Selective Oxidation of Advanced High Strength Steels

Experiments and Modelling

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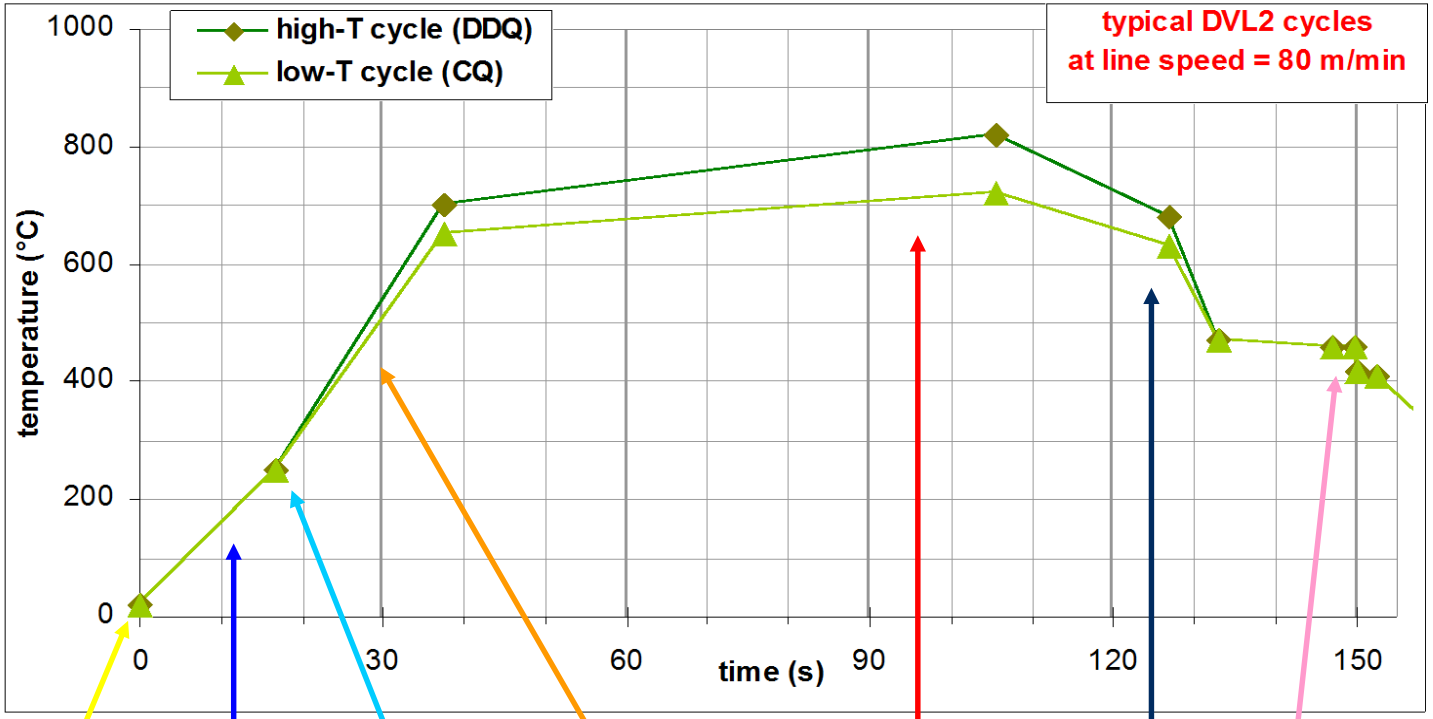
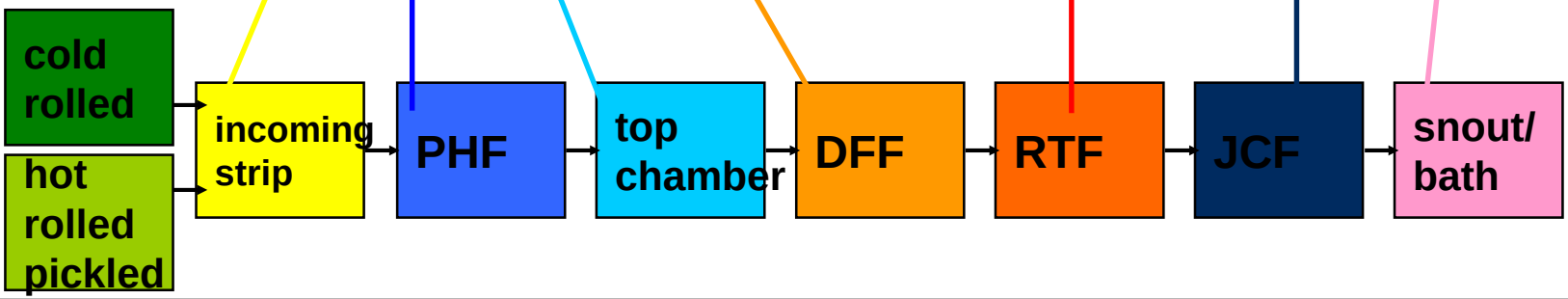
Modelling and Simulation of Annealing in Galvanizing Line

Temperature profile in industry

(a)



(b)

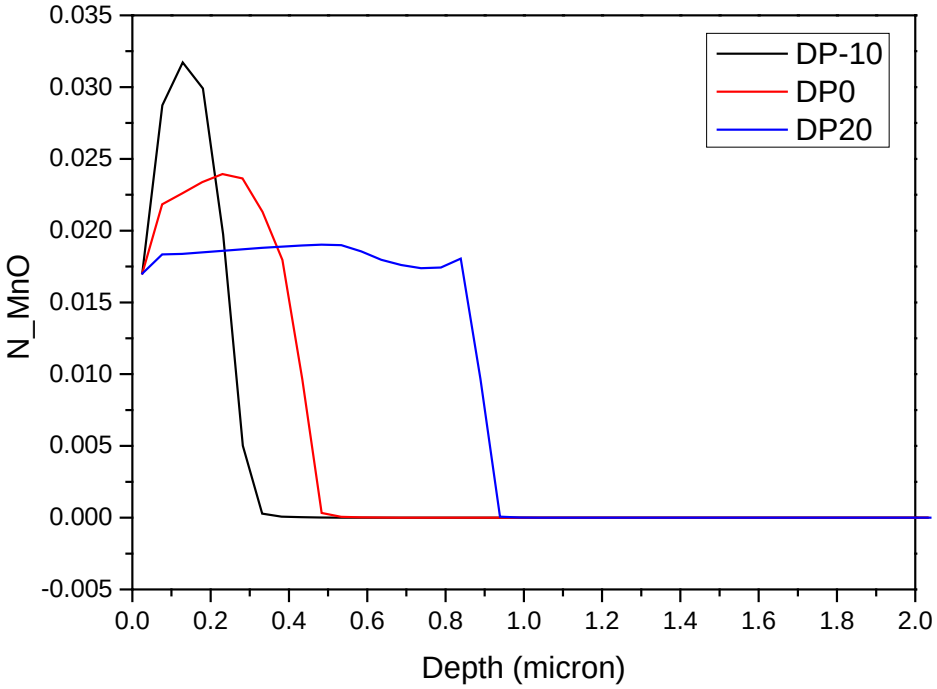


Simulation with varying temperature

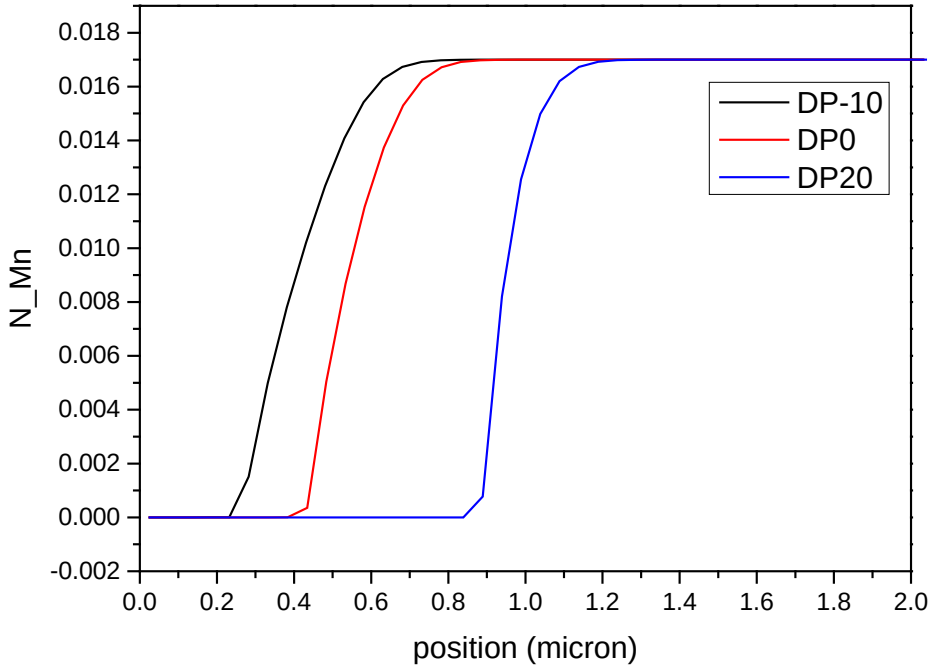
Fe-1.7Mn binary alloy

Simulated for constant dew points (DP) of -10, 0, and 20 ° C

Concentration of internal oxide precipitate



Concentration of dissolved Mn



Simulation based on “Flux model”

Advantages:

- Clear physical description (Fick’s 1st law)
- Can be applied to complex systems
  - Multiple element diffusion
  - Varying temperature and oxygen partial pressure with time
  - Phase transformation of alloy matrix during oxidation
- Both external and internal oxidation can be modelled

T.J. Nijdam and W.G. Sloof, *Modelling of composition and phase changes in multiphase alloys due to growth of an oxide layer*, Acta Materialia 56 (2008) 4972-4983.

Introduction to "Flux model"

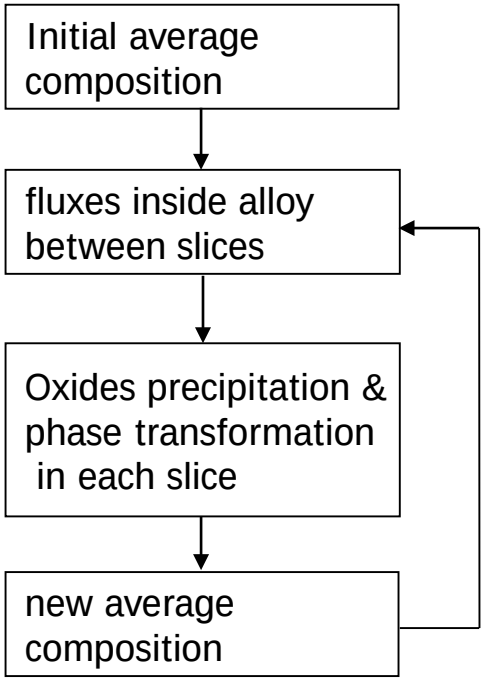
“Flux model”

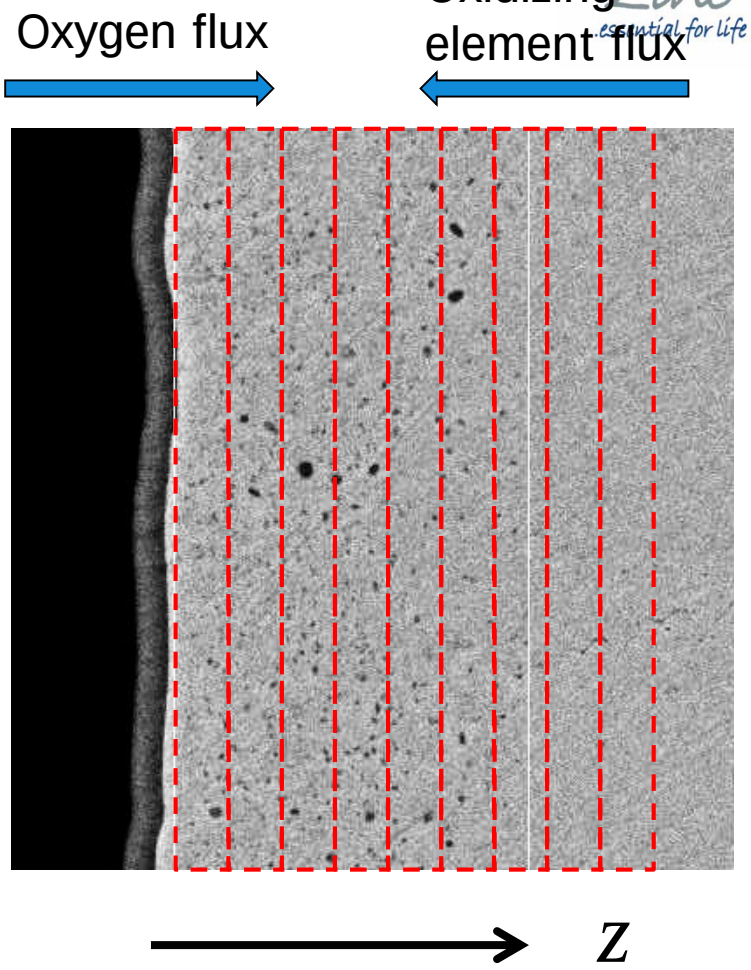
The alloy is divided into a series of thin slices

Elements diffuse between adjacent slices

When oxide precipitate, each slice is regarded as a closed system

Precipitation process is assumed to be infinite fast



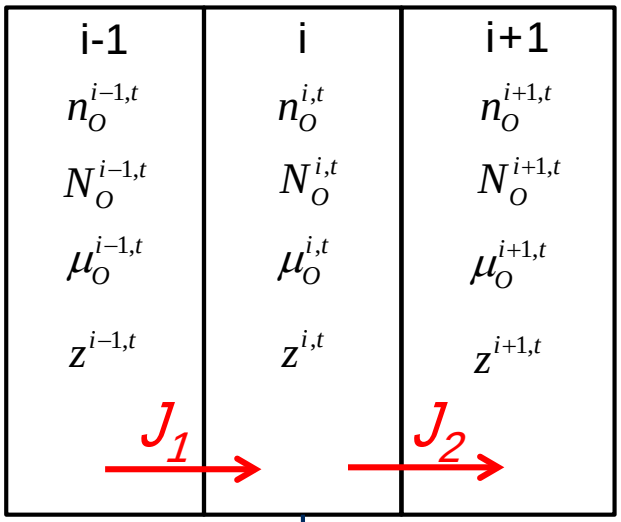


T.J. Nijdam and W.G. Sloof, *Modelling of composition and phase changes in multiphase alloys due to growth of an oxide layer*, Acta Materialia 56 (2008) 4972-4983.

