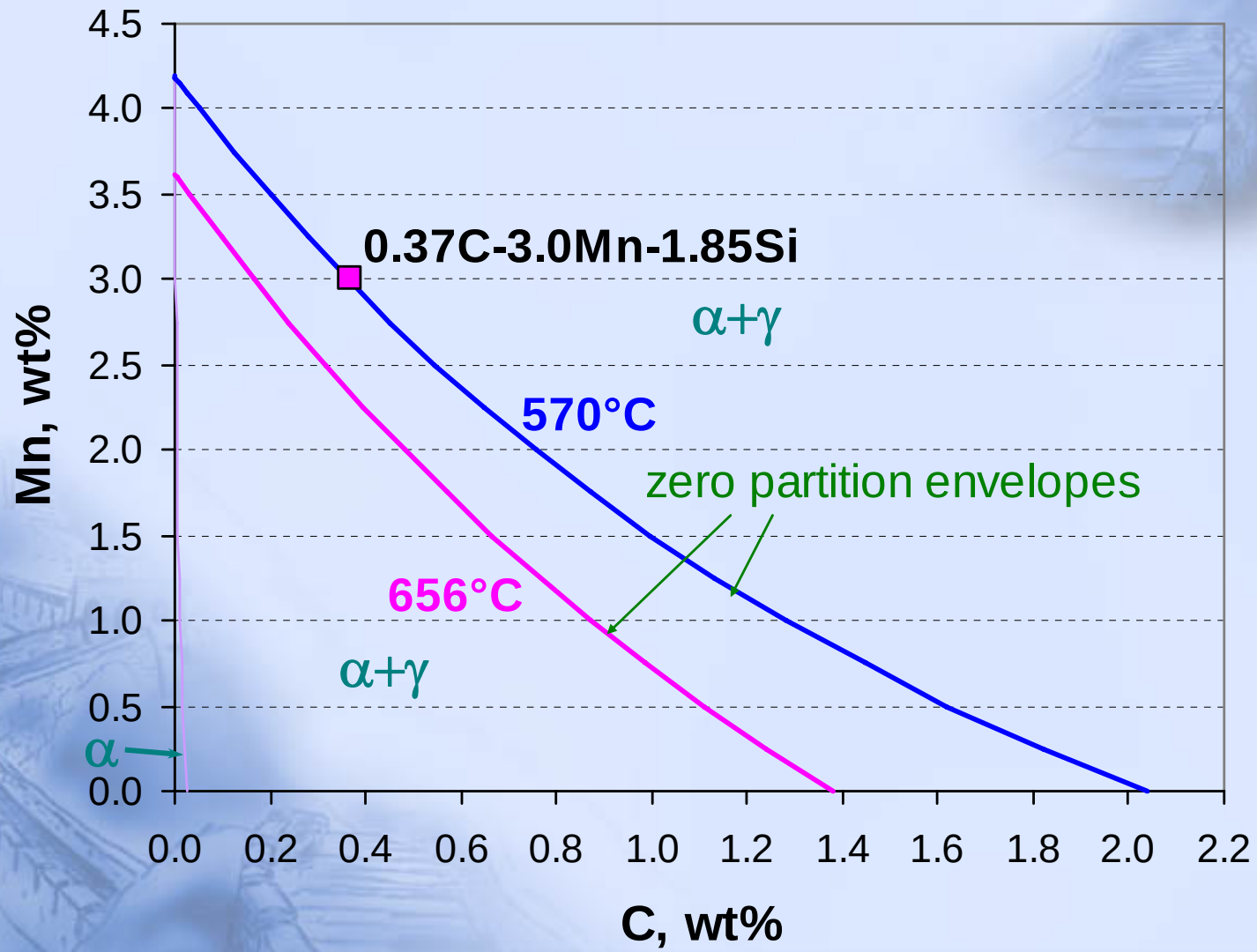
Homogenization:

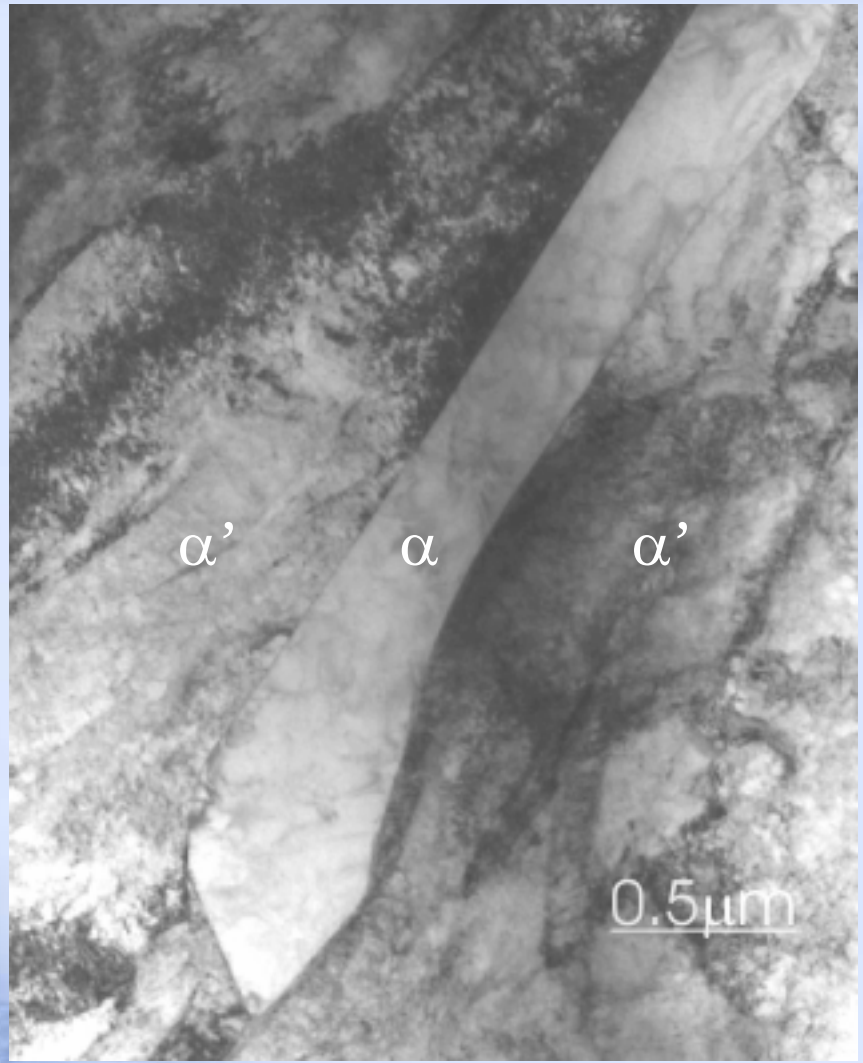
1200°C×96 hrs, furnace cooling.

Isothermal heat-treatment:



