TMS 2005 --- Diffusion Symposium

Characterization of Internal Oxidation

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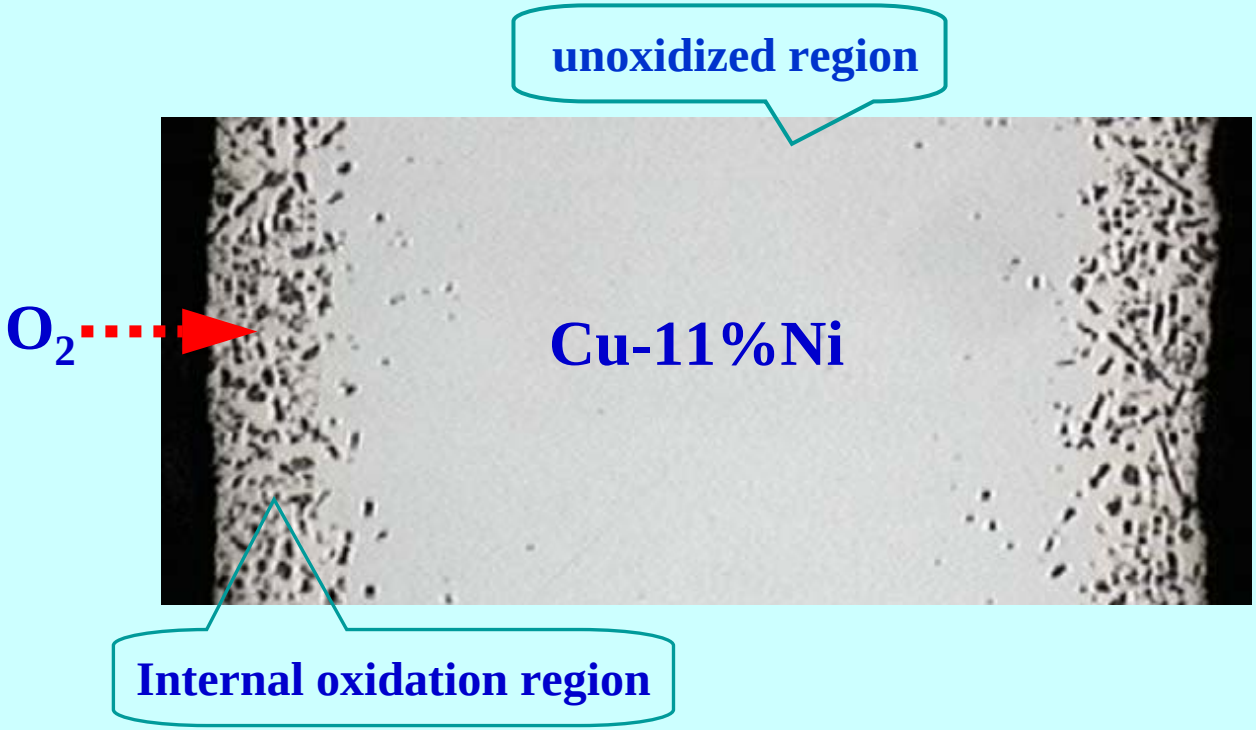
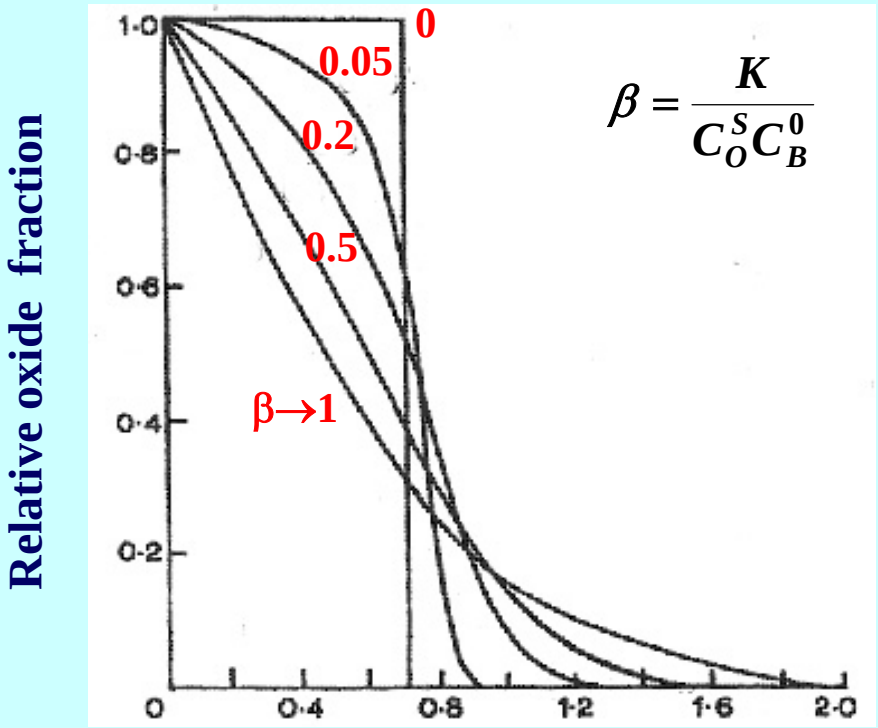
Internal Oxidation Characterization