“Flux Model”

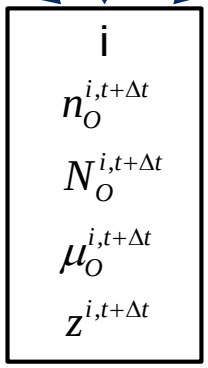
Diffusion of elements

t



Explicit method

t+Δt



$N_O^{i,t}$ O molar fraction in slice i at time t

$$N_O^{i,t} = \frac{n_O^{i,t}}{n_O^{i,t} + n_{Fe}^{i,t} + n_{Mn}^{i,t}}$$

$n_O^{i,t}$ Amount of O in slice i at time t, unit mole/area

$\mu_O^{i,t}$ Chemical potential of O in slice i at time t

$z^{i,t}$ Position of slice i at time t

$$n_O^{i,t+\Delta t} = n_O^{i,t} + (J_1 - J_2)\Delta t$$

Same applies to all other elements *k* (e.g. Fe, Mn)

“Flux Model”

Diffusion of elements

Modified flux equations (take oxygen as example):

$$J_2 = -\frac{RT}{V_m}\left(\frac{\sqrt{M_O^{i+1,t}N_O^{i+1,t}M_O^{i,t}N_O^{i,t}}}{z^{i+1,t}-z^{i,t}}\right)\times 2\sinh\left(\frac{\mu_O^{i+1,t}-\mu_O^{i,t}}{2RT}\right)$$

$$J_1 = -\frac{RT}{V_m}\left(\frac{\sqrt{M_O^{i,t}N_O^{i,t}M_O^{i-1,t}N_O^{i-1,t}}}{z^{i,t}-z^{i-1,t}}\right)\times 2\sinh\left(\frac{\mu_O^{i,t}-\mu_O^{i-1,t}}{2RT}\right)$$

V_m Molar volume of alloy

$M_O^{i,t}$ Mobility of O in slice i at time t $\quad M_O = \frac{D_O^{tracer}}{RT}$

Both D_k^{tracer} and $\mu_k^{i,t}$ is a function of local alloy composition, and can be obtained in thermocalc

For simplicity, D_k^{tracer} is considered independent of alloy composition, and equals to impurity diffusion coefficient

“Flux Model”

“3rd element effect” on diffusion of elements

When thermocalc is not used, taking Fe-Mn bianry alloy as an example

$$J_2 = -\frac{RT}{V_m}\left(\frac{\sqrt{M_O^{i+1,t} N_O^{i+1,t} M_O^{i,t} N_O^{i,t}}}{z^{i+1,t} - z^{i,t}}\right) \times 2\sinh\left(\frac{\mu_O^{i+1,t} - \mu_O^{i,t}}{2RT}\right)$$

$$\mu_O = \mu_O^0 + RT\ln a_O = \mu_O^0 + RT\ln N_O + RT\ln\gamma_O$$

$$\mu_O^{i+1,t} - \mu_O^{i,t} = RT(\ln N_O^{i+1,t} - \ln N_O^{i,t}) + RT(\ln\gamma_O^{i+1,t} - \ln\gamma_O^{i,t})$$

Recall that $\ln\gamma_O = \ln\gamma_O^0 + \varepsilon_O^{Mn} N_{Mn}$ Assuming that $\varepsilon_O^O \approx 0$

$$\mu_O^{i+1,t} - \mu_O^{i,t} = RT(\ln N_O^{i+1,t} - \ln N_O^{i,t}) + RT\,\varepsilon_O^{Mn}(N_{Mn}^{i+1,t} - N_{Mn}^{i,t})$$

Similarly, for Mn $\ln\gamma_{Mn} = \ln\gamma_{Mn}^0 + \varepsilon_{Mn}^{Mn} N_{Mn} + \varepsilon_{Mn}^{O} N_O$ $\varepsilon_O^{Mn} = \varepsilon_{Mn}^{O}$

$$\mu_{Mn}^{i+1,t} - \mu_{Mn}^{i,t} = RT(\ln N_{Mn}^{i+1,t} - \ln N_{Mn}^{i,t}) + RT\,\varepsilon_{Mn}^{Mn}(N_{Mn}^{i+1,t} - N_{Mn}^{i,t}) + RT\,\varepsilon_{Mn}^{O}(N_O^{i+1,t} - N_O^{i,t})$$

“Flux Model”

Diffusion of elements in “ideal” solution

When solution is ideal, i.e. thermodynamic and mobility solute interaction are neglected

Thus: $M_O^{i,t}$ Independent of local alloy composition

$$\varepsilon_O^{Mn} = \varepsilon_{Mn}^{O} = 0 \qquad \varepsilon_{Mn}^{Mn} = 0$$

Then:
$$\mu_O^{i+1,t} - \mu_O^{i,t} = RT(\ln N_O^{i+1,t} - \ln N_O^{i,t})$$

$$\mu_{Mn}^{i+1,t} - \mu_{Mn}^{i,t} = RT(\ln N_{Mn}^{i+1,t} - \ln N_{Mn}^{i,t})$$

Flux equations reduce to:
$$J_O = -\frac{RT}{V_m}\left(\frac{M_O\sqrt{N_O^{i+1,t}N_O^{i,t}}}{z^{i+1,t} - z^{i,t}}\right) \times 2\sinh\left(\frac{\ln N_O^{i+1,t} - \ln N_O^{i,t}}{2}\right)$$

$$J_{Mn} = -\frac{RT}{V_m}\left(\frac{M_{Mn}\sqrt{N_{Mn}^{i+1,t}N_{Mn}^{i,t}}}{z^{i+1,t} - z^{i,t}}\right) \times 2\sinh\left(\frac{\ln N_{Mn}^{i+1,t} - \ln N_{Mn}^{i,t}}{2}\right)$$

“Flux Model”

“3rd element effect” on oxides precipitation in each slice

Take Fe-Mn binary alloy as an example

t+Δt

Before precipitation

Slice i

$n_O^{i,t+\Delta t}$

$n_{Mn}^{i,t+\Delta t}$

$n_{Fe}^{i,t+\Delta t}$

$N_O^{i,t+\Delta t}$

$N_{Mn}^{i,t+\Delta t}$

$N_{Fe}^{i,t+\Delta t}$

$\mu_O^{i,t+\Delta t}$

$\mu_{Mn}^{i,t+\Delta t}$

$\mu_{Fe}^{i,t+\Delta t}$

$n_{MnO}^{i,t}$

$z^{i,t+\Delta t}$

$$N_O^{i,t+\Delta t} = \frac{n_O^{i,t+\Delta t}}{n_O^{i,t+\Delta t} + n_{Fe}^{i,t+\Delta t} + n_{Mn}^{i,t+\Delta t}}$$

$$N_{Mn}^{i,t+\Delta t} = \frac{n_{Mn}^{i,t+\Delta t}}{n_O^{i,t+\Delta t} + n_{Fe}^{i,t+\Delta t} + n_{Mn}^{i,t+\Delta t}}$$

before precipitation, the amount of MnO at new time step is the same as previous time step

if $N_O^{i,t+\Delta t} \times N_{Mn}^{i,t+\Delta t} \geq Ksp^0 \times \exp\left[-N_{Mn}^{i,t+\Delta t}(\varepsilon_{Mn}^{Mn} + \varepsilon_O^{Mn})\right]$ Precipitation occur

"Flux Model"

"3rd element effect" on oxides precipitation in each slice

t+Δt
Before precipitation

Slice i

$n_O^{i,t+\Delta t}$
$n_{Mn}^{i,t+\Delta t}$
$n_{Fe}^{i,t+\Delta t}$
$N_O^{i,t+\Delta t}$
$N_{Mn}^{i,t+\Delta t}$
$N_{Fe}^{i,t+\Delta t}$
$\mu_O^{i,t+\Delta t}$
$\mu_{Mn}^{i,t+\Delta t}$
$\mu_{Fe}^{i,t+\Delta t}$
$n_{MnO}^{i,t}$
$z^{i,t+\Delta t}$

If thermodynamic tools are not used, the following 3 equations with 3 unknowns are solved to obtain new composition of slice *i* after precipitation

$$n_O^{i,t+\Delta t} + n_{MnO}^{i,t} = n_O^{i,t+\Delta t}(new) + n_{MnO}^{i,t+\Delta t}$$

$$n_{Mn}^{i,t+\Delta t} + n_{MnO}^{i,t} = n_{Mn}^{i,t+\Delta t}(new) + n_{MnO}^{i,t+\Delta t}$$

$$N_O^{i,t+\Delta t}(new) \times N_{Mn}^{i,t+\Delta t}(new) = Ksp^0 \times \exp\left[-N_{Mn}^{i,t+\Delta t}(new)(\varepsilon_{Mn}^{Mn} + \varepsilon_O^{Mn})\right]$$

t+Δt
After precipitation

Slice i

$n_O^{i,t+\Delta t}(new)$
$n_{Mn}^{i,t+\Delta t}(new)$
$n_{Fe}^{i,t+\Delta t}$
$N_O^{i,t+\Delta t}(new)$
$N_{Mn}^{i,t+\Delta t}(new)$
$N_{Fe}^{i,t+\Delta t}(new)$
$\mu_O^{i,t+\Delta t}(new)$
$\mu_{Mn}^{i,t+\Delta t}(new)$
$\mu_{Fe}^{i,t+\Delta t}(new)$
$n_{MnO}^{i,t+\Delta t}$
$z^{i,t+\Delta t}(new)$

“Flux Model”

Oxides precipitation in each slice in ideal solution

t+Δt
Before precipitation

Slice i

$n_O^{i,t+\Delta t}$
$n_{Mn}^{i,t+\Delta t}$
$n_{Fe}^{i,t+\Delta t}$
$N_O^{i,t+\Delta t}$
$N_{Mn}^{i,t+\Delta t}$
$N_{Fe}^{i,t+\Delta t}$
$\mu_O^{i,t+\Delta t}$
$\mu_{Mn}^{i,t+\Delta t}$
$\mu_{Fe}^{i,t+\Delta t}$
$n_{MnO}^{i,t}$
$z^{i,t+\Delta t}$

if $N_O^{i,t+\Delta t} \times N_{Mn}^{i,t+\Delta t} \geq Ksp^0$ Precipitation occur

the following 3 equations with 3 unknowns are solved to obtain new composition of slice *i* after precipitation

$$n_O^{i,t+\Delta t} + n_{MnO}^{i,t} = n_O^{i,t+\Delta t}(new) + n_{MnO}^{i,t+\Delta t}$$

$$n_{Mn}^{i,t+\Delta t} + n_{MnO}^{i,t} = n_{Mn}^{i,t+\Delta t}(new) + n_{MnO}^{i,t+\Delta t}$$

$$N_O^{i,t+\Delta t}(new) \times N_{Mn}^{i,t+\Delta t}(new) = Ksp^0$$

t+Δt
After precipitation

Slice i

$n_O^{i,t+\Delta t}(new)$
$n_{Mn}^{i,t+\Delta t}(new)$
$n_{Fe}^{i,t+\Delta t}$
$N_O^{i,t+\Delta t}(new)$
$N_{Mn}^{i,t+\Delta t}(new)$
$N_{Fe}^{i,t+\Delta t}(new)$
$\mu_O^{i,t+\Delta t}(new)$
$\mu_{Mn}^{i,t+\Delta t}(new)$
$\mu_{Fe}^{i,t+\Delta t}(new)$
$n_{MnO}^{i,t+\Delta t}$
$z^{i,t+\Delta t}(new)$

Current simulations with “Flux model”

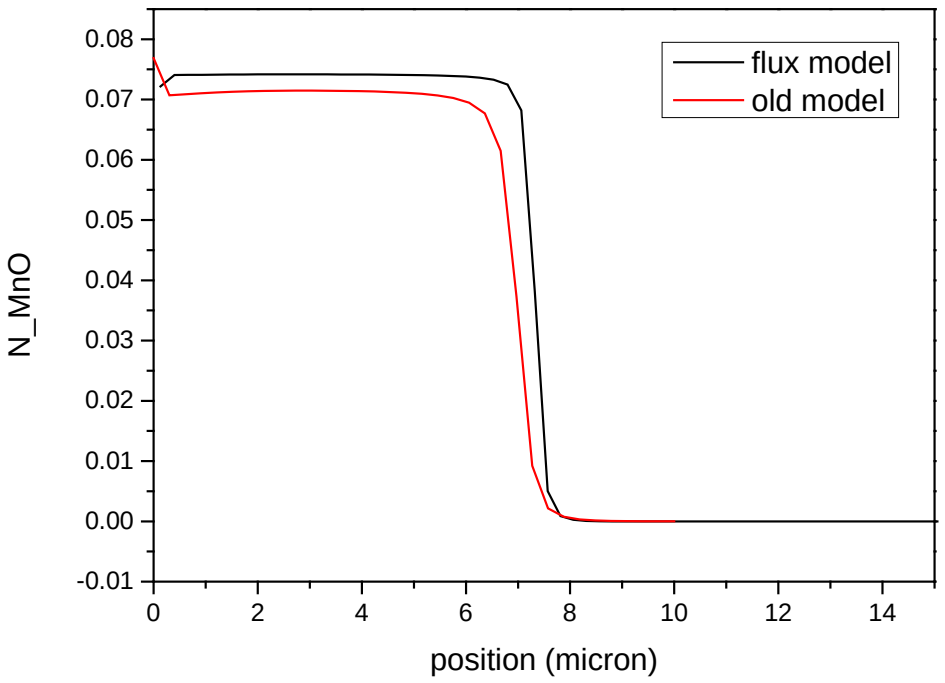
- 1D numerical model for internal oxidation based on Fick’s 1st law
- Include effect of solute interaction on element diffusion (non-ideal behaviour)
- Include effect of solute interaction on oxide precipitation (non-ideal behaviour)
- Incorporate phase transformation of matrix (oxidation induced element depletion) for binary alloys
- Element diffusion in multi-phase matrix is well described
- Can be coupled with thermodynamic database thermocalc

Fe-Mn binary alloy, ideal solution, single phase, constant temperature

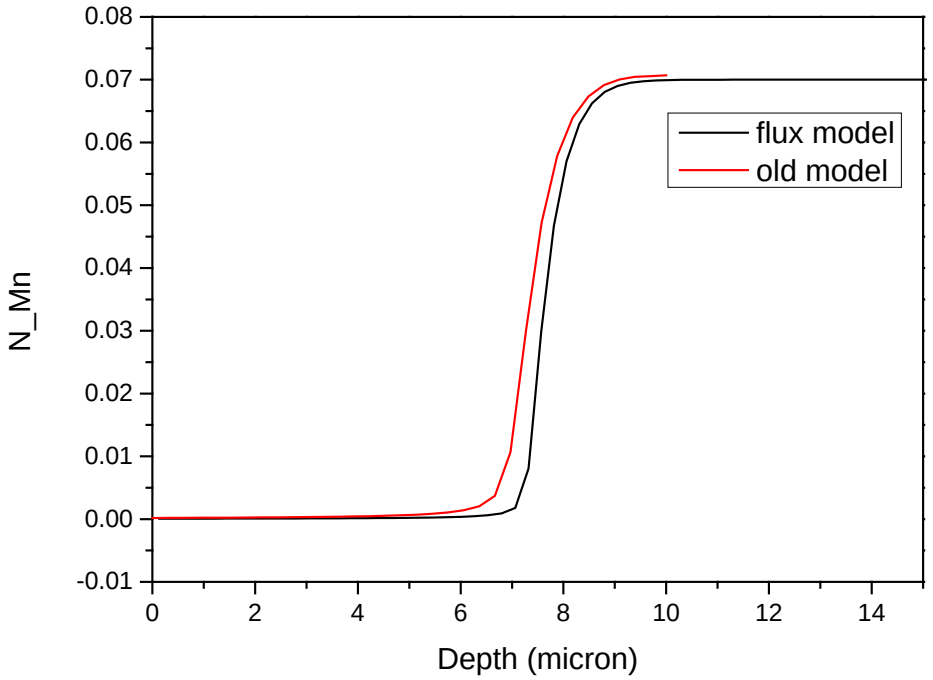
Comparison with old numerical model

Fe-7Mn, 950C, 4hours, ideal solution, DP 10 ° C

Concentration of oxide precipitate



Concentration of dissolved Mn

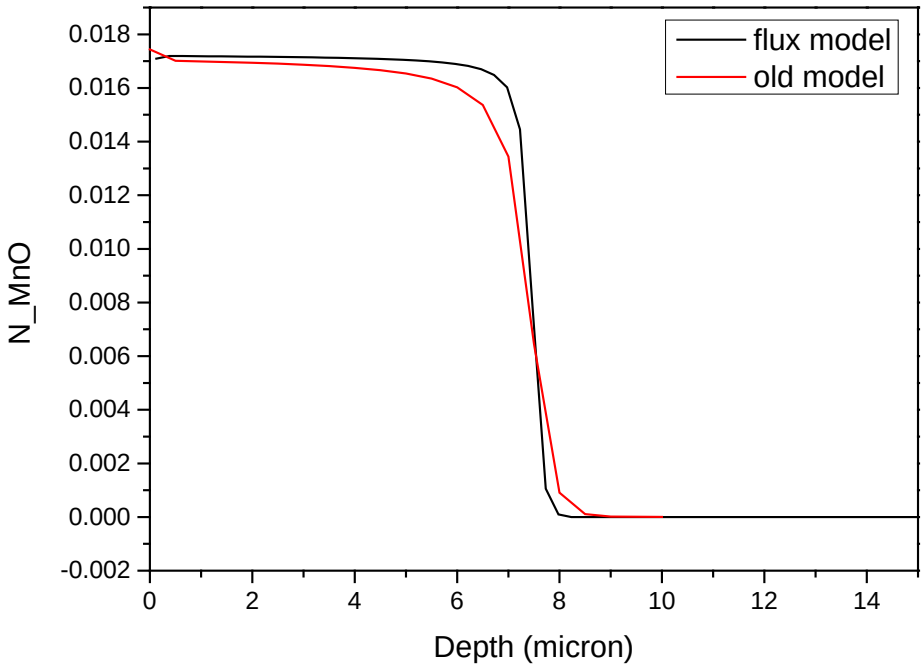


Flux model shows similar prediction in internal oxidation kinetics as old numerical model