- zero partition envelopes at 570°C and 656°C



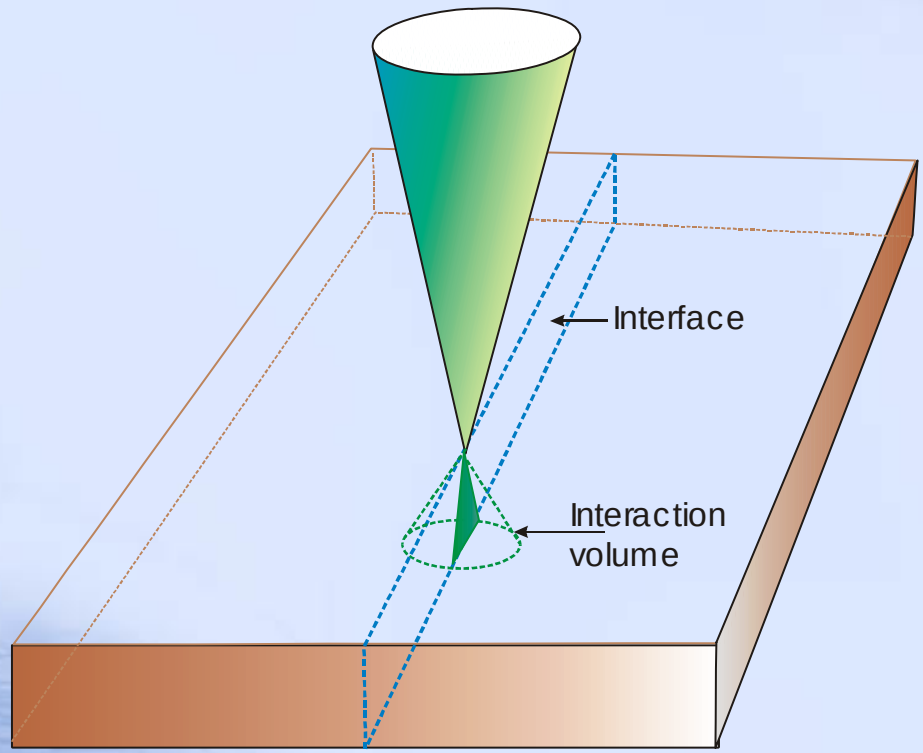


Grain boundary ferrite in Fe-0.37C-3Mn-1.8Si,
1 hour at 656°C

STEM analysis

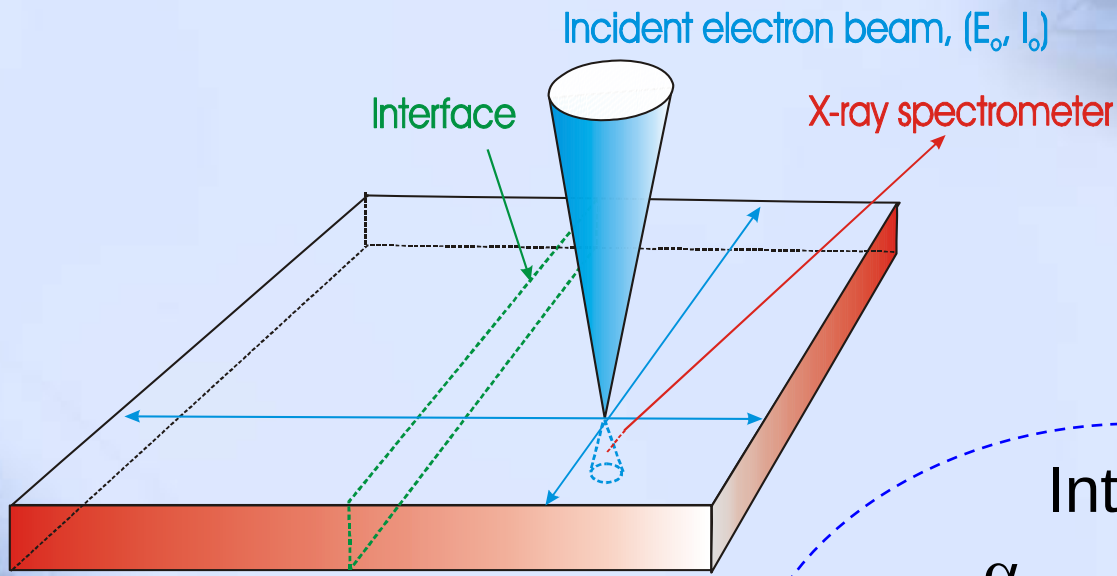
Edge-on condition

Beam spreading in Transmission:



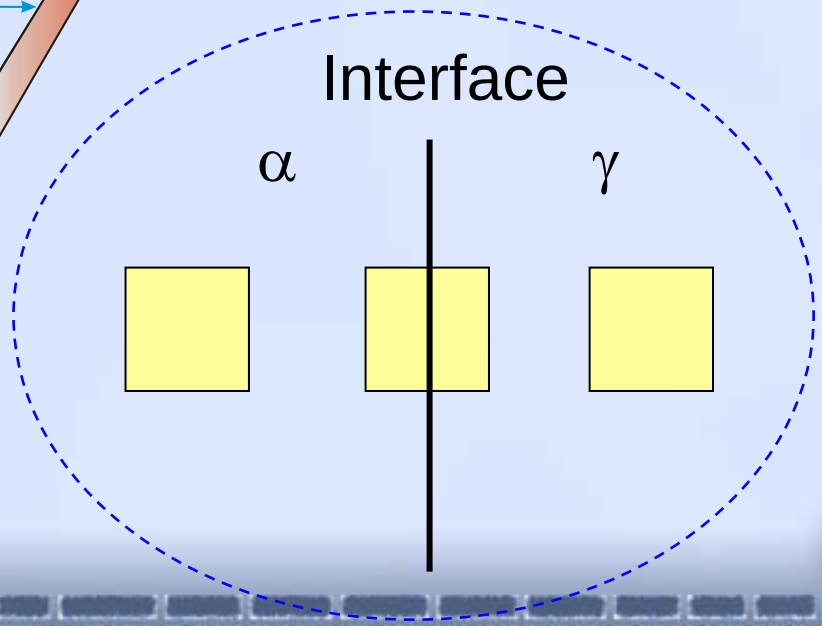
STEM MICROANALYSIS

Scanning Mode

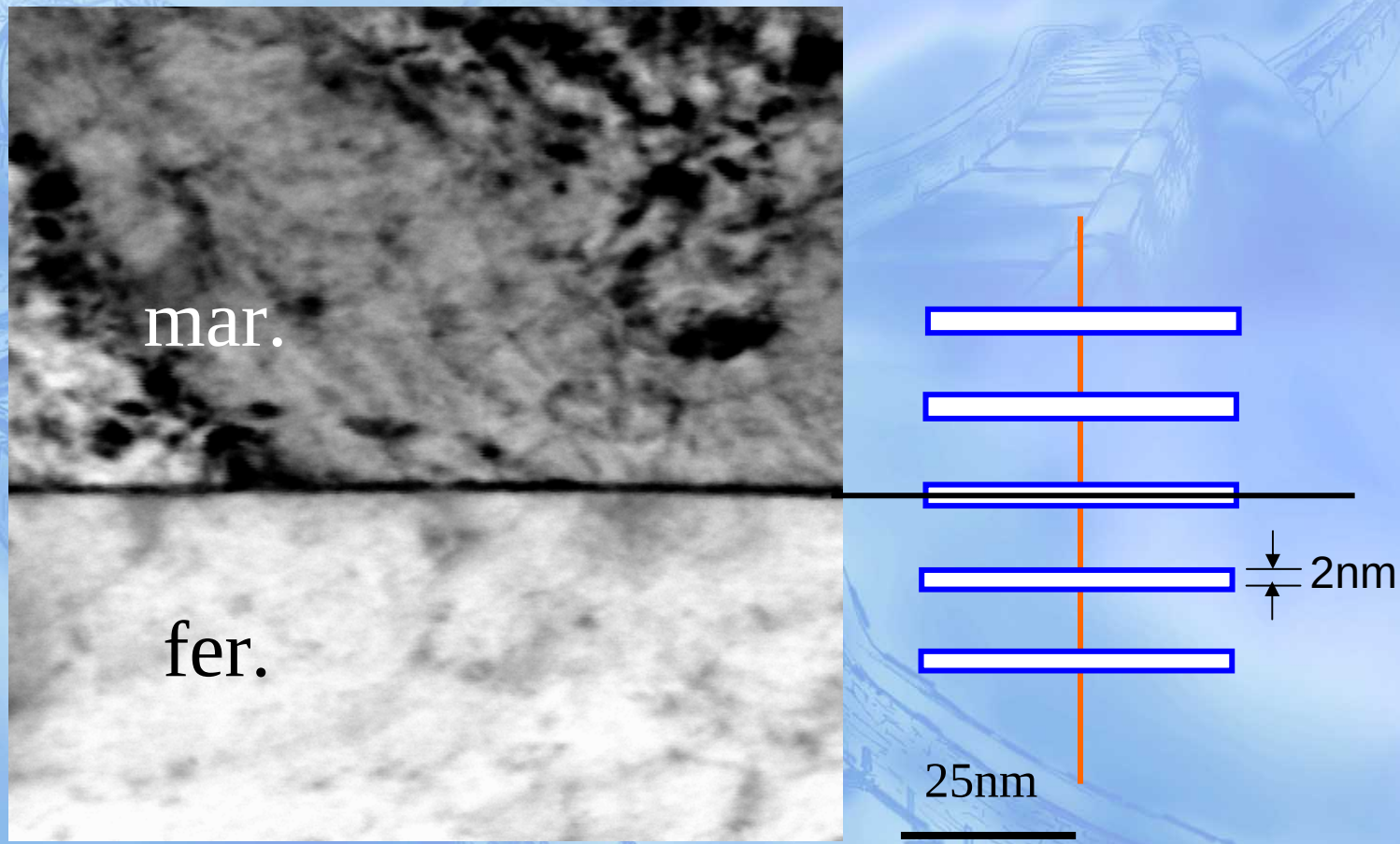


Experimental conditions:
E_o=250KeV, I_0=10^{-10}A,

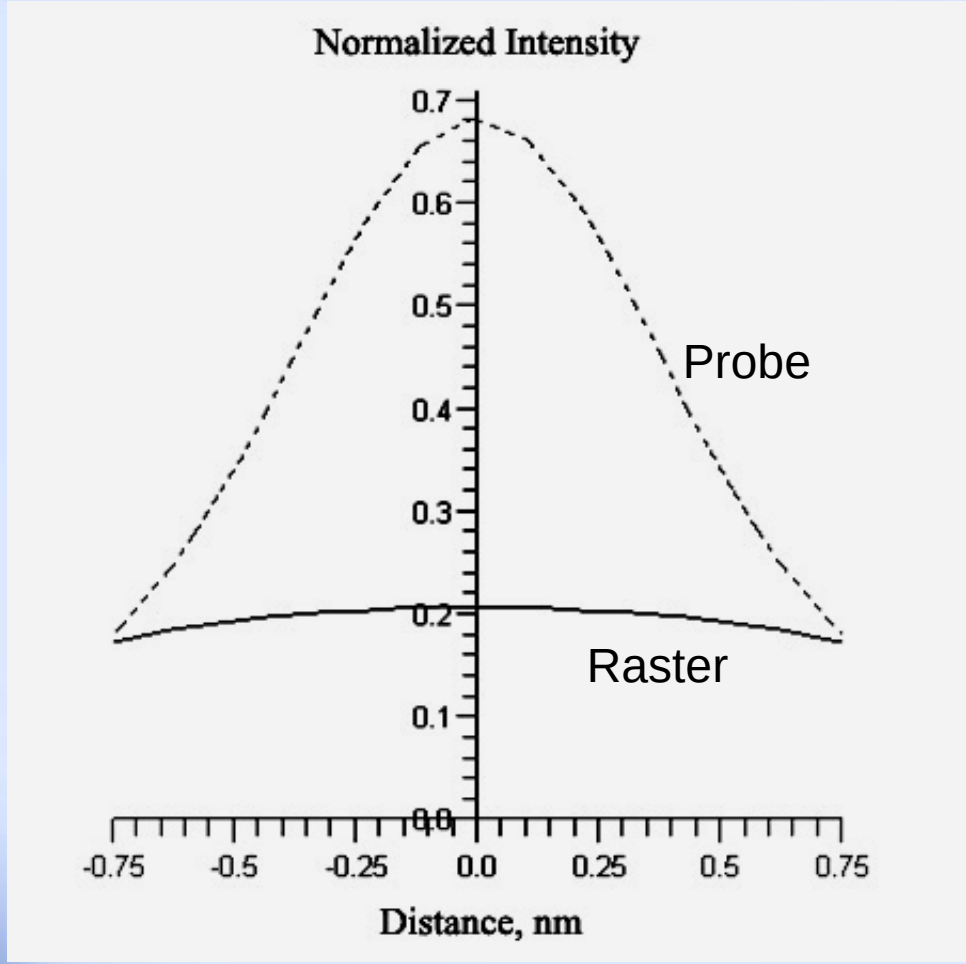
Area scanned: 16X16 nm
Counting time: 1000 s
min. detectable Mo in Fe:
3 x 10^{17} atoms/m^2



Raster scanning: Collecting time >= 150 s

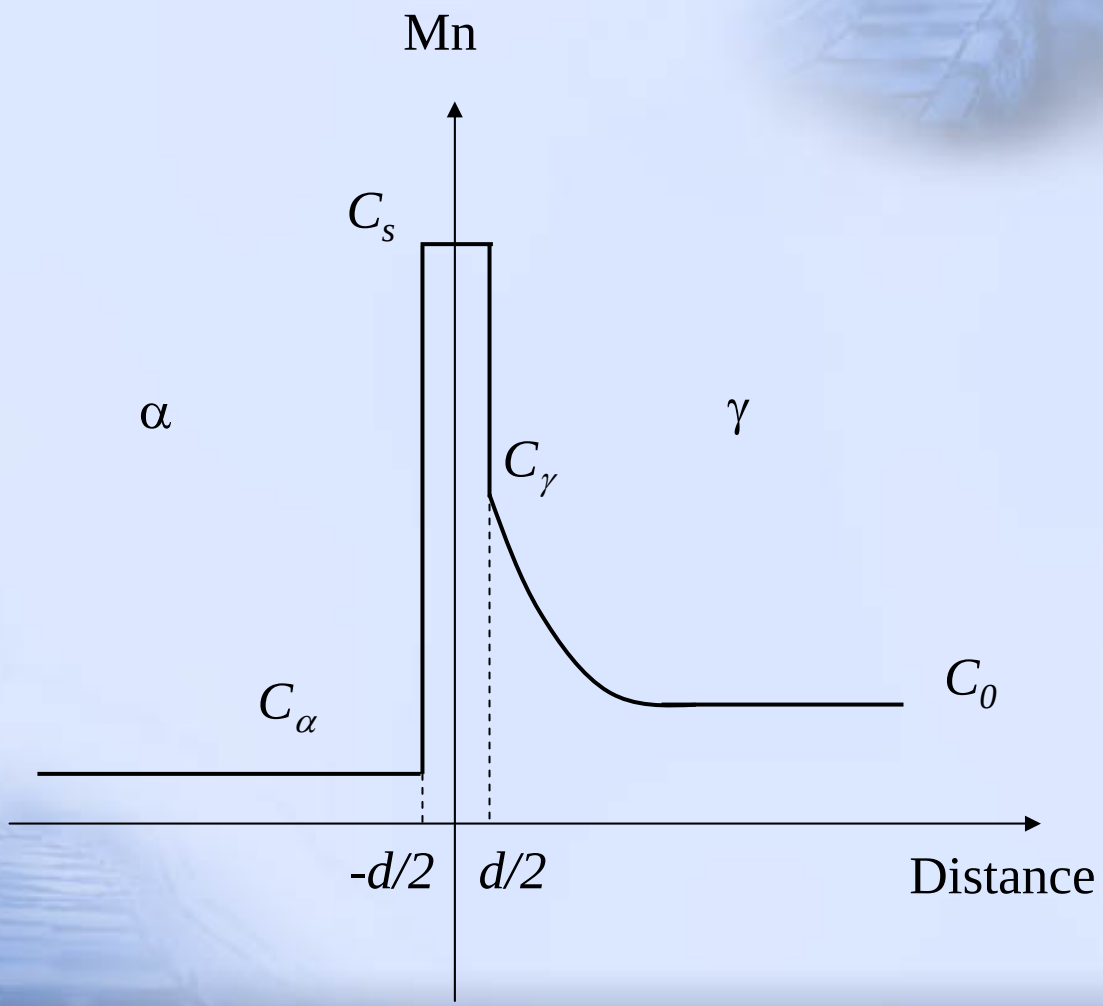


STEM image of an edge-on α/γ interface:



Normalized electron intensity distribution within a 1.5nm-wide interface after the electrons passed through a 200-nm thick foil in a raster window and a probe beam analysis.

An illustration of Mn profile across an α / γ interface. Cs is assumed to be a constant across the interface.