- Phases present --- XRD
- Oxide fraction profile --- Image analysis
- Concentration profile --- EDX
- Thickness of internal oxidation region

Oxide Fraction Profile

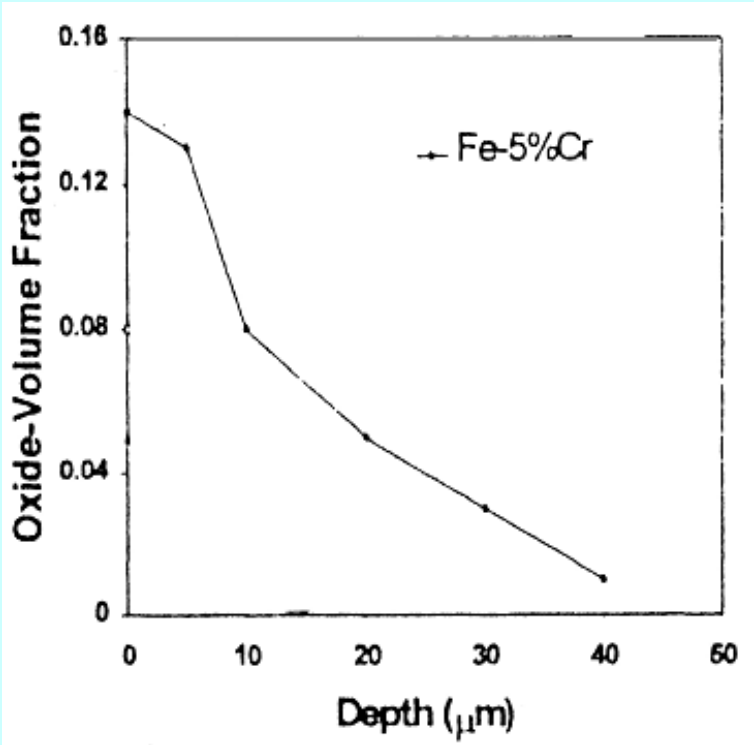
Simulation results for saturated case in literature :