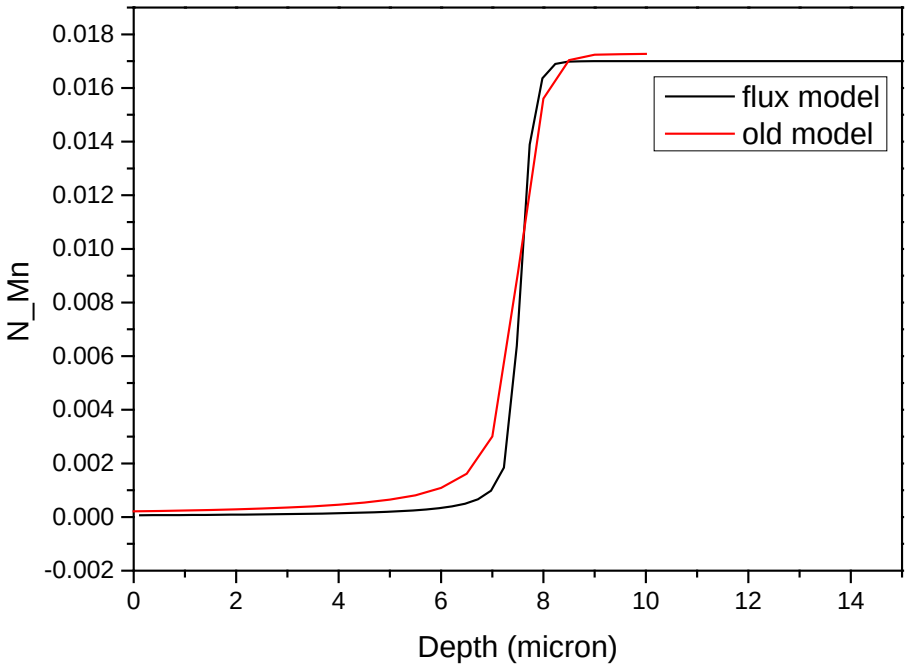
Comparison with old numerical model

Fe-1.7Mn, 950C, 1 hour, ideal solution, DP 10 ° C

Concentration of oxide precipitate



Concentration of dissolved Mn

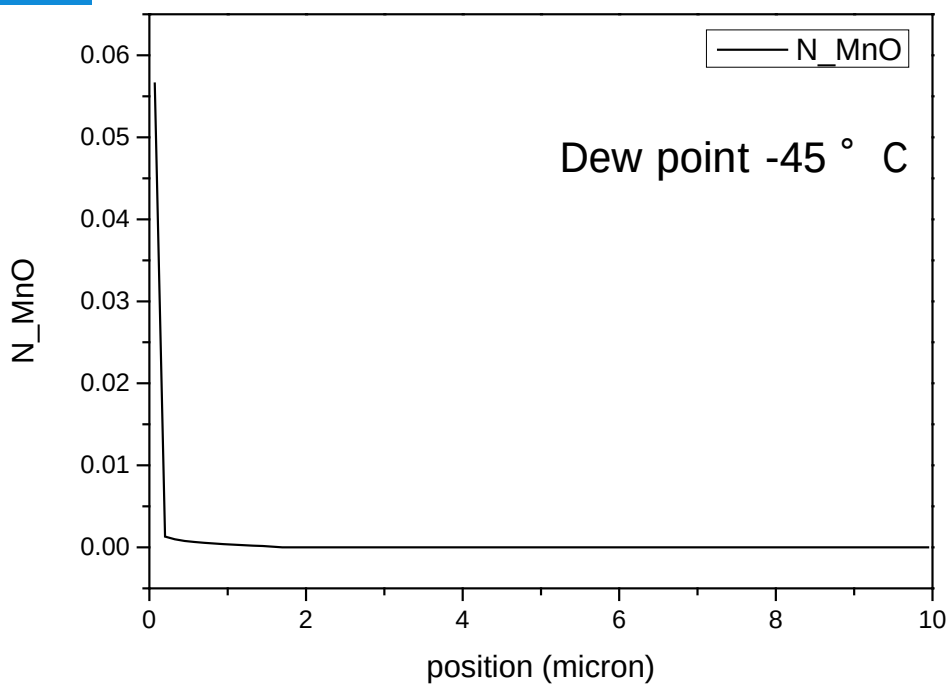


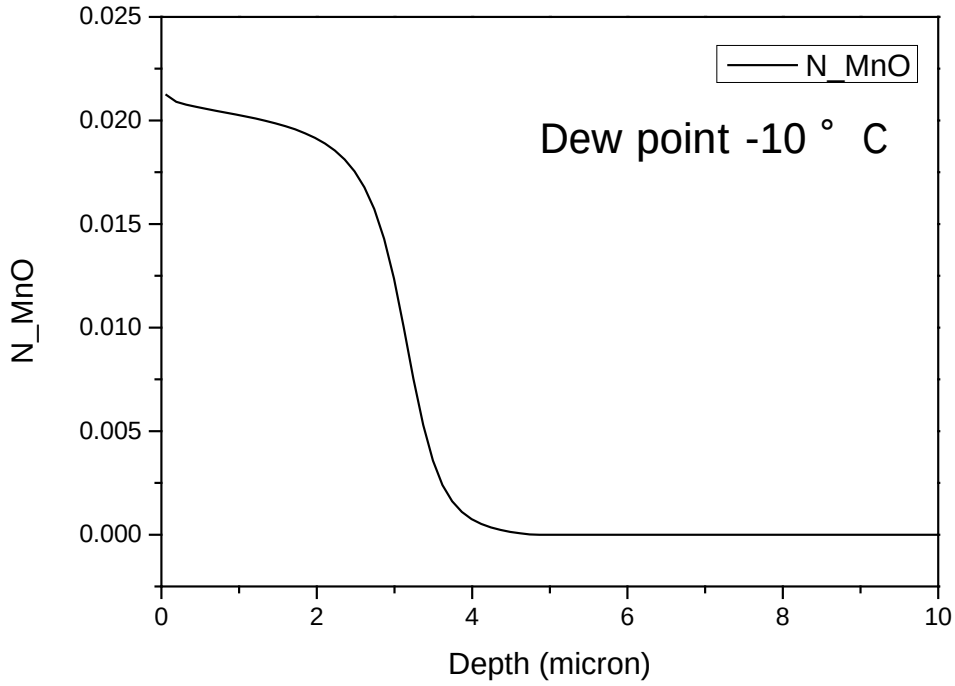
Flux model shows similar prediction in internal oxidation kinetics as old numerical model

Internal/external oxidation

Fe-1.7Mn, 950C, ideal solution, 1hour

Concentration of oxide precipitate



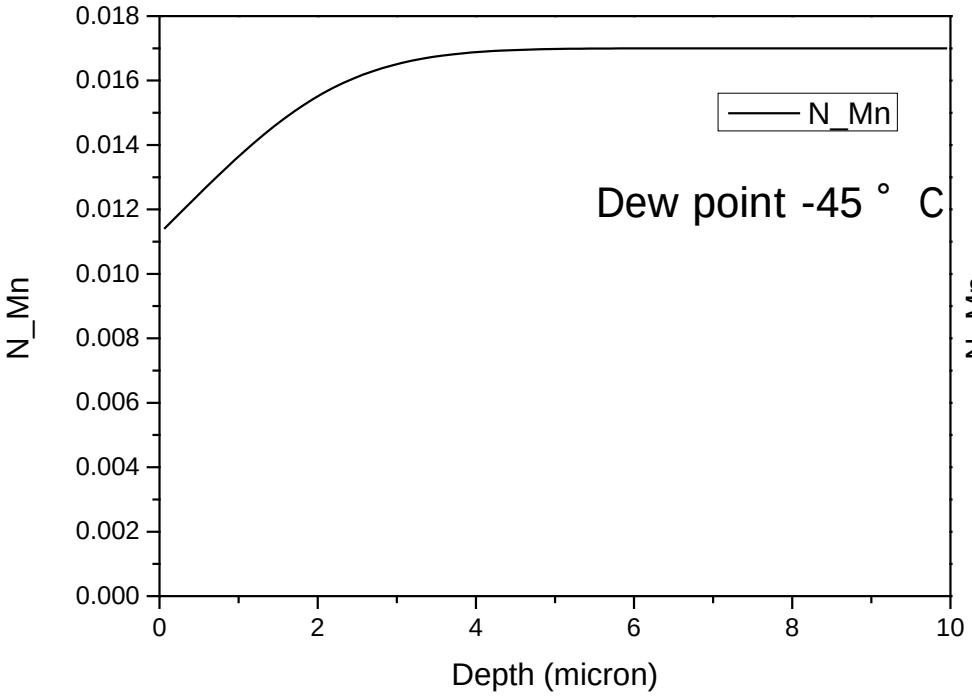


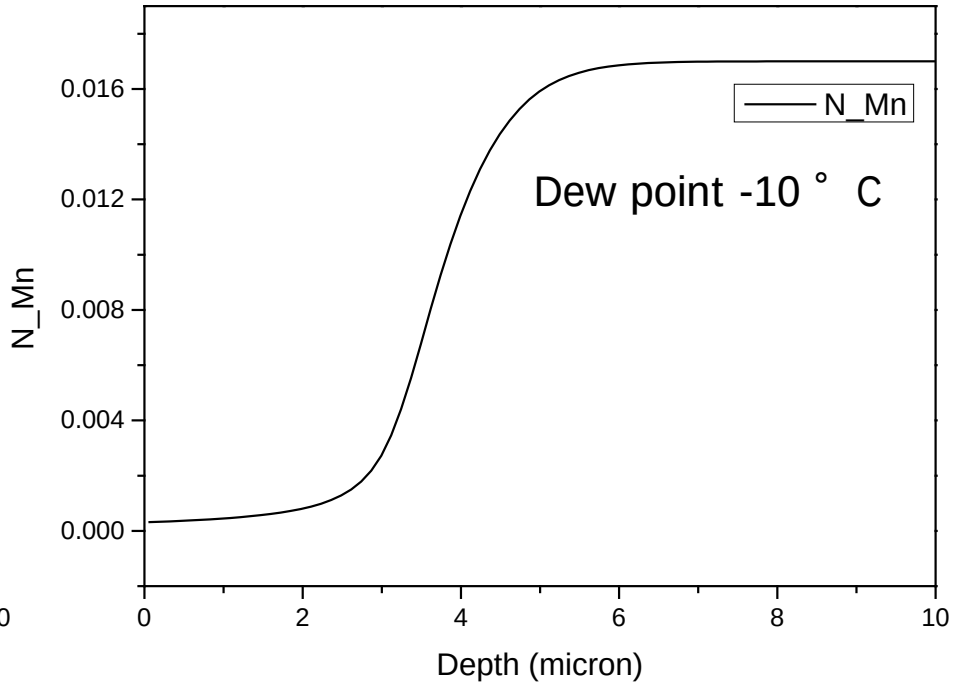
Internal oxidation model can also indicate external oxidation mode from the depth profile of oxide and oxidizing element

Internal/external oxidation

Fe-1.7Mn, 950C, ideal solution, 1hour

Concentration of oxidizing element



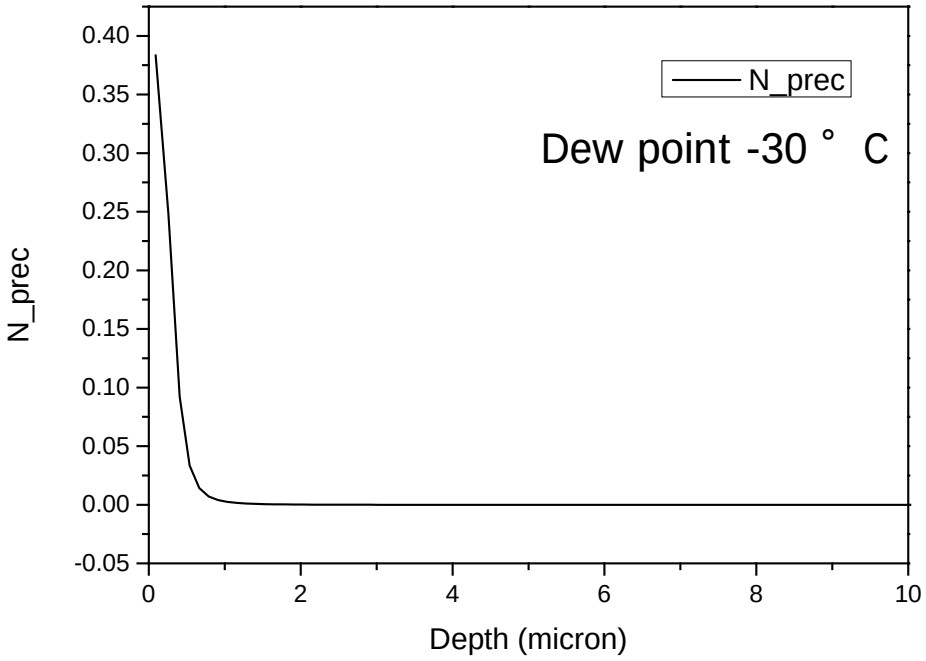


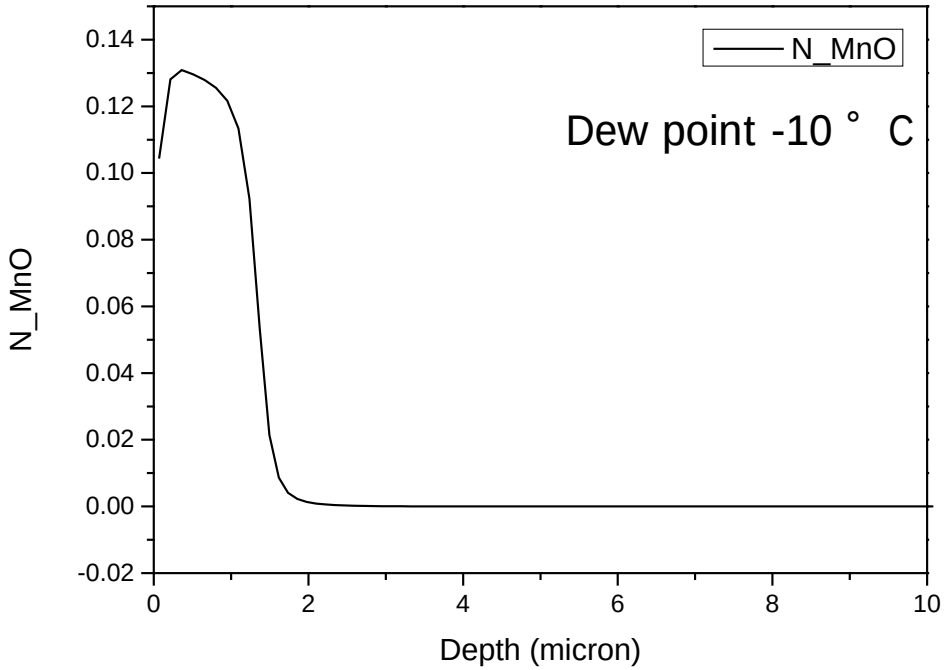
Internal oxidation model can also indicate external oxidation mode from the depth profile of oxide and oxidizing element