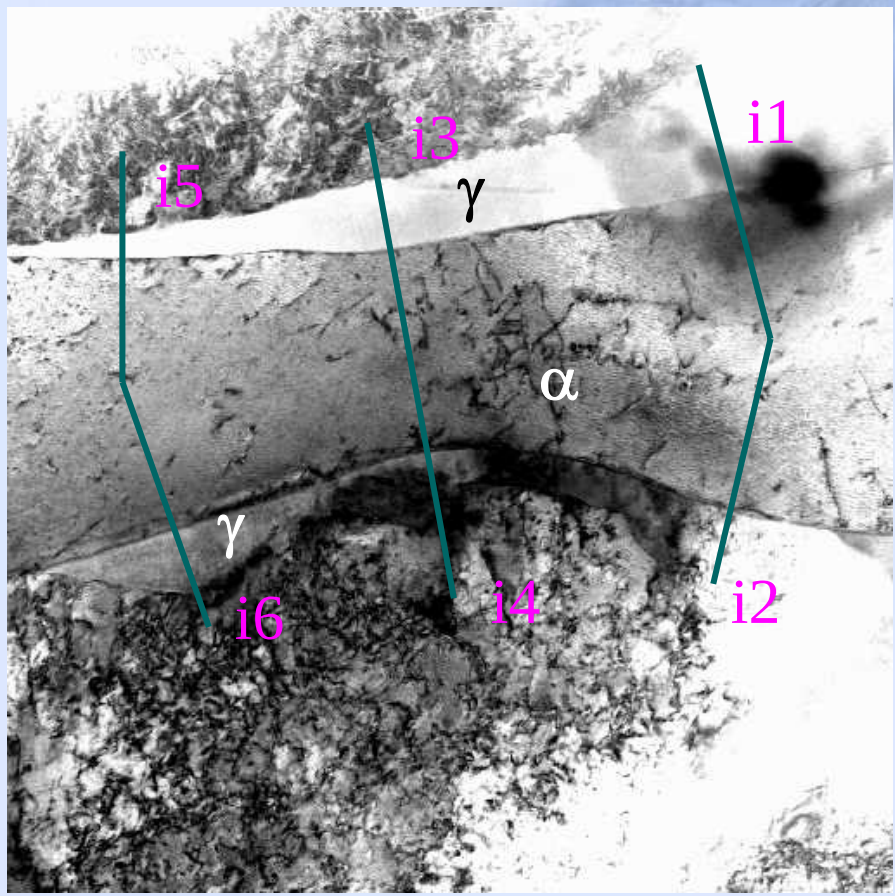
900°C×15min

656°C ×1hr

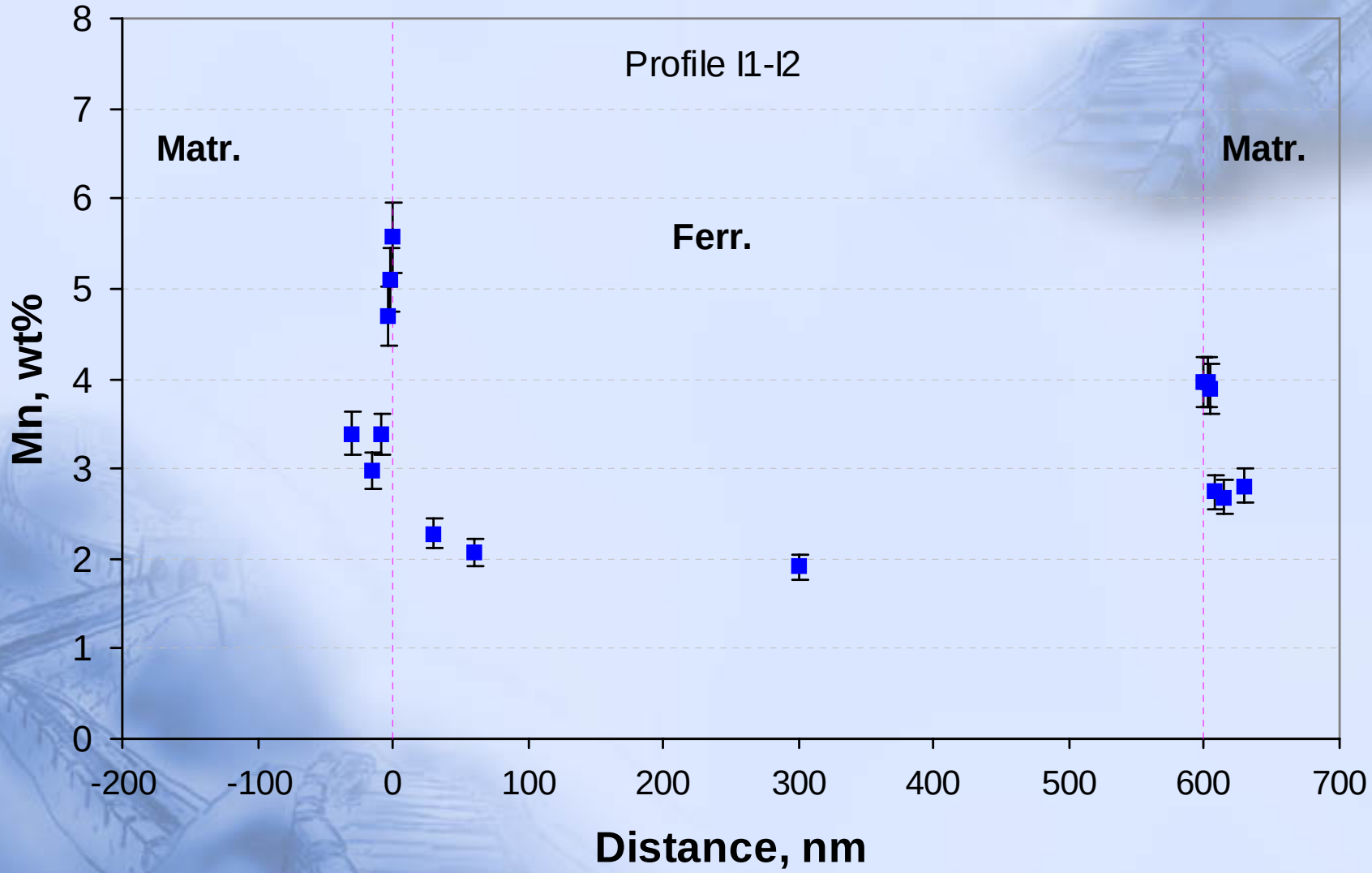
310°C ×12hr

WC

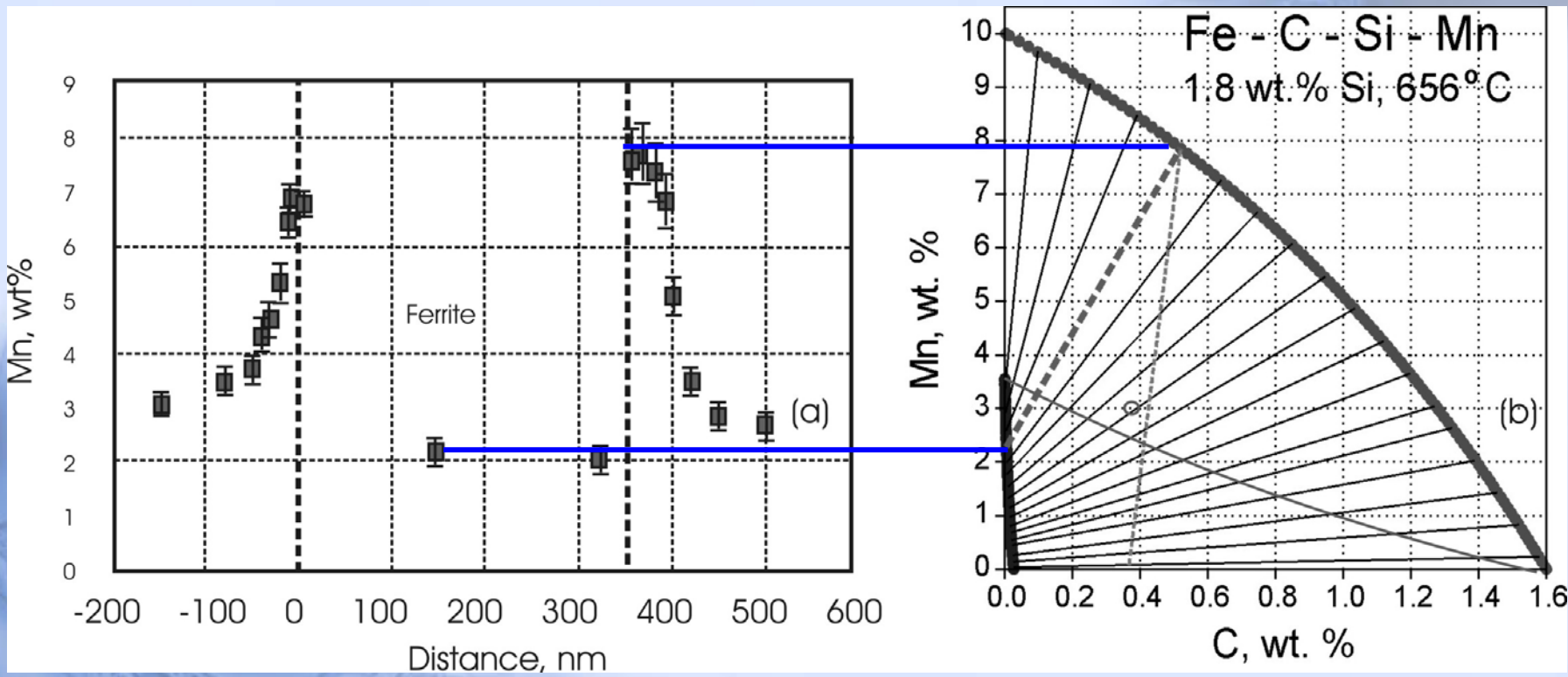
Grain size: 50 μm