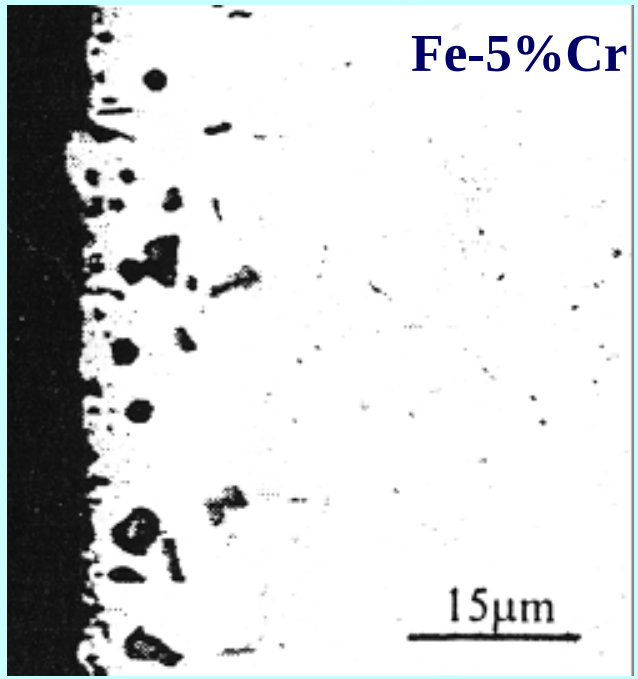


* E. K. Ohriner and J. E. Morral, Scripta Metallurgica, 13 (1979) 7.

Oxide Fraction Profile

Experimental results in literature:



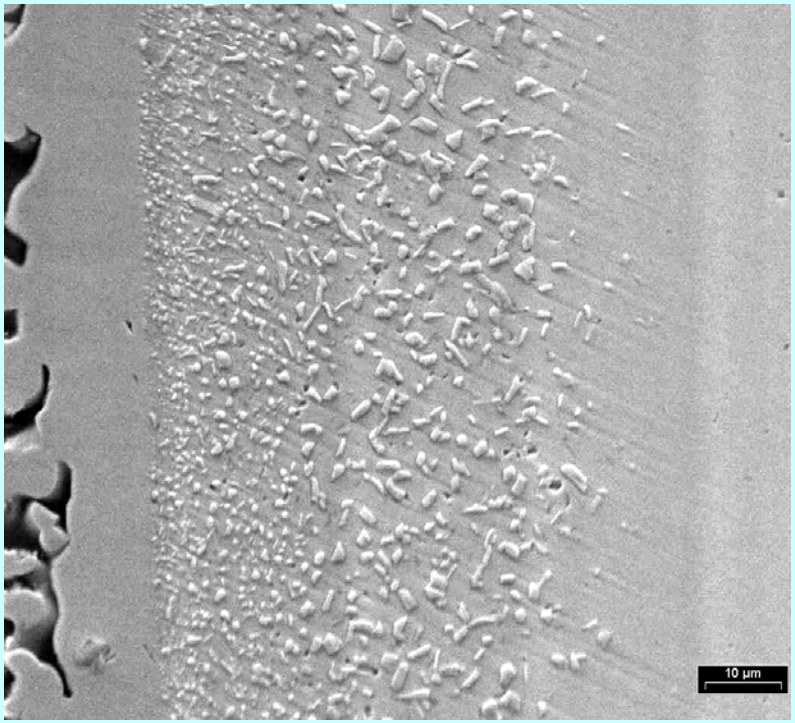


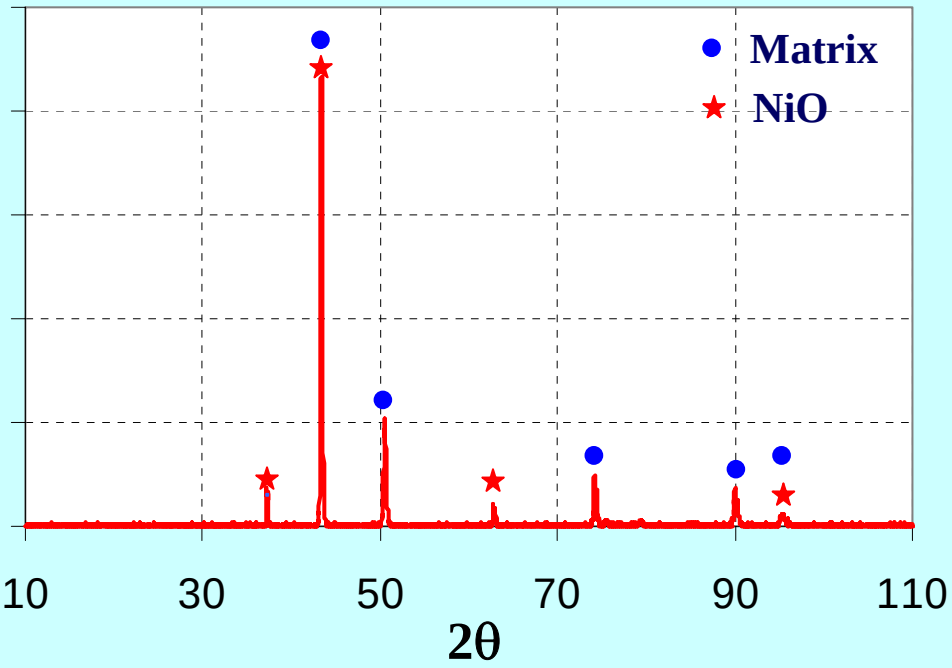
Fe-Cr alloys internally oxidized at 1000 °C for 20 hours with Po_2=8.7×10^{-17}atm.*