Internal/external oxidation

Fe-7Mn, 950C, ideal solution, 1hour

Concentration of oxide precipitate



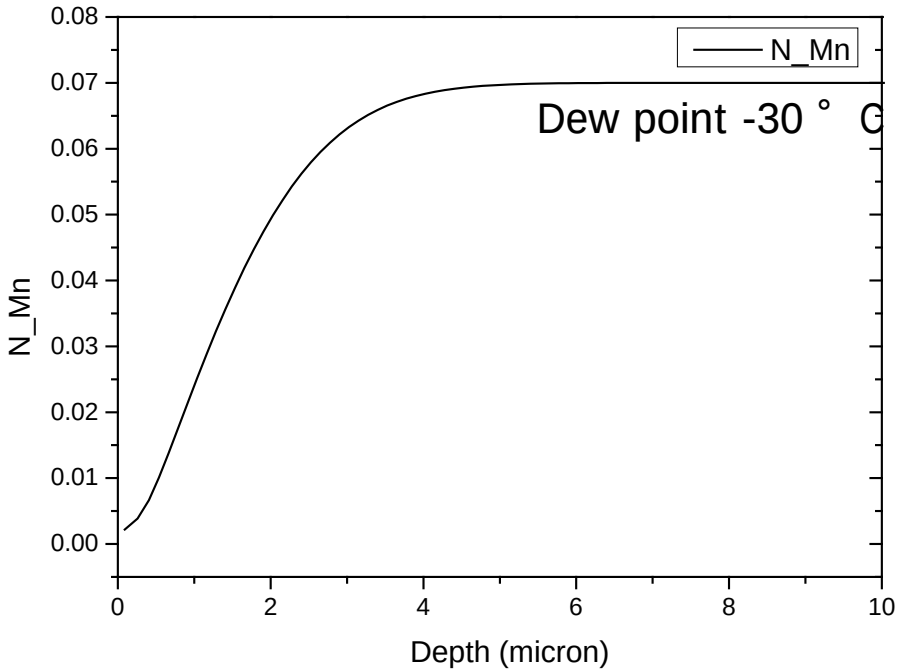


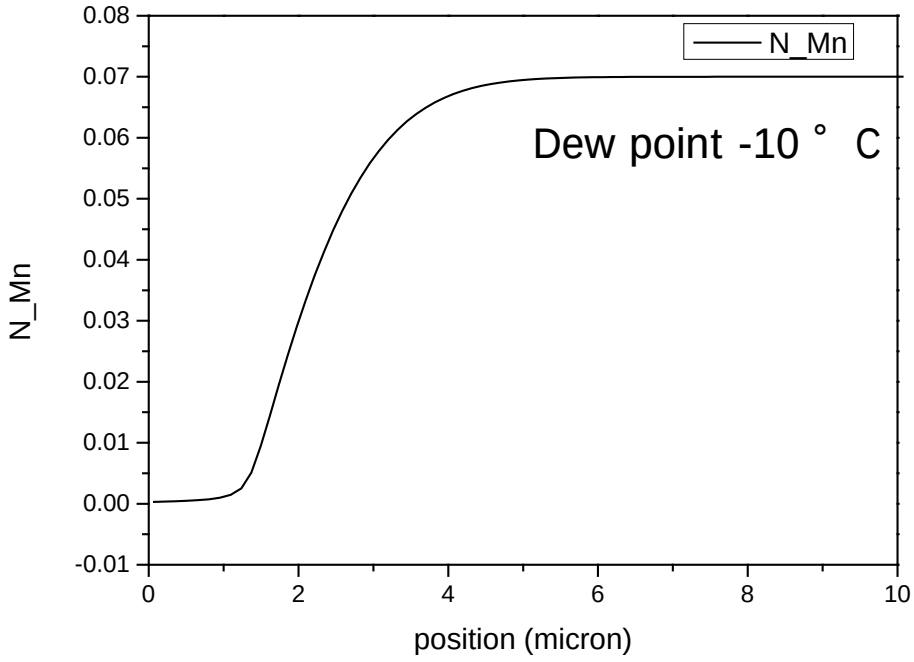
Internal oxidation model can also indicate external oxidation mode from the depth profile of oxide and oxidizing element

Internal/external oxidation

Fe-7Mn, 950C, ideal solution, 1hour

Concentration of oxidizing element





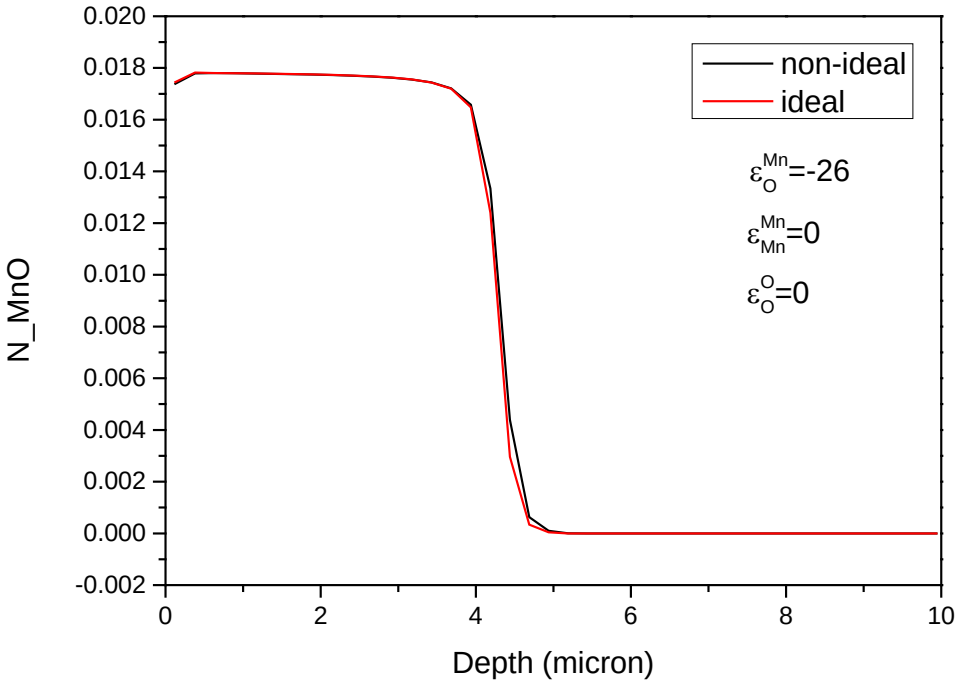
Internal oxidation model can also indicate external oxidation mode from the depth profile of oxide and oxidizing element

Fe-Mn binary alloy, solute interaction, single phase, constant temperature

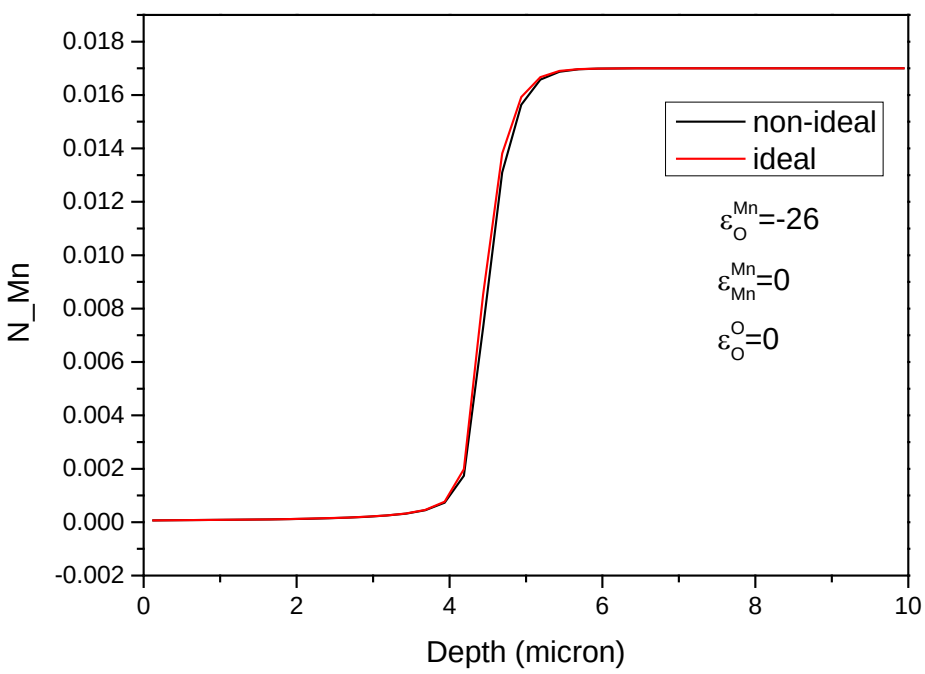
Effect of Mn-O solute interaction

Fe-1.7Mn, 950C, 20min, dew point 10° C

Concentration of oxide precipitate



Concentration of oxidizing element



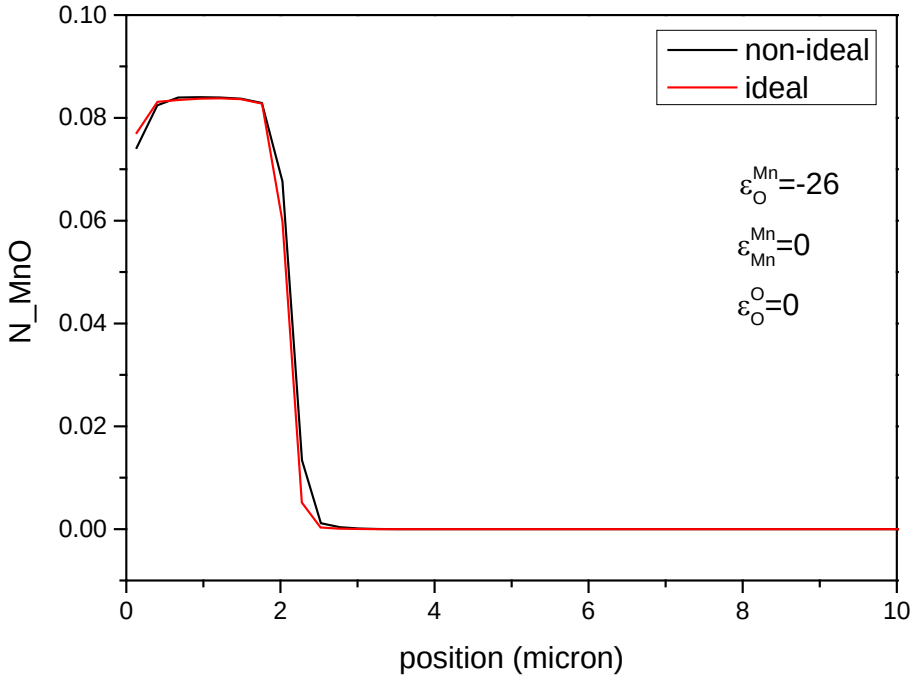
Mn-O solute interaction affects both diffusion and the Ksp of MnO

However, Effect of Mn-O solute interaction is small on internal oxidation kinetics

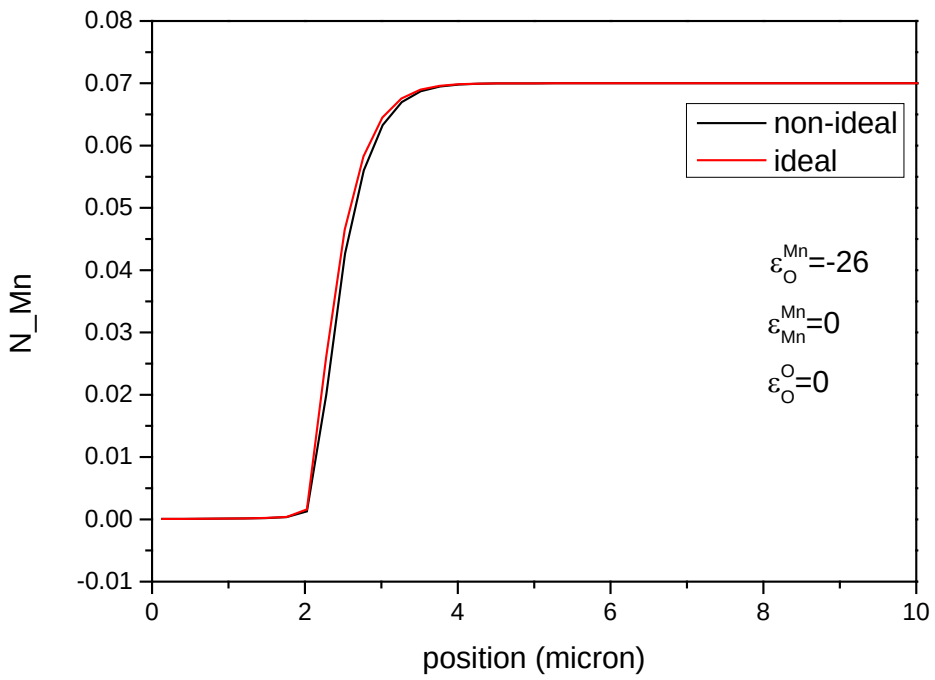
Effect of Mn-O solute interaction

Fe-7Mn, 950C, 20min, dew point 10° C

Concentration of oxide precipitate



Concentration of oxidizing element



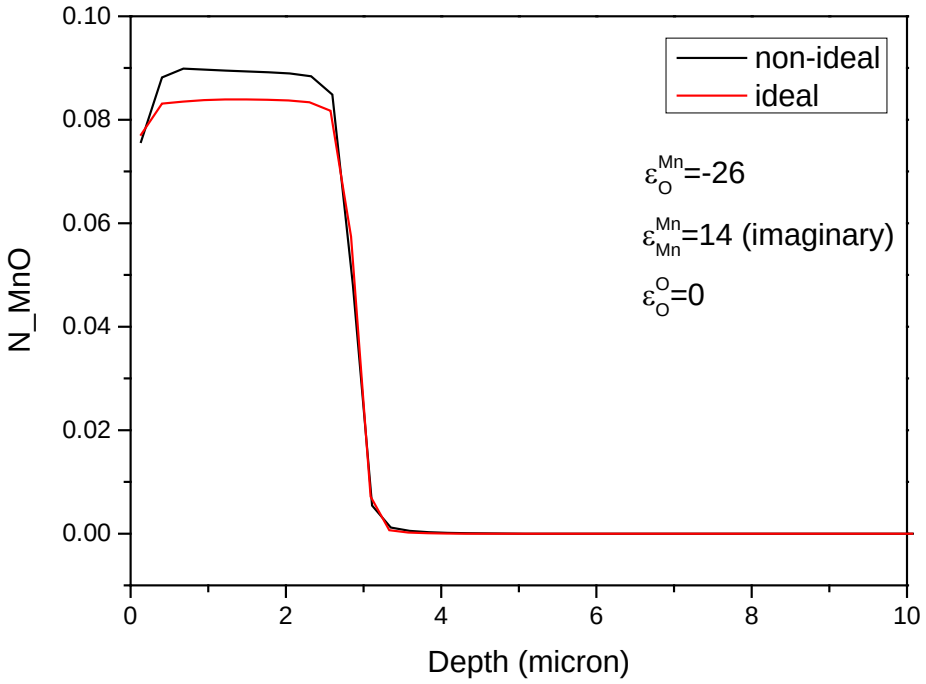
Mn-O solute interaction affects both diffusion and the Ksp of MnO

However, Effect of Mn-O solute interaction is small on internal oxidation kinetics