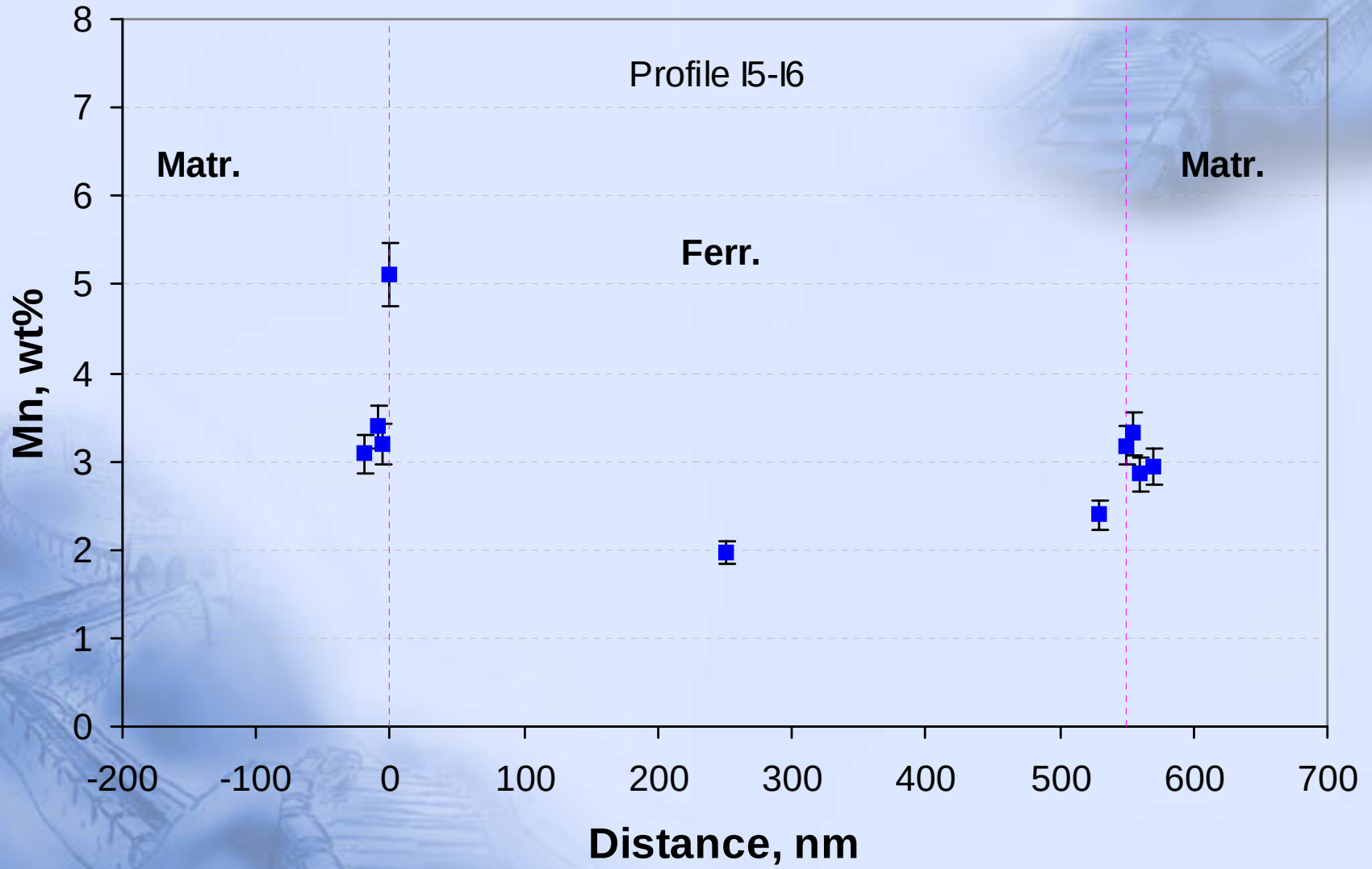


250 nm

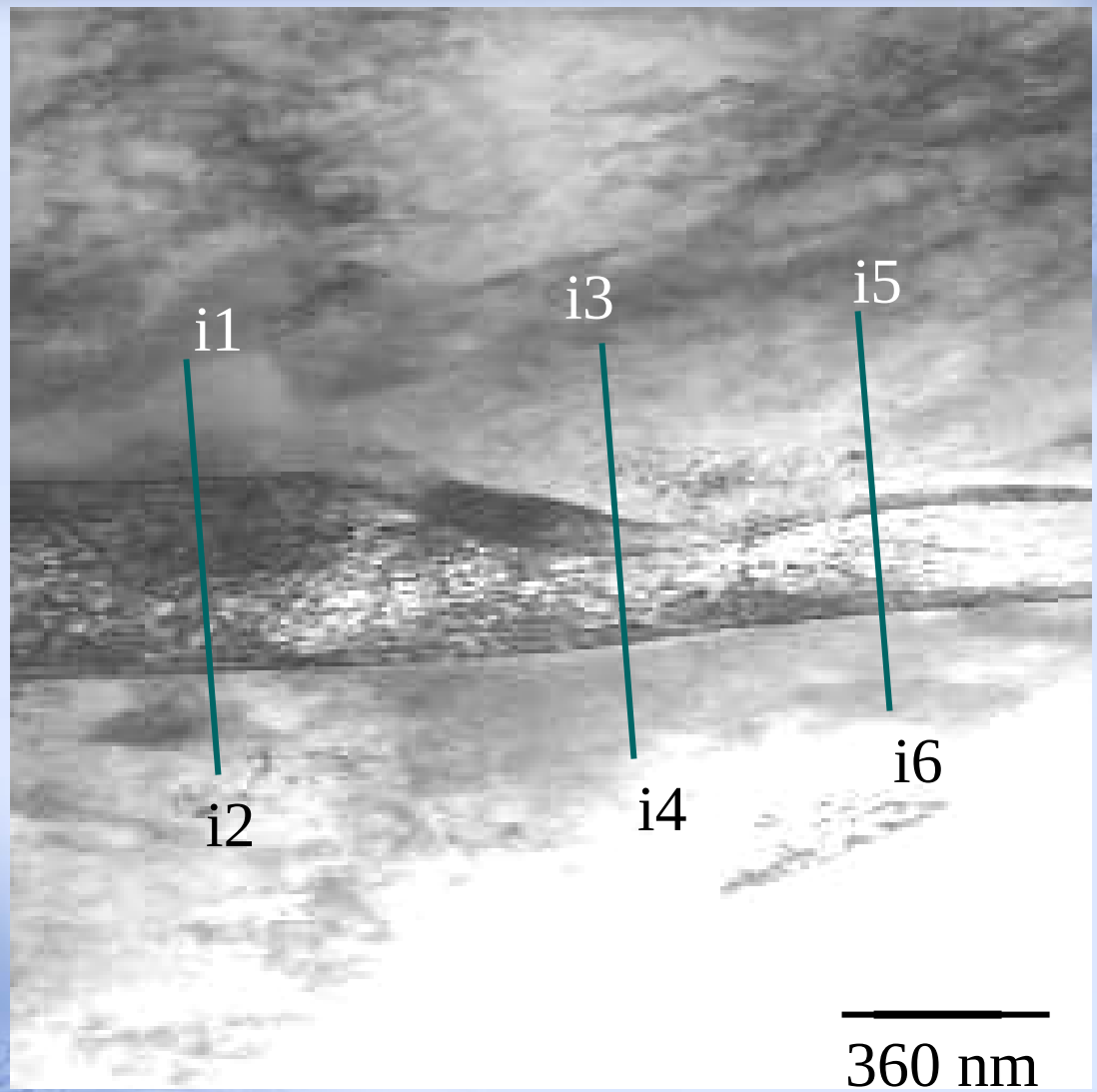

Profile I1-I2
Matr.
Ferr.
Matr.
Mn, wt%
Distance, nm
0
1
2
3
4
5
6
7
8
-200
-100
0
100
200
300
400
500
600
700