*** O. Ahmed and D. J. Yong, Electrochemical Society Proceedings, 38 (1999) 77.**

Oxide Fraction Profile

Cu-7% Ni internally oxidized at 900° C in Rhines Pack



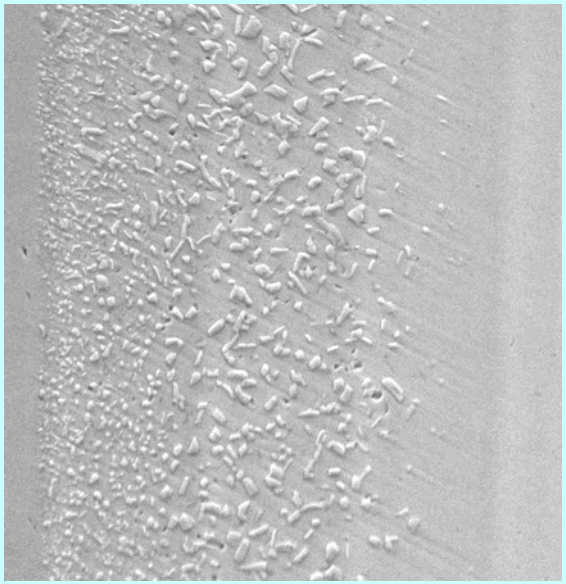


SEM

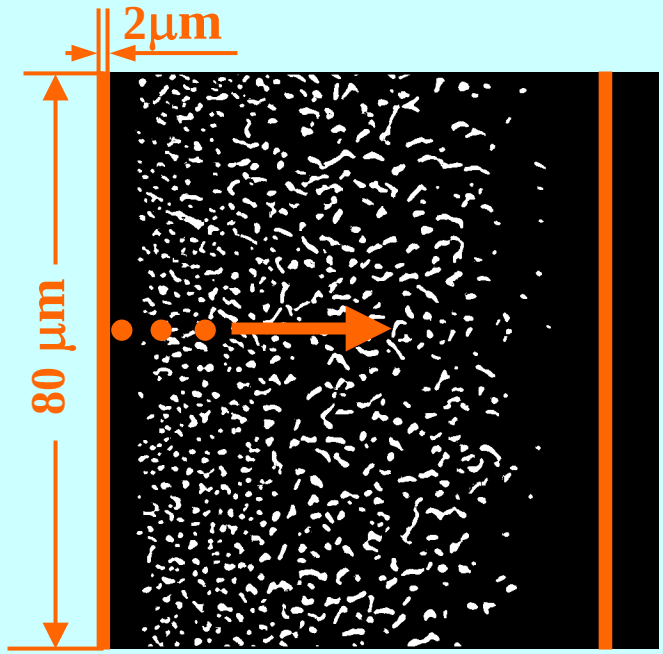
XRD patterns

Oxide Fraction Profile

Image analysis: oxide area fraction profile