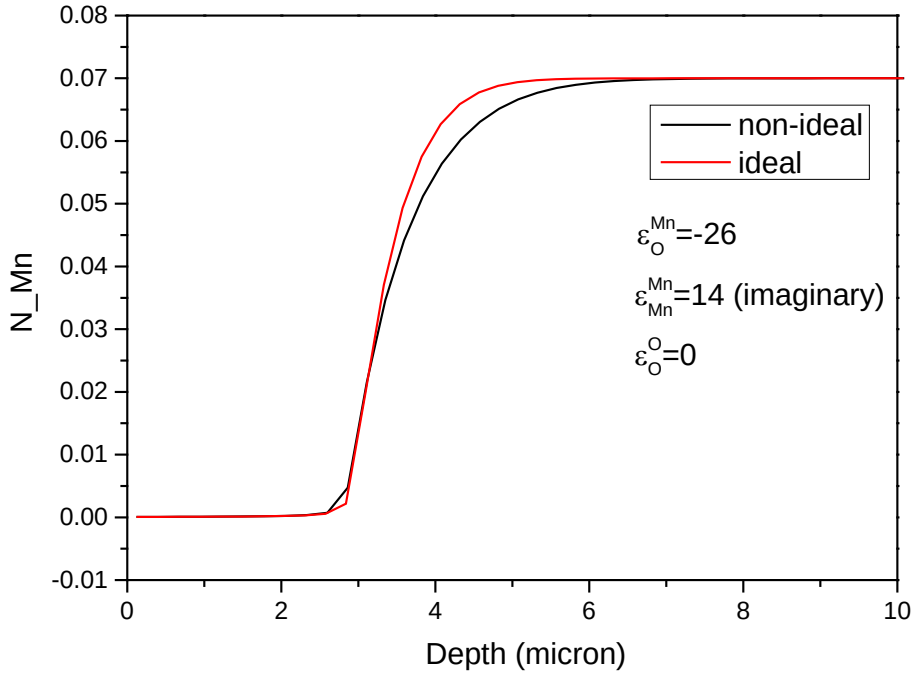
Effect of Mn-Mn solute interaction

Fe-7Mn, 950C, 40min, dew point 10° C

Concentration of oxide precipitate



Concentration of oxidizing element

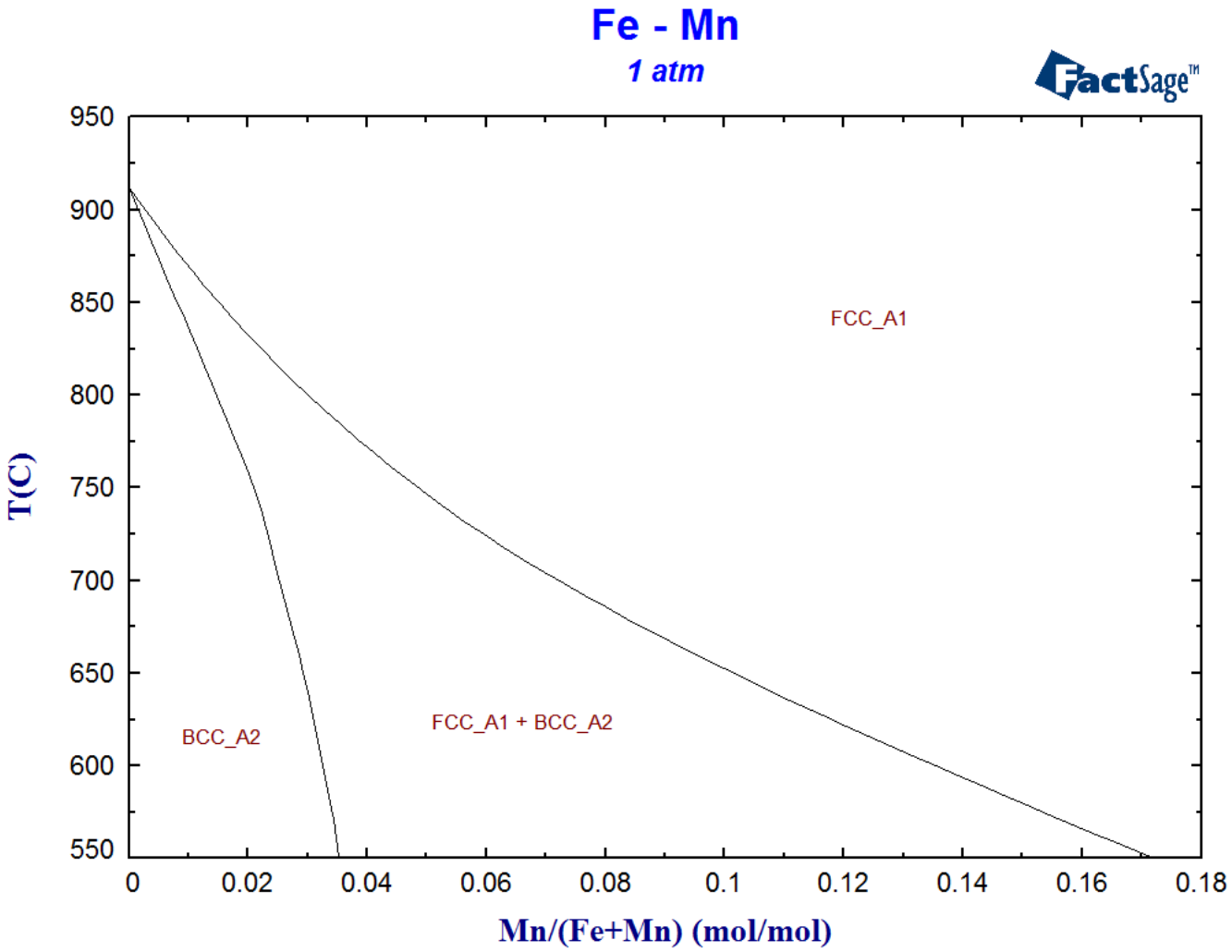


Mn-Mn solute interaction may affect diffusion of Mn and thus affect the oxide enrichment in IOZ

However, the real Mn-Mn solute interaction is small according to Factsage $\varepsilon_{Mn}^{Mn} = 0.7$

Fe-Mn binary alloy, ideal solution, phase transformation, constant temperature

Phase diagram of Fe-Mn binary alloy

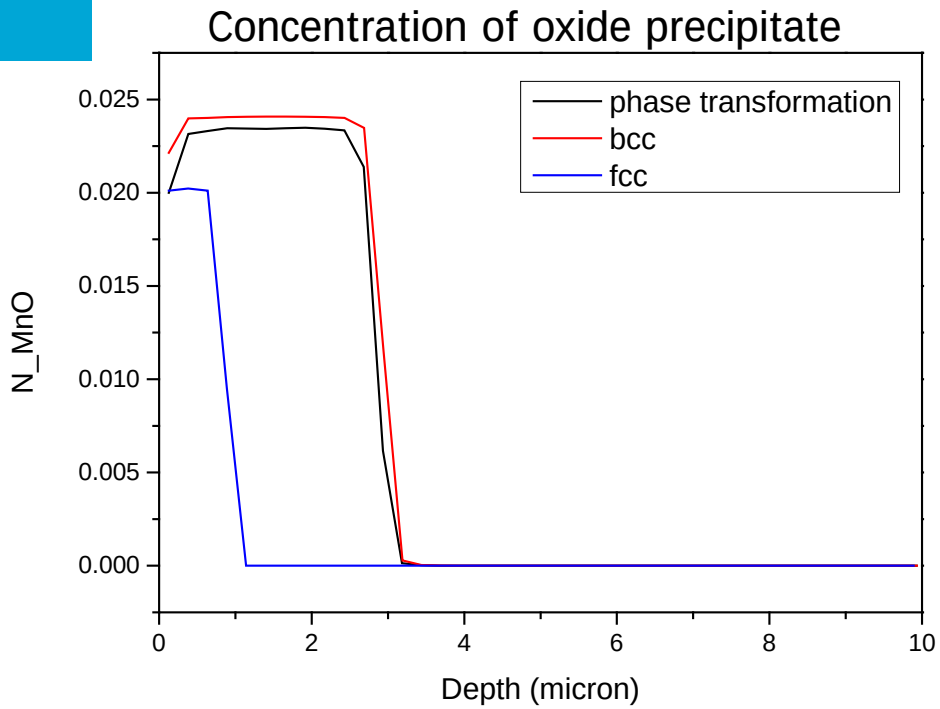


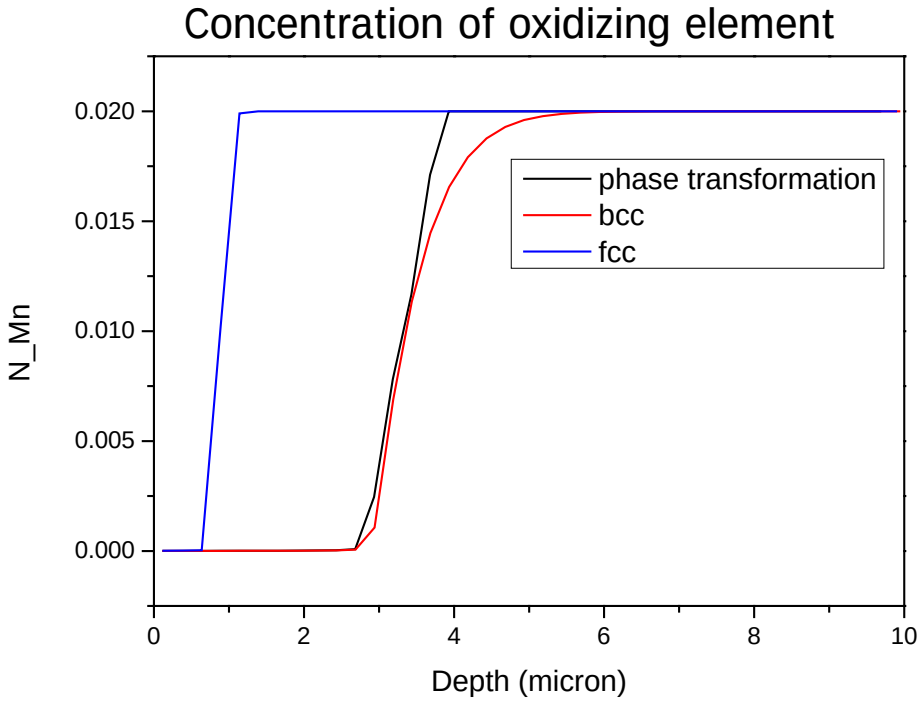
Phase diagram calculated in Factsage

Similar as the phase diagram calculated in thermocalc

Effect of phase transformation

Fe-2Mn, 800C, 20min, dew point 10° C





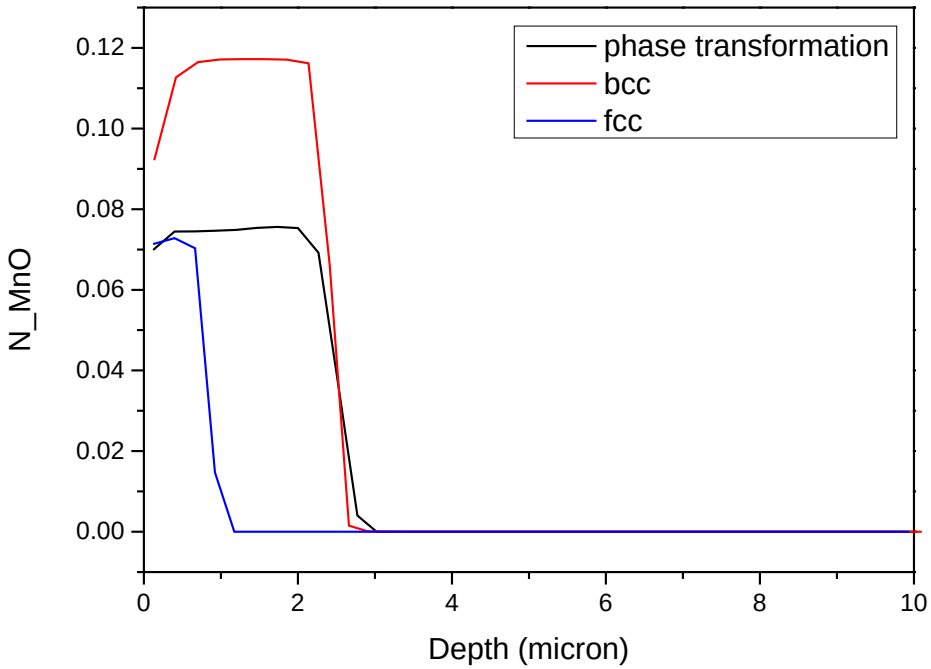
Internal oxidation kinetics is faster in bcc phase due to fast diffusion of O

Phase transformation from fcc to bcc phase increases kinetics of internal oxidation

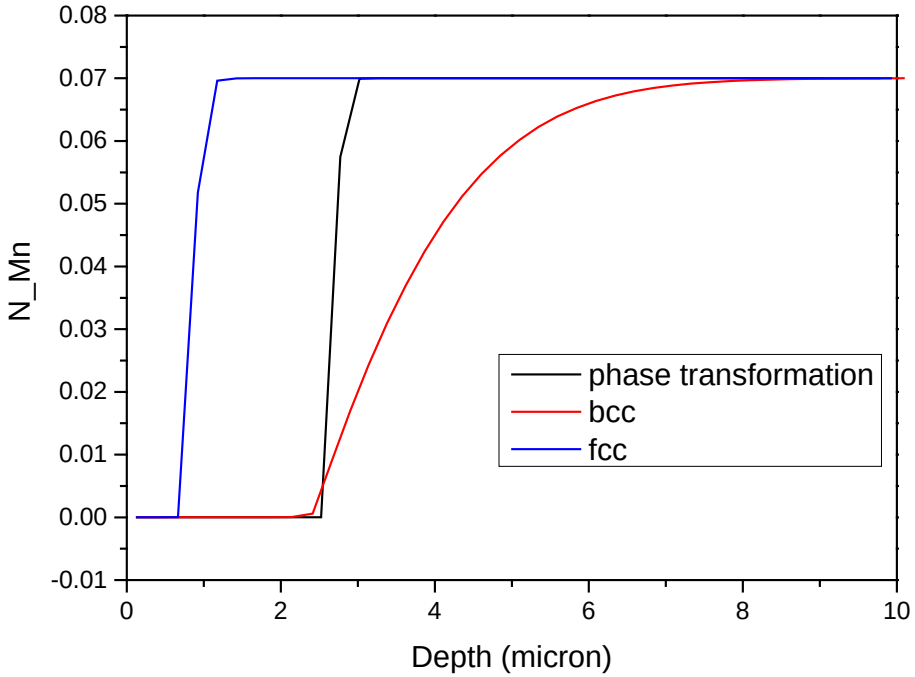
Effect of phase transformation

Fe-7Mn, 800C, 1h, dew point 10° C

Concentration of oxide precipitate



Concentration of oxidizing element

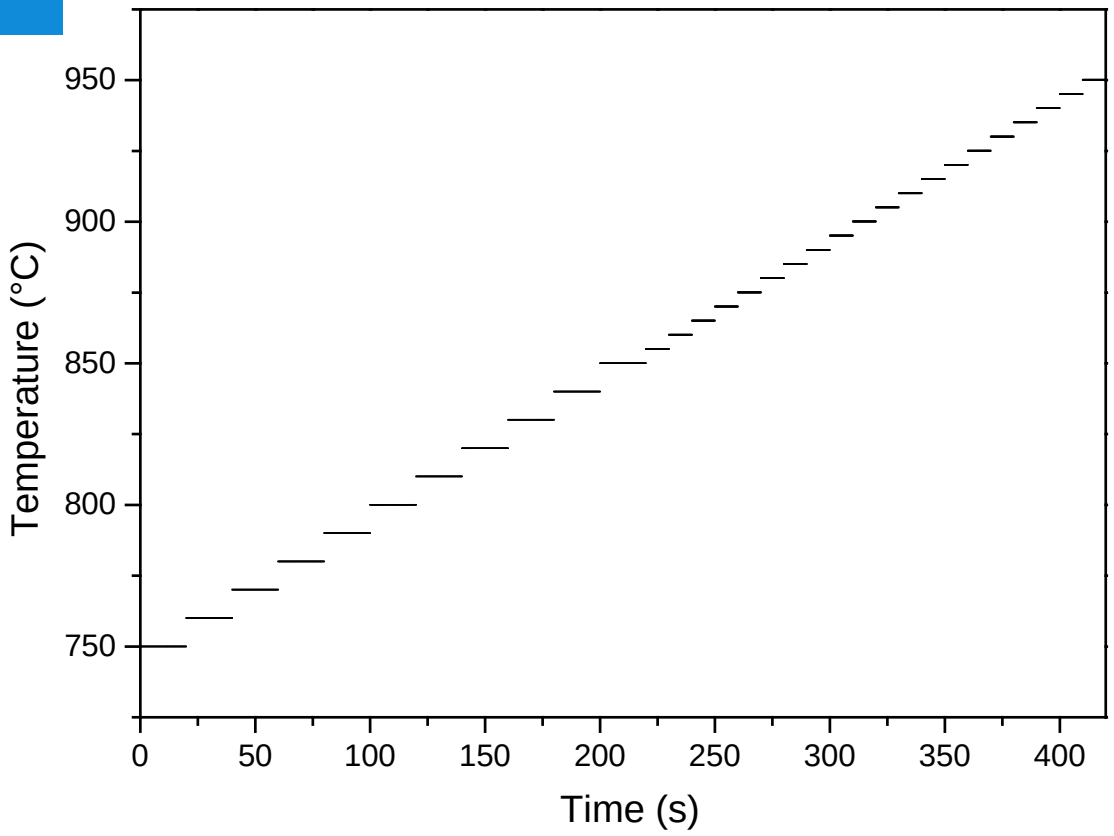


Phase transformation affects both kinetics of internal oxidation and solute enrichment in IOZ