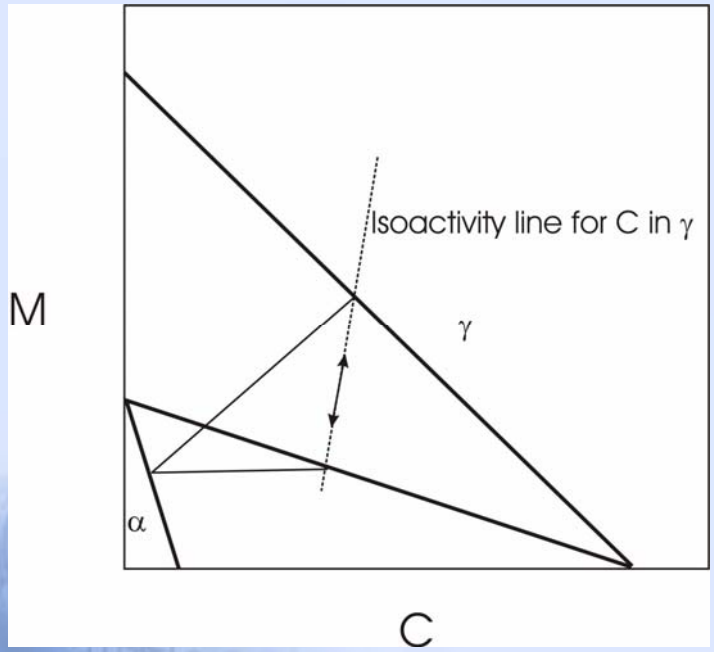
P3-F1

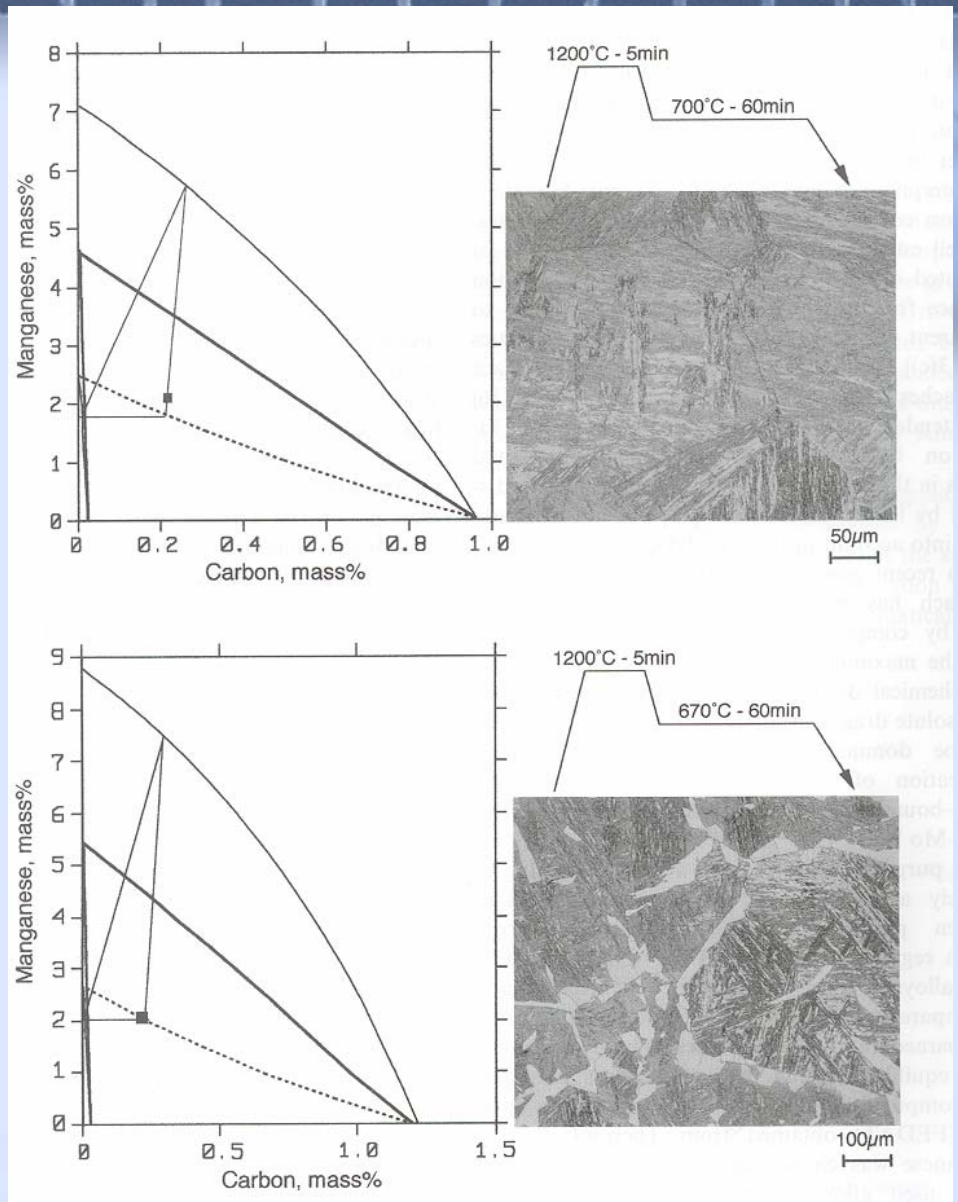

Mn, wt%
Ferrite
(a)
Distance, nm
Fe - C - Si - Mn
1.8 wt.% Si, 656°C
Mn, wt. %
(b)
C, wt. %


Profile I5-I6
Matr.
Ferr.
Matr.
Mn, wt%
Distance, nm
0
1
2
3
4
5
6
7
8
-200
-100
0
100
200
300
400
500
600
700

P3-F1

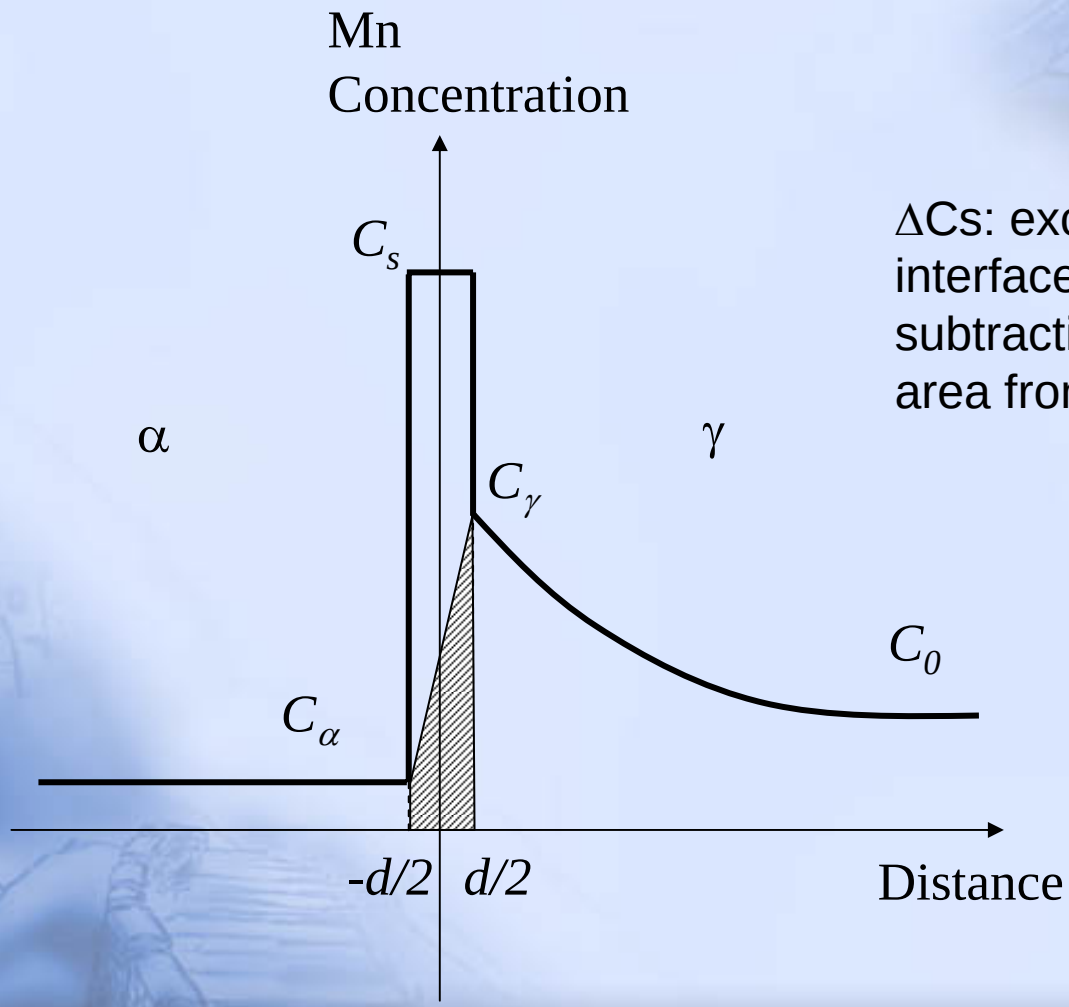

i1
i2
i3
i4
i5
i6
360 nm





Oi, Lux, Purdy
Acta Mat., **48**, 2000, 2147

An illustration of Mn profile across an α / γ interface.



ΔCs: excess Mn at interface, obtained by subtracting the shadow area from Cs

A simulation to obtain Cs

$$I^*(x, x_0, y_0, t) = \iiint\int I(x, x_0, y_0, t)C(x)dxdx_0dy_0dt$$

$$= \int_0^h \int_{-\frac{l}{2}}^{+\frac{l}{2}} \int_{-\frac{w}{2}}^{+\frac{w}{2}} \int_{-\infty}^{+\infty} \left[\frac{I_e C(x)}{\pi(2\sigma^2 + \beta t^3)} \exp\left(-\frac{(x - x_0)^2 + y_0^{\,2}}{2\sigma^2 + \beta t^3} \right) \right] dxdx_0dy_0dt$$

$$\beta = 500\left(\frac{4Z}{E_0}\right)^2 \frac{\rho}{A}$$

I: the electron probe distribution

I_e: the total current in the incident probe

x0, y0: the position of the incident beam relative the original point

x, t: 3-dimensional axes h: the thickness of the sample

A: atomic weight Z: atomic number

E_0: incident beam energy (eV)

ρ: density (g/cm^3)

σ: standard deviation (=0.33)

Description of the segregation at the interface

Boundary coverage Γ :

$$\Gamma = \rho_{ave.} \frac{A_A}{A_B} \Delta C_s w_i$$

ρ_{ave}: density of the interface in atoms/nm^3

ΔC_s: composition of the pure segregation (excess Mn at interface)

A_A and A_B : atomic masses of the segregant and the matrix

w_i: assumed width of interface

Monolayer: Γ/18.90

A value of monolayers contains a^{-2} segregant atoms per unit area where a^3 is the atomic volume of the segregant.

α Mn: cubic, 8.89Å, 58 atoms

1 monolayer = 18.90 atoms/nm^2

Interface: Type I

No spike observed at the interface.

The Mn concentrations both at the interface and adjacent matrix are close to the bulk composition.

Interface designation	Mn apparent concentration, (Cg) in mass %	Mn segregation at interface, (monolayers)
1	3.2	0.07±0.03
2	3.1	0.09±0.03
3	3.9	0.12±0.04
4	4.0	0.27±0.06

Interface: Type II

Mn spike is much larger than 10 nm.