Fe-Mn binary alloy, ideal solution, phase transformation, temperature profile

Temperature profile in simulation

Linear increase from 750 to 950℃



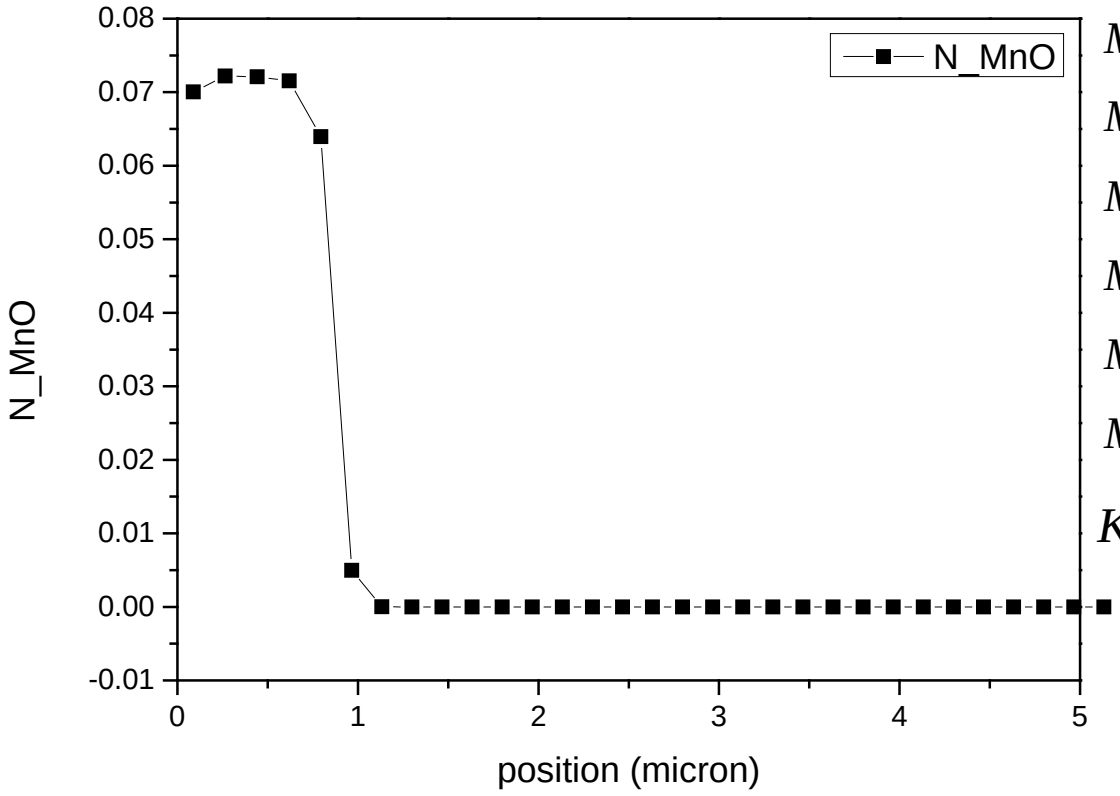
750-850℃: step size 10℃, 20s per step

850-950℃: step size 5℃, 10s per step

Simulation with varying temperature

Fe-7Mn, ideal solution, two phases, DP 10 ° C

Ferrite-austenite phase transformation is considered



$$M_{O,bcc} = 0.037 \times 10^8 \exp(-98000 / RT) / RT$$

$$M_{O,fcc} = 5.75 \times 10^8 \exp(-168000 / RT) / RT$$

$$M_{Mn,bcc} = 0.756 \times 10^8 \exp(-224500 / RT) / RT$$

$$M_{Mn,fcc} = 0.16 \times 10^8 \exp(-261700 / RT) / RT$$

$$M_{Fe,bcc} = 1.02 \times 10^8 \exp(-244300 / RT) / RT$$

$$M_{Fe,fcc} = 4.08 \times 10^8 \exp(-311100 / RT) / RT$$

$$Ksp_{fcc} = 10^{(-10766.4/T - 0.81)}$$

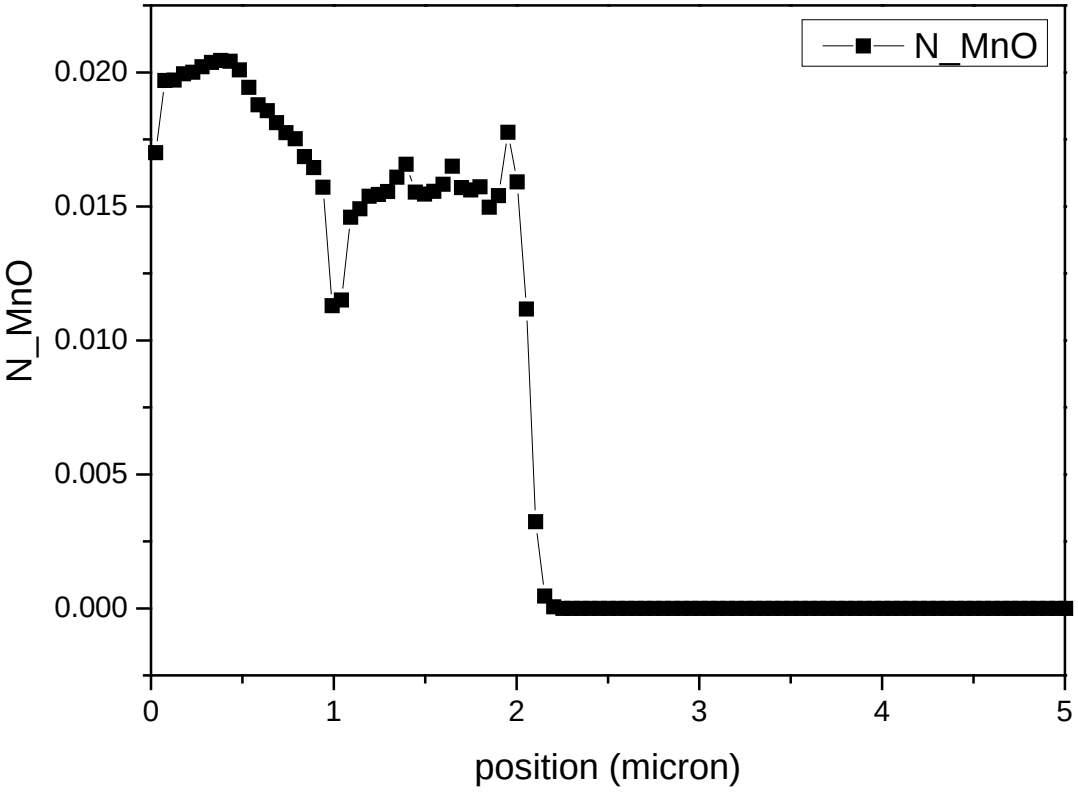
Slice size: 0.17 micron (original)

Redissolution of oxide is neglected

Simulation with varying temperature

Fe-1.7Mn, ideal solution, two phases, DP 10 ° C

Ferrite-austenite phase transformation is considered



$$M_{O,bcc} = 0.037 \times 10^{8} \exp(-98000 / RT) / RT$$

$$M_{O,fcc} = 5.75 \times 10^{8} \exp(-168000 / RT) / RT$$

$$M_{Mn,bcc} = 0.756 \times 10^{8} \exp(-224500 / RT) / RT$$

$$M_{Mn,fcc} = 0.16 \times 10^{8} \exp(-261700 / RT) / RT$$

$$M_{Fe,bcc} = 1.02 \times 10^{8} \exp(-244300 / RT) / RT$$

$$M_{Fe,fcc} = 4.08 \times 10^{8} \exp(-311100 / RT) / RT$$

$$Ksp_{fcc} = 10^{(-10766.4/T - 0.81)}$$

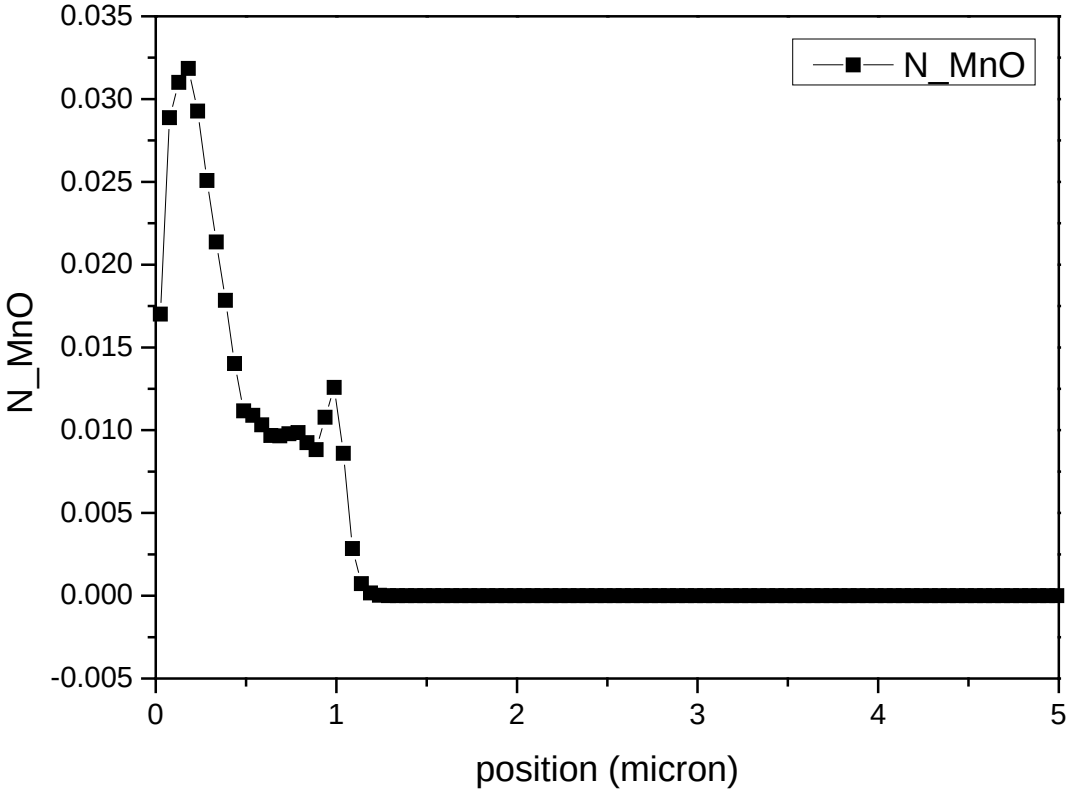
Slice size: 0.05 micron (original)

Redissolution of oxide is neglected

Simulation with varying temperature

Fe-1.7Mn, ideal solution, two phases, DP -10 ° C

Ferrite-austenite phase transformation is considered



$$M_{O,bcc} = 0.037 \times 10^{8} \exp(-98000 / RT) / RT$$

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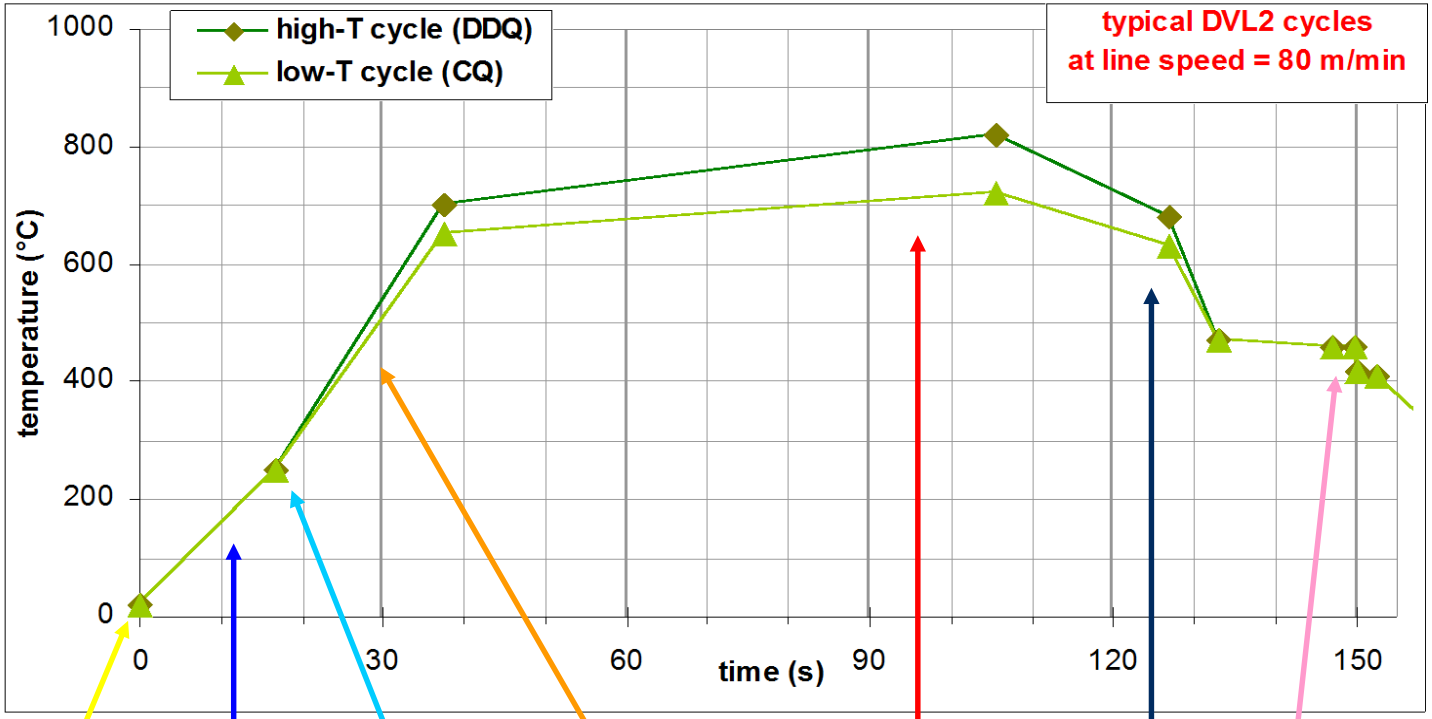
$$Ksp_{fcc} = 10^{(-10766.4/T - 0.81)}$$

Slice size: 0.05 micron (original)

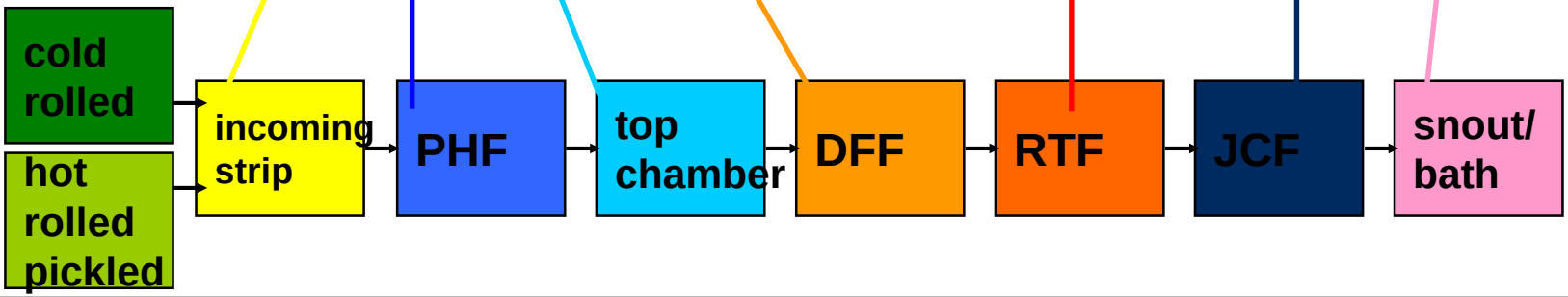
Redissolution of oxide is neglected

Temperature profile in industry

(a)

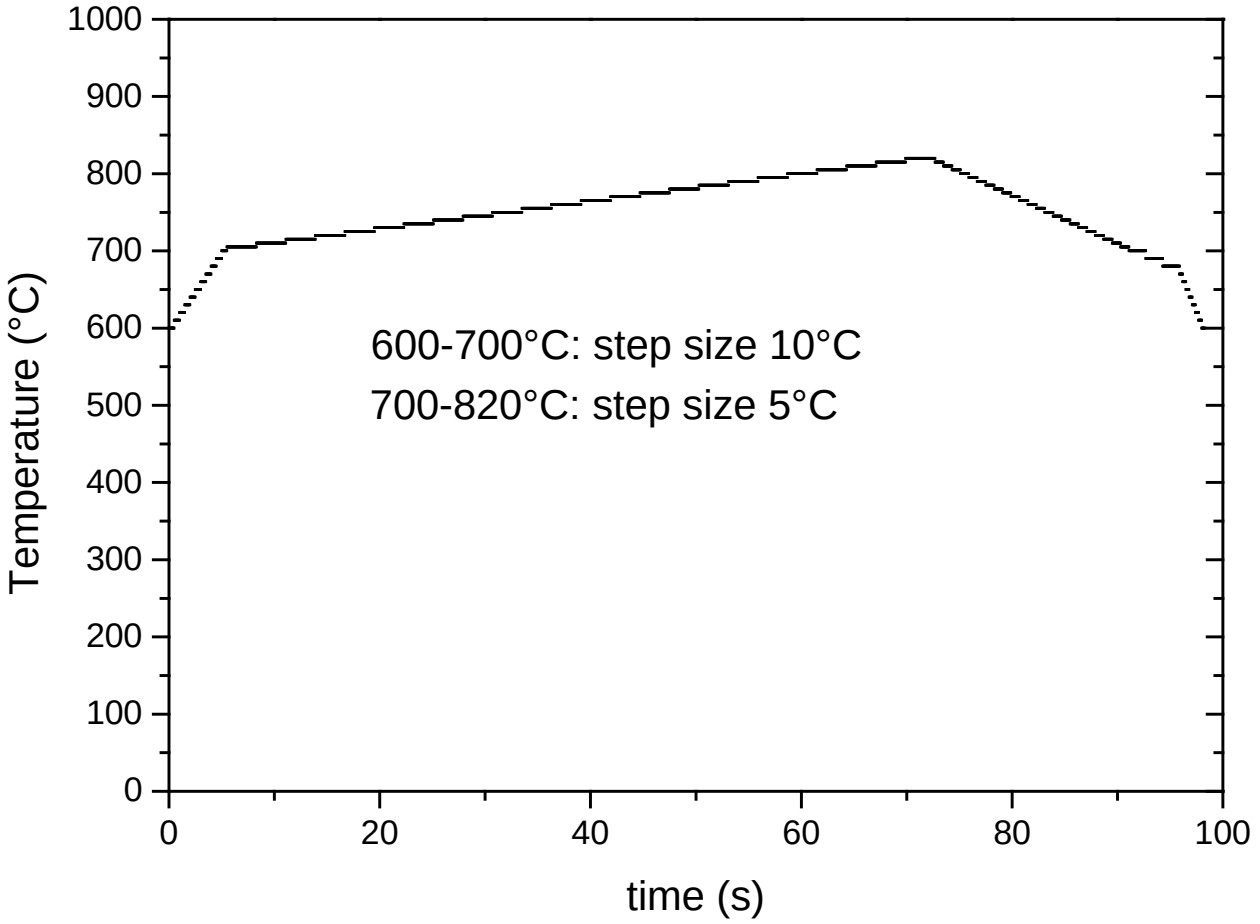


(b)



Temperature profile in simulation

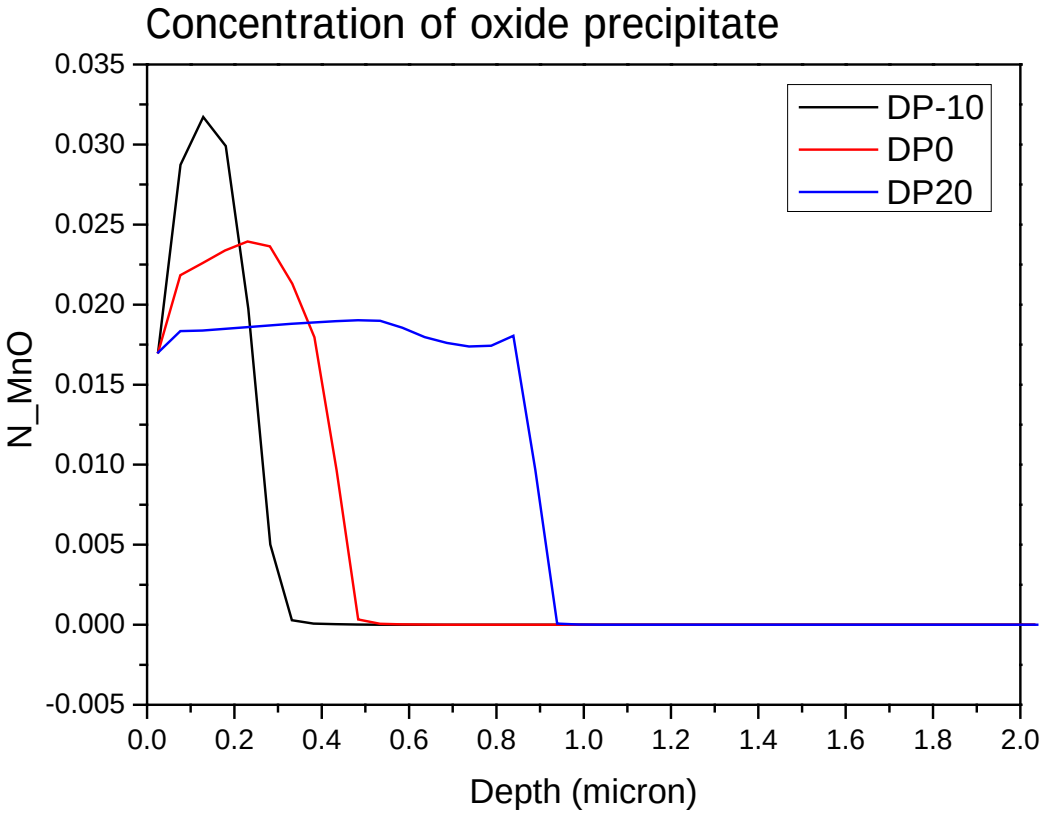
Assuming that no precipitation occur below 600C



Simulation with industrial temperature profile

Fe-1.7Mn, ideal solution, two phases, DP 10 ° C

Ferrite-austenite phase transformation is considered



$$M_{O,bcc} = 0.037 \times 10^8 \exp(-98000 / RT) / RT$$

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$$M_{Mn,fcc} = 0.16 \times 10^8 \exp(-261700 / RT) / RT$$

$$M_{Fe,bcc} = 1.02 \times 10^8 \exp(-244300 / RT) / RT$$

$$M_{Fe,fcc} = 4.08 \times 10^8 \exp(-311100 / RT) / RT$$

$$Ksp_{fcc} = 10^{(-10766.4/T - 0.81)}$$

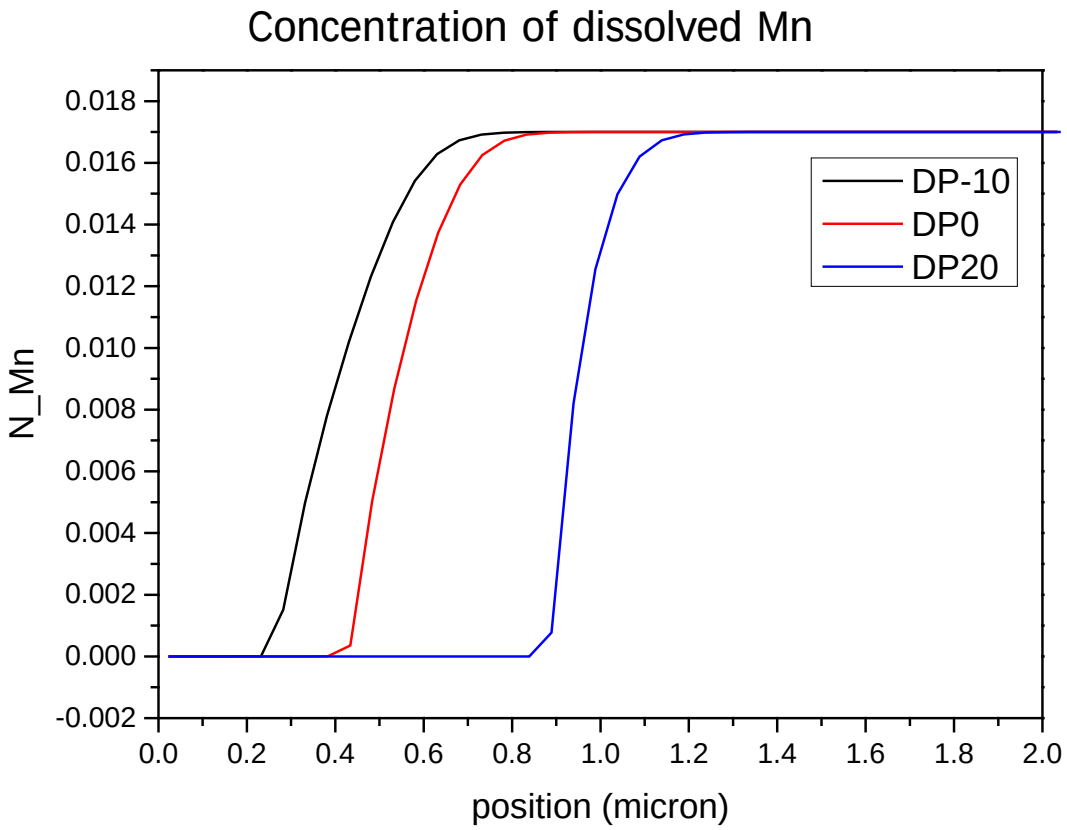
Slice size: 0.05 micron (original)

Redissolution of oxide is neglected

Simulation with industrial temperature profile

Fe-1.7Mn, ideal solution, two phases, DP 10 ° C

Ferrite-austenite phase transformation is considered



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$$M_{Fe,fcc} = 4.08 \times 10^{8} \exp(-311100 / RT) / RT$$

$$Ksp_{fcc} = 10^{(-10766.4/T - 0.81)}$$

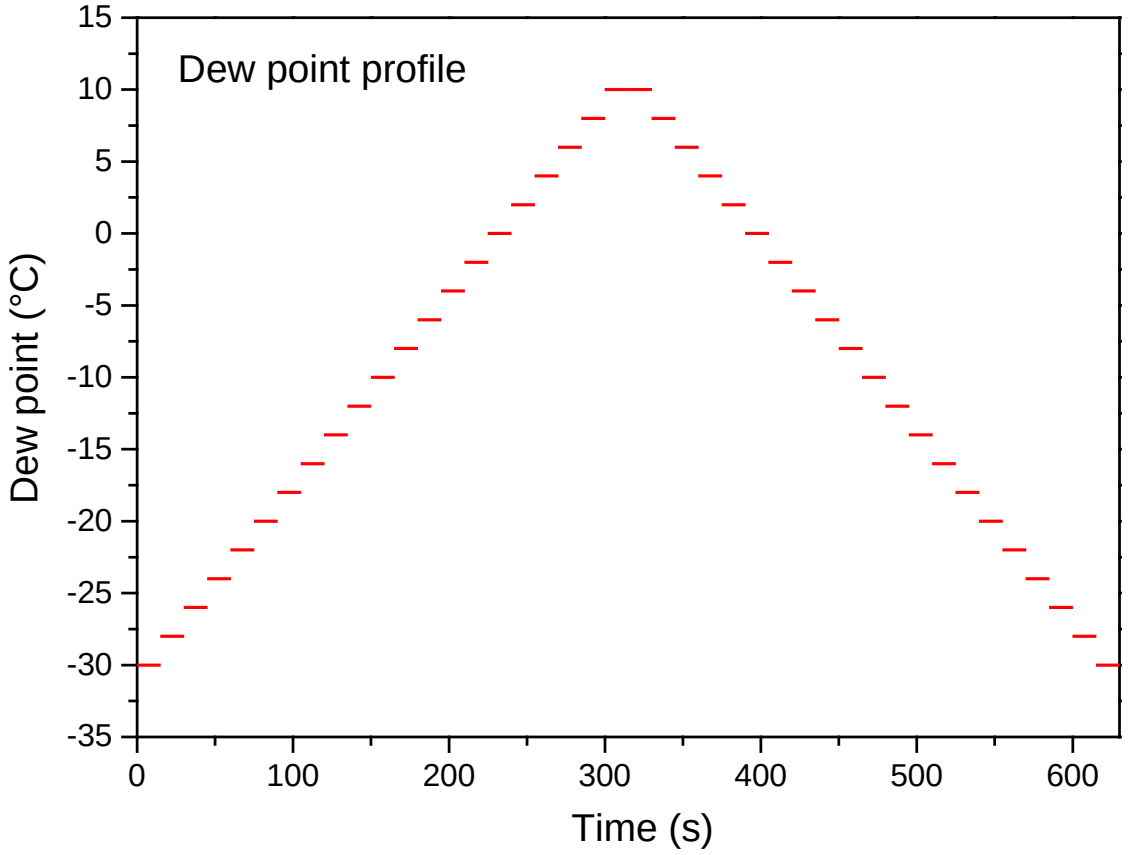
Slice size: 0.05 micron (original)