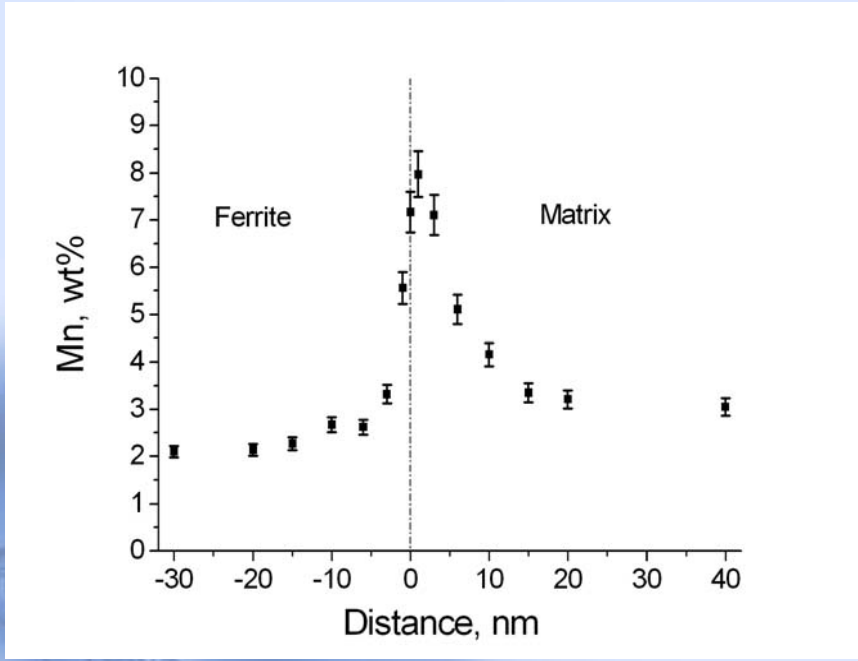
Interface designation	Mn concentration, (Cg) in mass % from extrapolation to interface position.	Mn segregation at interface, (monolayers)
1	5.0	0.31±0.07
2	6.7	0.39±0.09
3	7.2	0.42±0.10
4	7.3	0.44±0.10
5	7.4	0.46±0.10
6	7.7	0.46±0.10
7	8.1	0.50±0.11
8	7.2	0.59±0.12
9	7.2	0.73±0.14
10	7.9	0.88±0.16

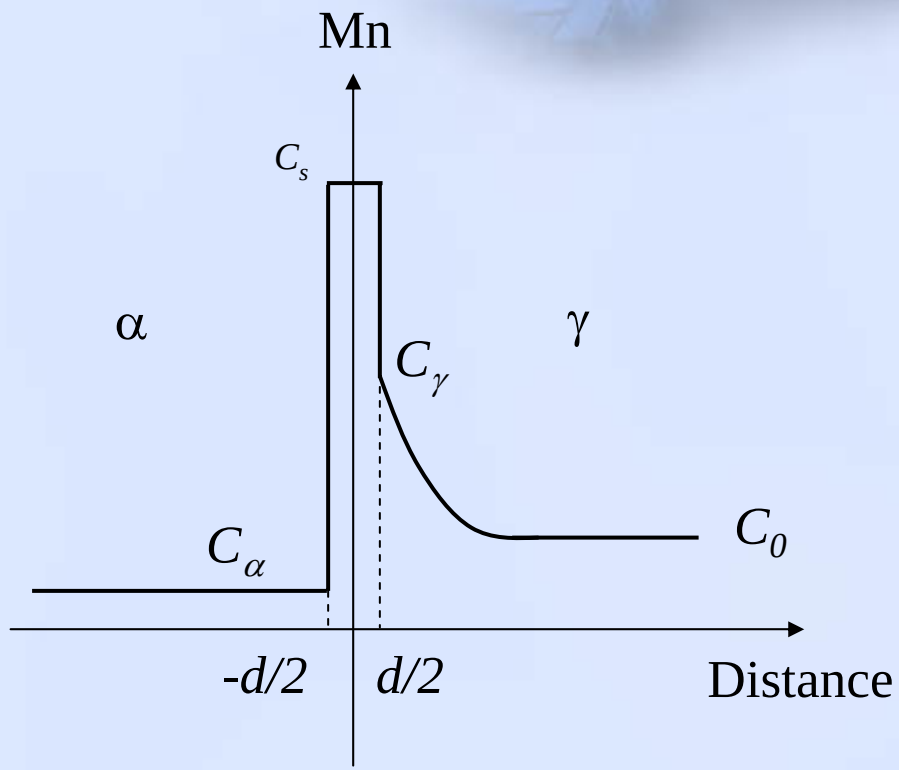
Interface: Type III

No obvious Mn spike observed.

Interface designation	Mn apparent concentration, (Cg) in mass %	Mn segregation at interface, (monolayers)	Mn segregation, (monolayer) subtracting a 10nm Mn spike
1	5.1	0.44±0.08	0.12±0.05
2	5.4	0.52±0.10	0.17±0.06
3	5.6	0.38±0.08	0.18±0.06
4	5.7	0.53±0.10	0.22±0.07
5	6.3	0.60±0.11	0.34±0.08
6	6.6	0.74±0.13	0.47±0.10
7	6.9	0.77±0.14	0.47±0.11
8	7.2	1.02±0.17	0.60±0.12
9	8.7	1.25±0.21	0.87±0.17
10	9.8	1.48±0.24	1.10±0.20

A measured Mn profile across a ferrite/martensite interface. A spike less than 10 nm is hard to be detected due to the limitation of the instrument.





Summary (1)

1. At 656°C all observed ferrite particles are partitioned in a Fe-0.37C-3.0Mn-1.85Si alloy;
2. Extended Mn profiles are observed at some interfaces. The extracted diffusion coefficient of Mn is larger than Wells and Mehl's value; it is thought that excess vacancies are responsible.
3. Mn profiles differ from one interface to another, even for a given ferrite crystal. We attribute this to a small variation of Mn concentration in the initial austenite.

Summary (2)

4. The majority of the interfaces studied approached a local equilibrium composition; the mobile interfaces tended to possess a similar level of Mn segregation, of the order of a half-monolayer. It is thought that this represents an equilibrium value.

5. The results fell into three groups:

   1) One set for which there is little or no apparent segregation

   of Mn; these interfaces are thought to be immobile;

   2) A second set for which extended Mn profiles were found in the prior austenite. For these, local equilibrium concentrations as well as interfacial segregation values could be inferred.

   3) A third group for which, due to instrumental limitations, no unambiguous interfacial segregation measurements could be made. For these, it was not possible to distinguish between segregation to the interface and a limited Mn spike in austenite.