Redissolution of oxide is neglected

Fe-Mn binary alloy, ideal solution, dew point profile, constant temperature

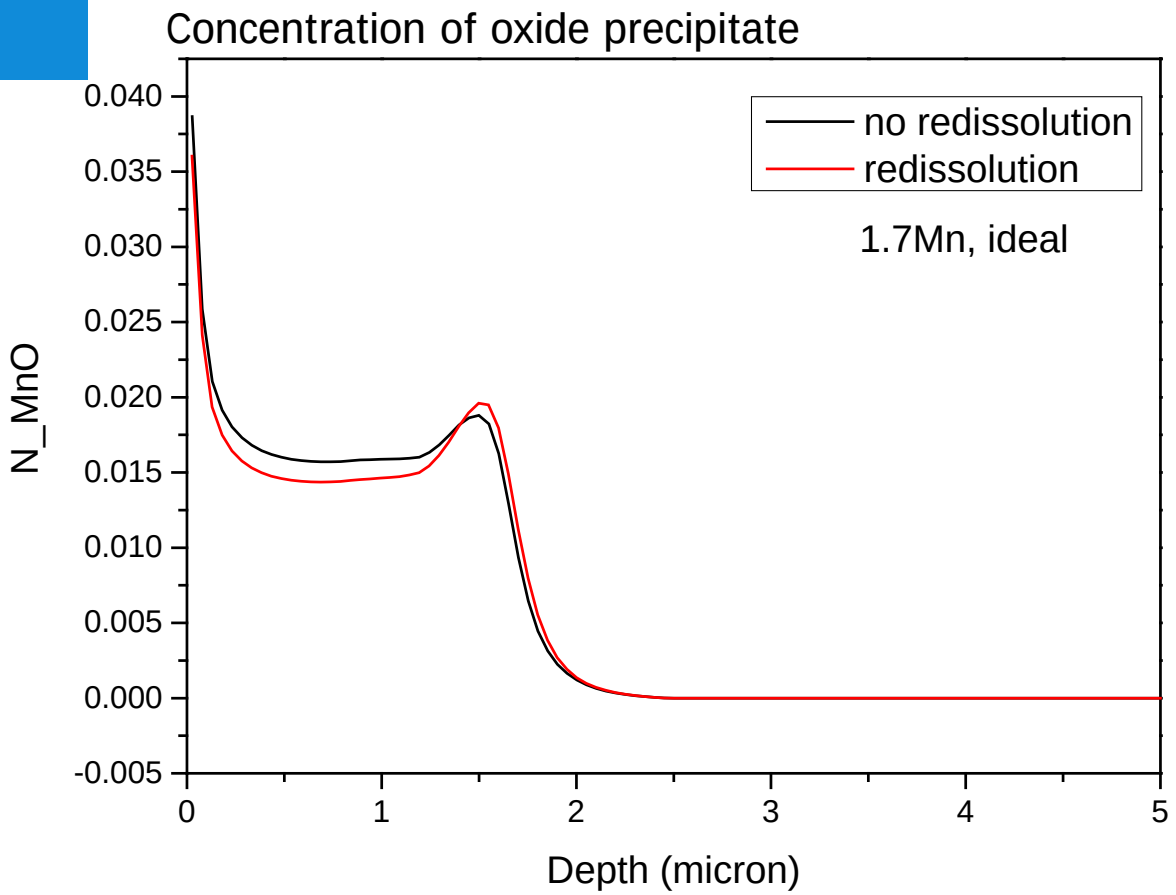
Dew point profile in simulation

Dew point step size is 2℃, duration time 15 seconds per step



Simulation with varying dew point

Fe-1.7Mn, ideal solution, constant temperature at 950C



$$M_O = 35 / RT$$

$$M_{Mn} = 4 \times 10^{-4} / RT$$

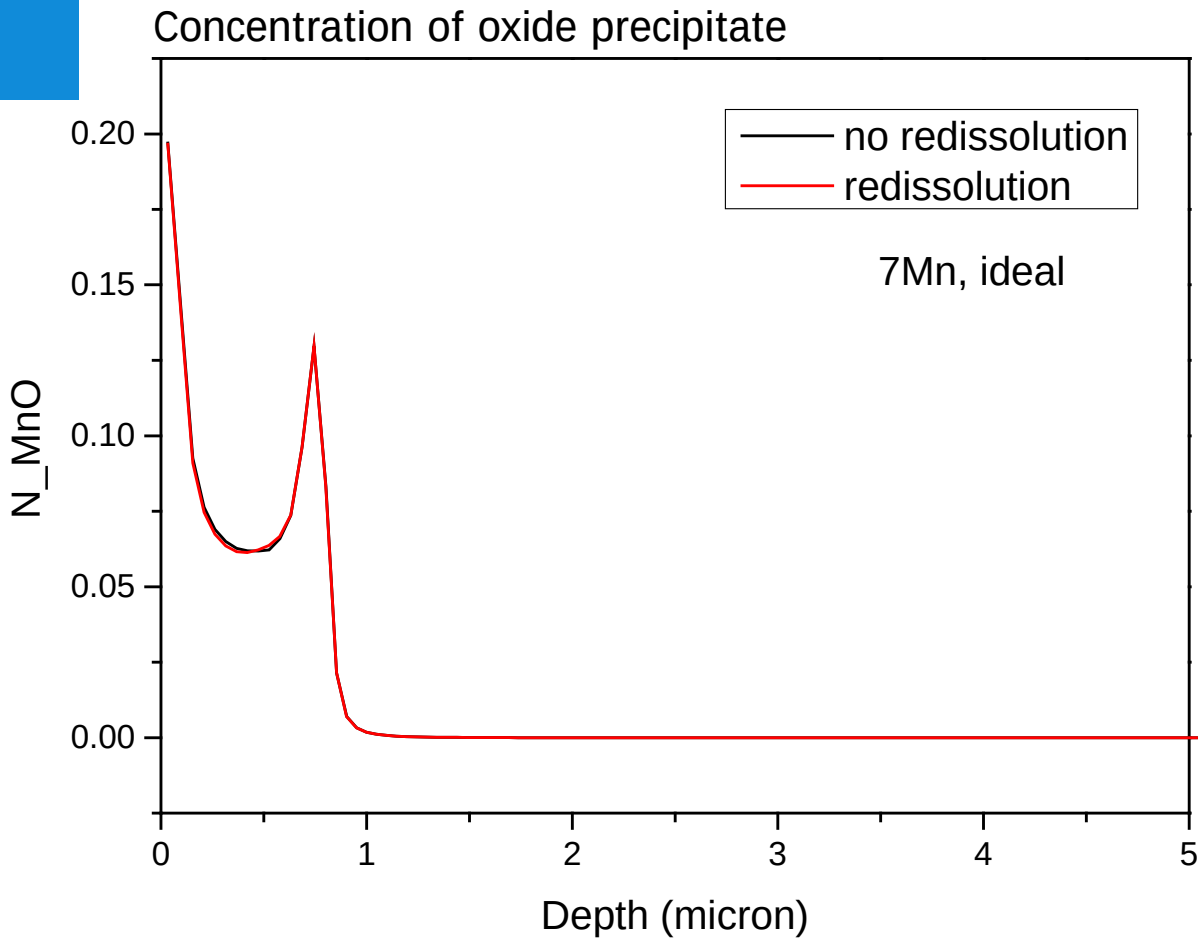
$$M_{Fe} = 4.08 \times 10^{8} \exp(-311100 / RT) / RT$$

$$Ksp = 2.4 \times 10^{-10}$$

Slice size: 0.05 micron (original)

Simulation with varying dew point

Fe-7Mn, ideal solution, constant temperature at 950C



$$M_O = 35 / RT$$

$$M_{Mn} = 4 \times 10^{-4} / RT$$

$$M_{Fe} = 4.08 \times 10^{8} \exp(-311100 / RT) / RT$$

$$Ksp = 2.4 \times 10^{-10}$$

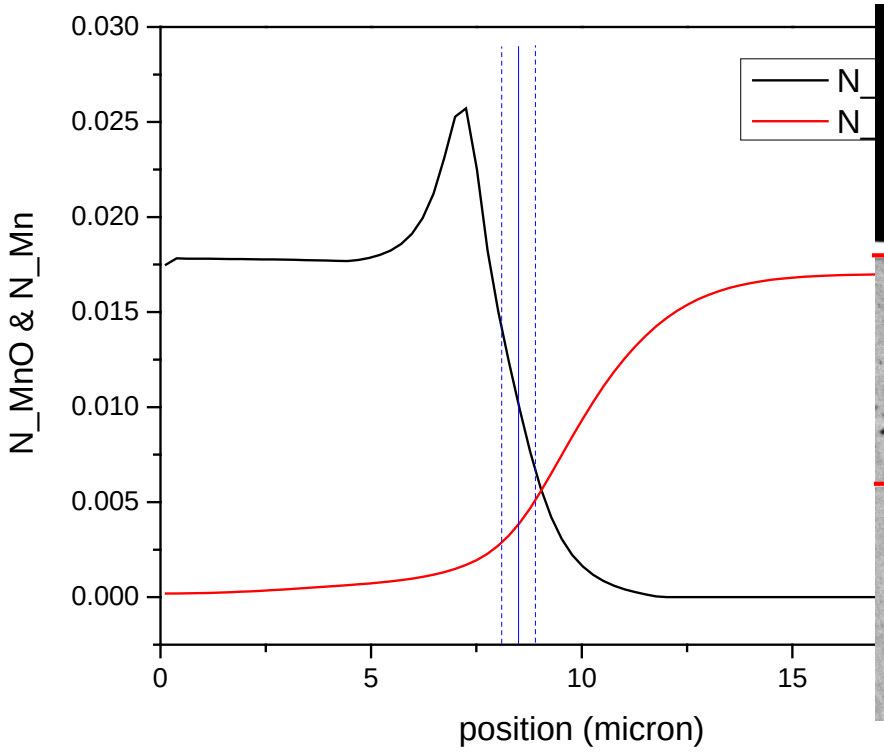
Slice size: 0.05 micron (original)

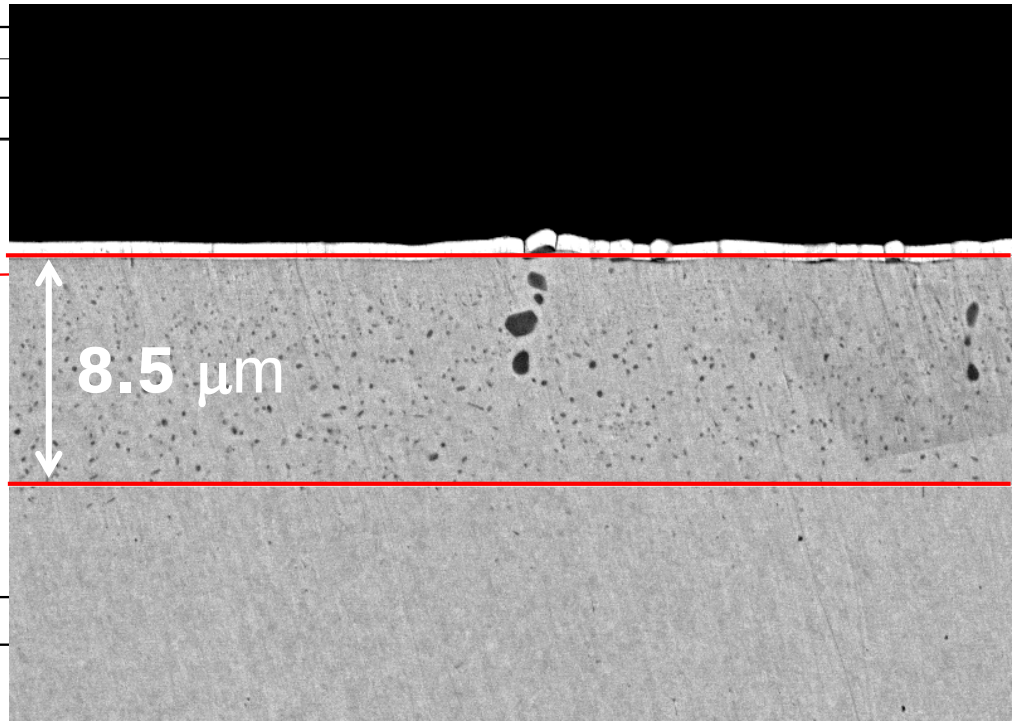
Simulation with varying dew point

Fe-1.7Mn, ideal solution, constant temperature at 950C

Annealed at DP10 for 1 hour and then DP-10 for 3 hours

Concentration of oxide precipitate and dissolved Mn



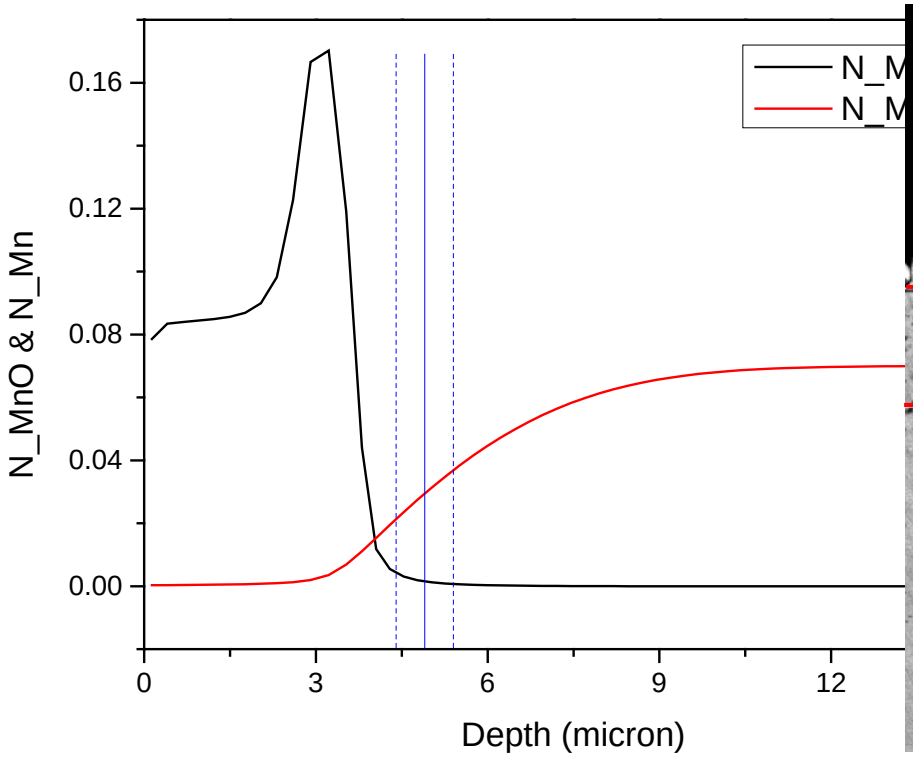


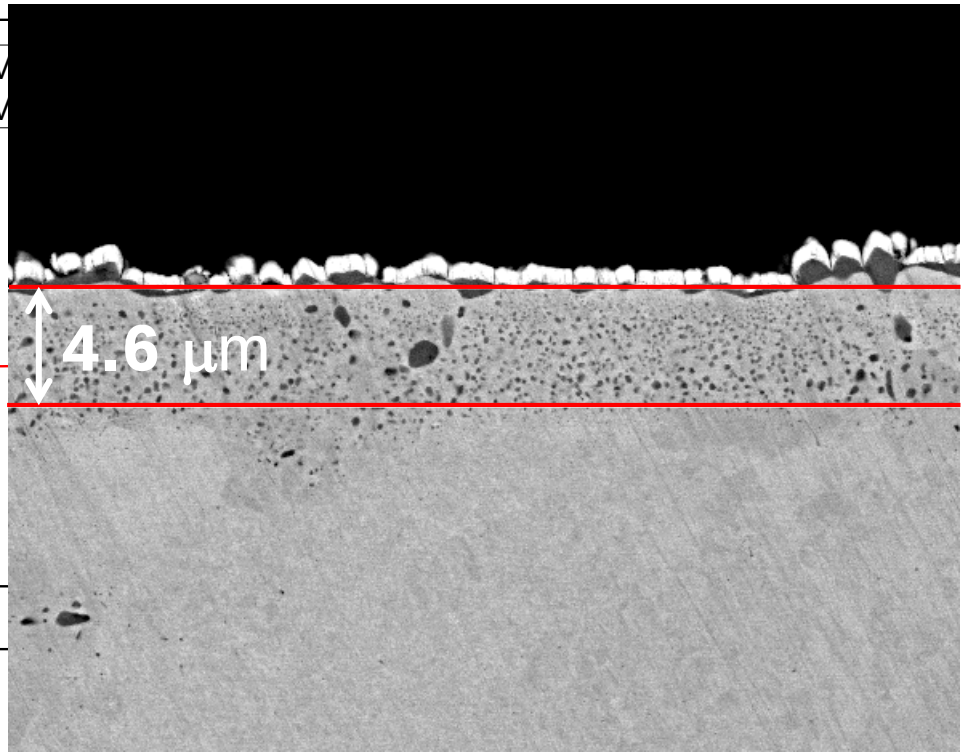
Simulation with varying dew point

Fe-7Mn, ideal solution, constant temperature at 950C

Annealed at DP10 for 1 hour and then DP-10 for 3 hours

Concentration of oxide precipitate and dissolved Mn





3

Outlook

Development of our simulation tool

- Optimizing current simulation program for faster computation
- Coupling our simulation program with thermocalc and Factsage
- Extend simulation tool to three type of oxide precipitates
- Include formation of mixed oxide (Mn,Fe)O
- Include phase transformation in oxidation of ternary alloys
- Incorporation of solute interaction in simulation program for oxidation of ternary alloys with more than one type of oxides formed