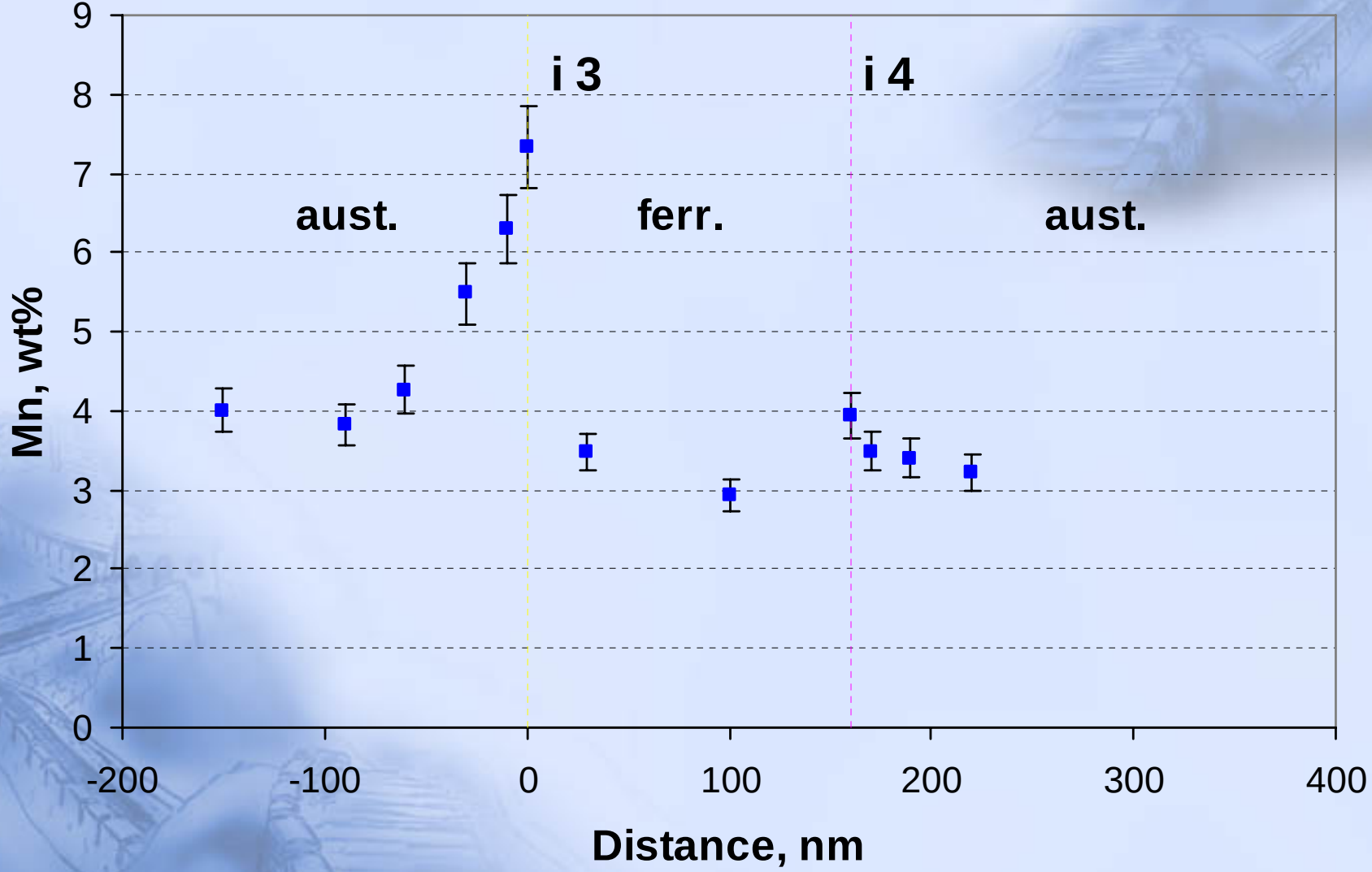
Acknowledgements

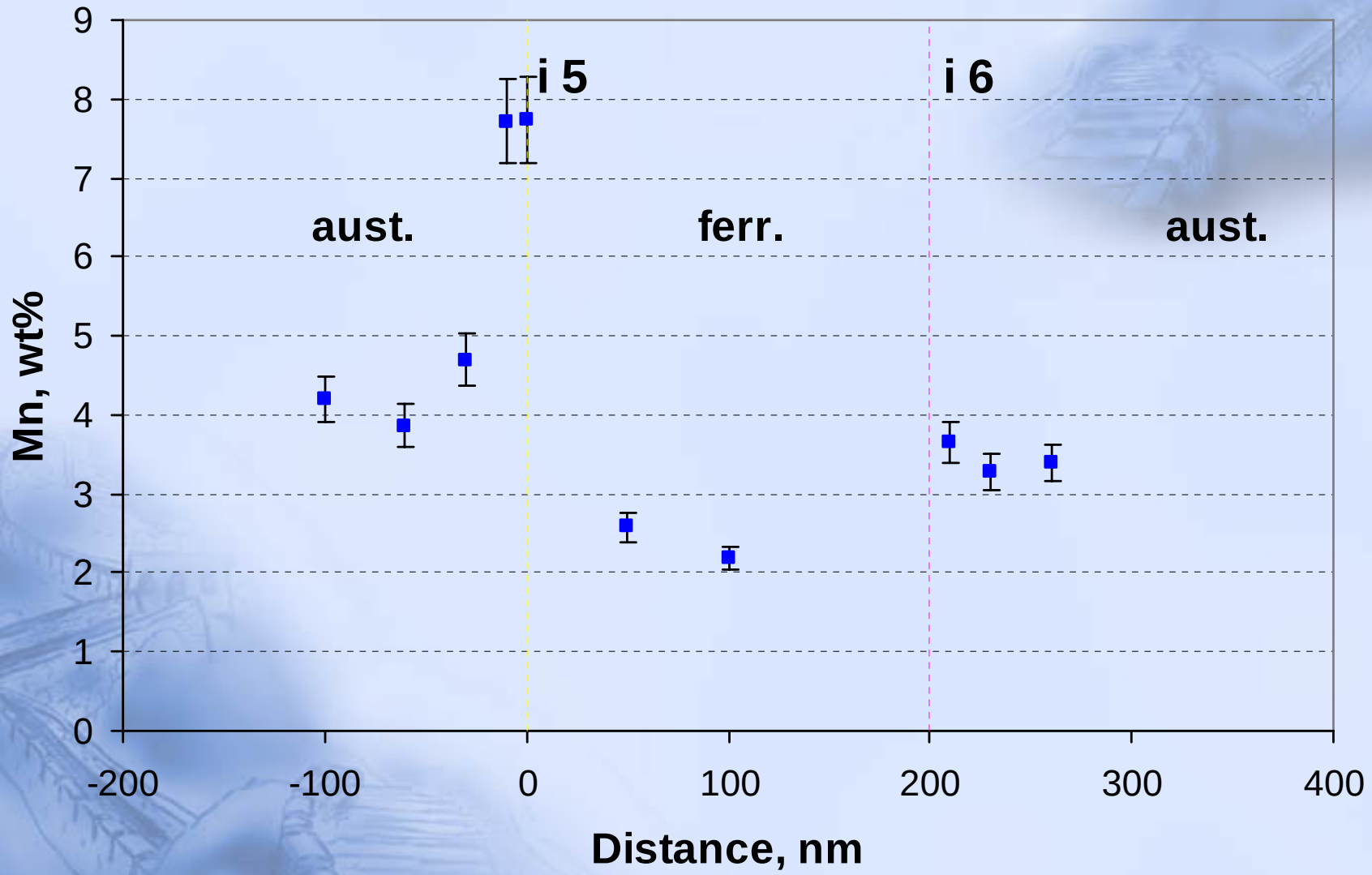
- Drs.H.Zurob, D.Malakhov, A.Perovic
- Drs. H.I.Aaronson, M.Enomoto
- Messrs. J.Garrett, F.Pearson, A.Duft, C.Butcher

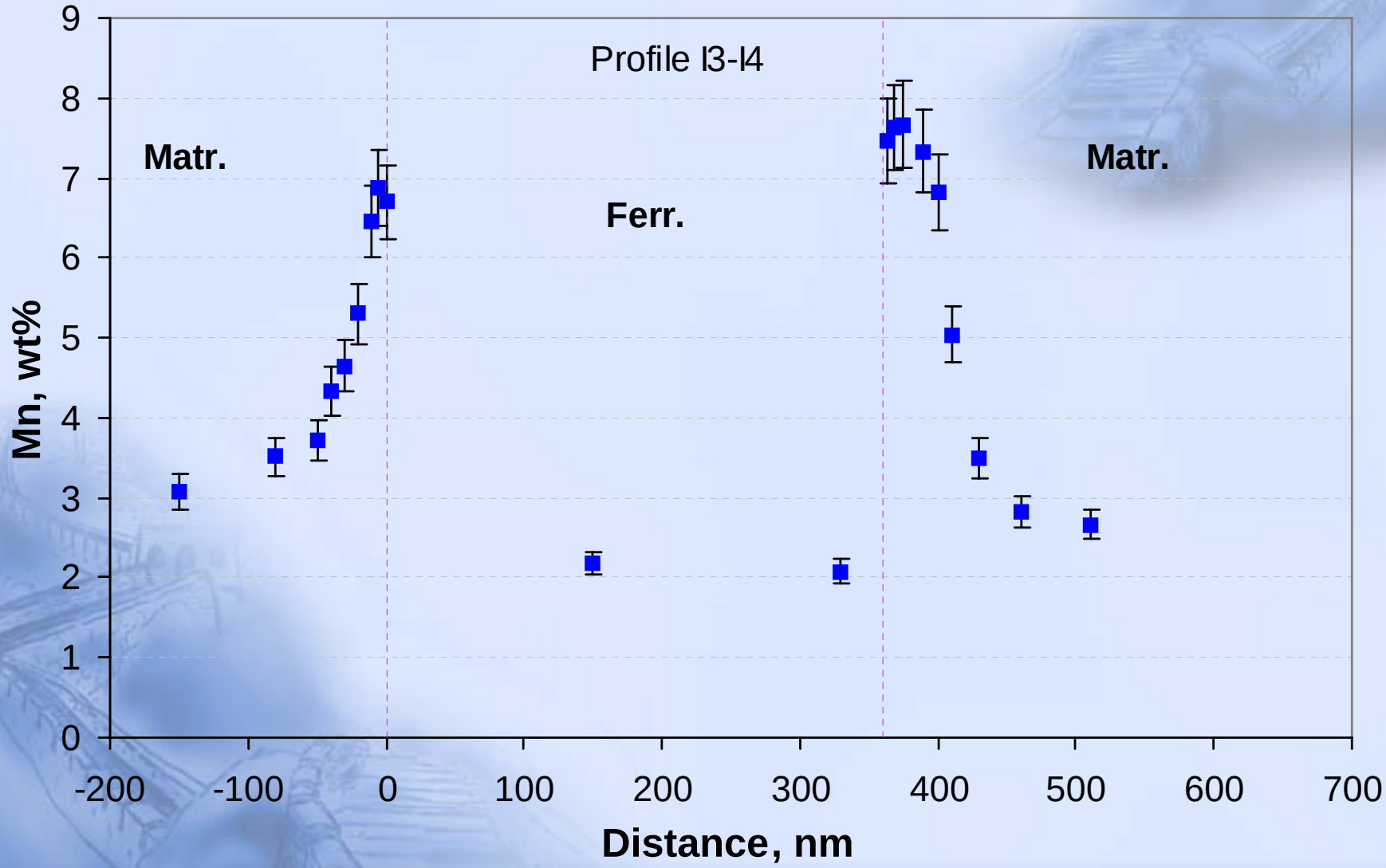

Thank you for your attention!

An example of Computed interfacial segregation; variation with assumed width of the interface (w) and foil thickness (h).

Assumed interface width (nm)	Segregation (monolayers)		
	h =150nm	h =200nm	h = 250nm
0.001	0.52±0.08	0.63±0.10	0.72±0.11
1.0	0.53±0.11	0.64±0.13	0.74±0.14
1.5	0.55±0.12	0.66±0.15	0.76±0.15


i 3
i 4
aust.
ferr.
aust.
Mn, wt%
Distance, nm
9
8
7
6
5
4
3
2
1
0
-200
-100
0
100
200
300
400


i 5
i 6
aust.
ferr.
aust.
Mn, wt%
Distance, nm
9
8
7
6
5
4
3
2
1
0
-200
-100
0
100
200
300
400


Profile I3-I4
Matr.
Ferr.
Matr.
Mn, wt%
Distance, nm
0
1
2
3
4
5
6
7
8
9
-200
-100
0
100
200
300
400
500
600
700

P3-F1

A transition from Para-E to P-LE at 751°C