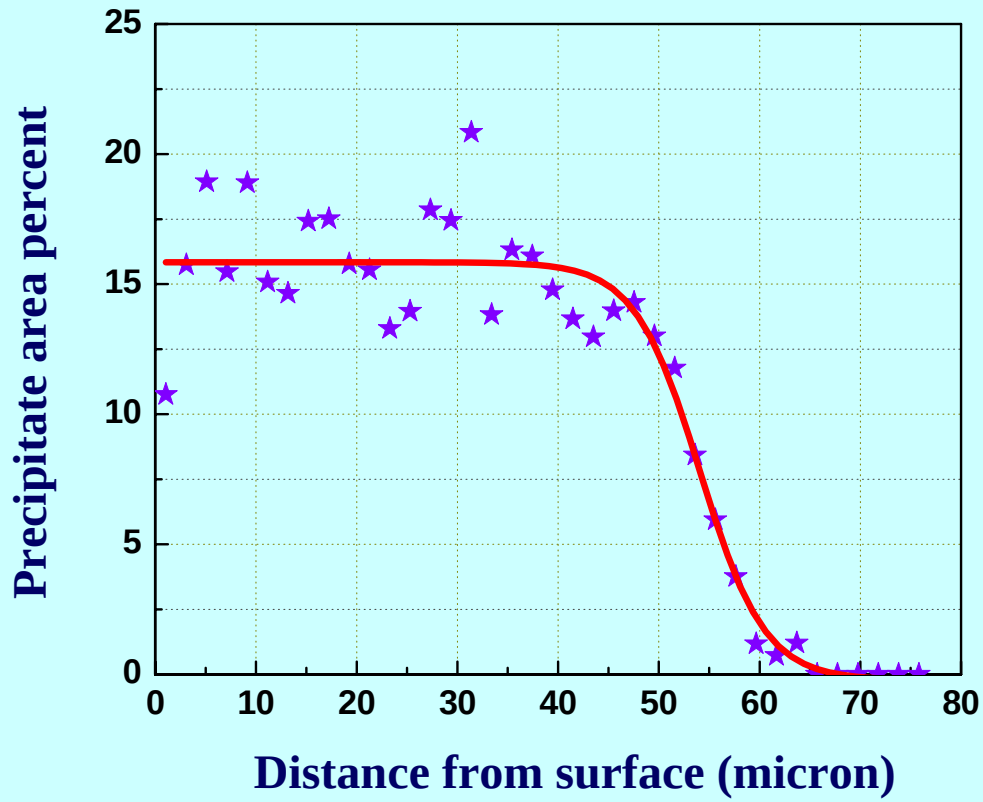
grey scale



binary mode

Oxide Fraction Profile

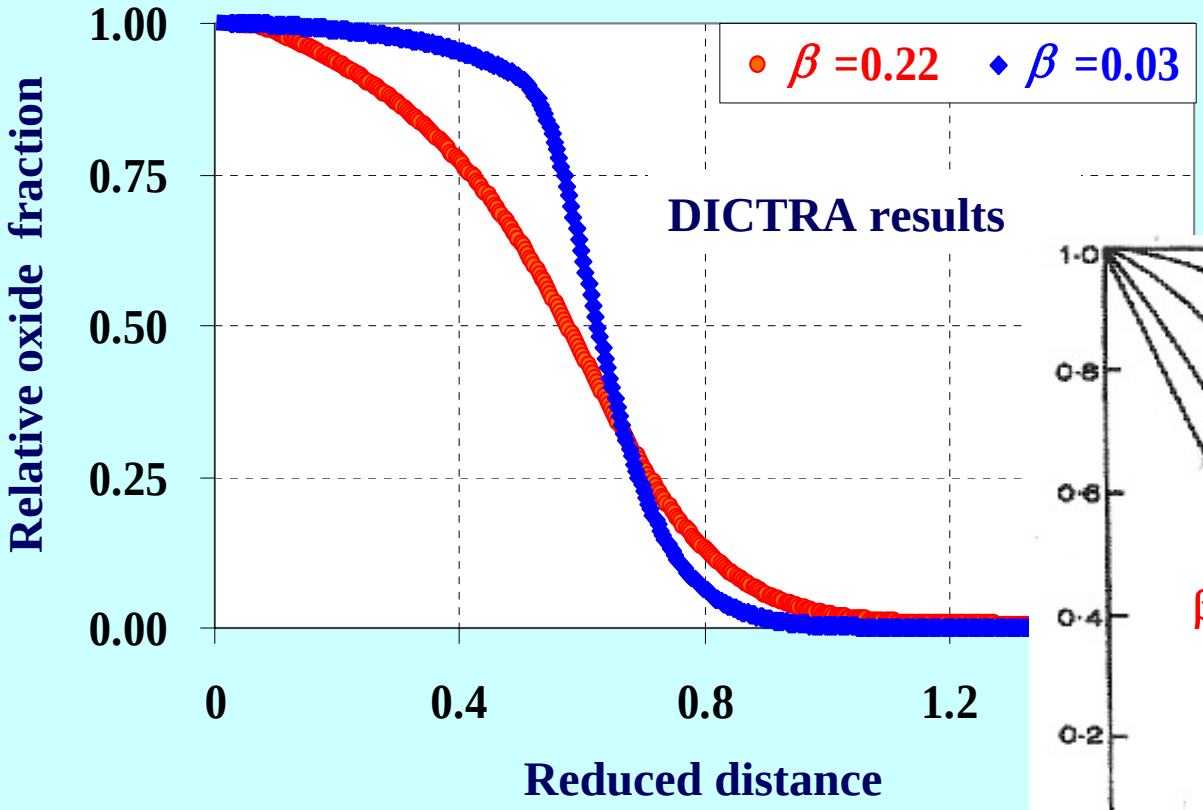
NiO area fraction versus distance

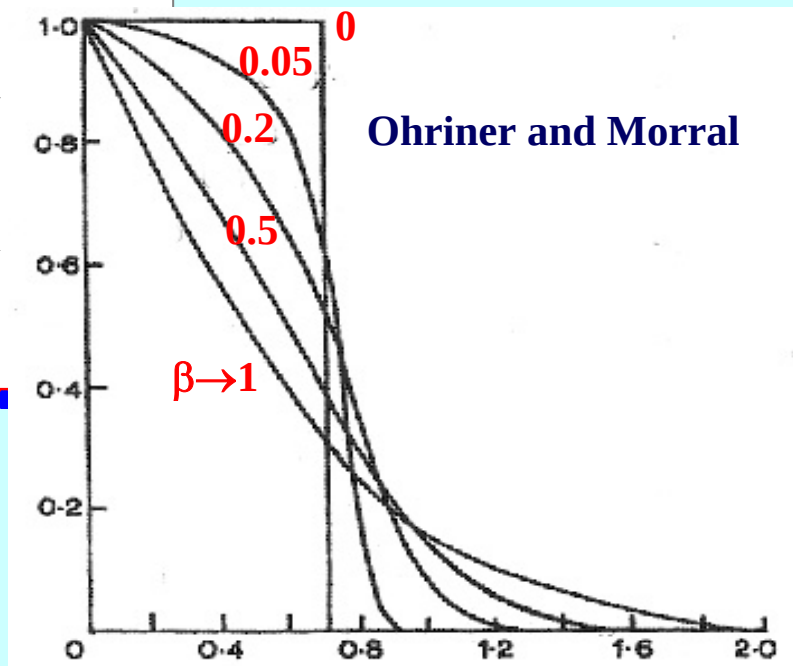


Cu-7% Ni alloys internally oxidized at 900° C for 1 hour

Oxide Fraction Profile

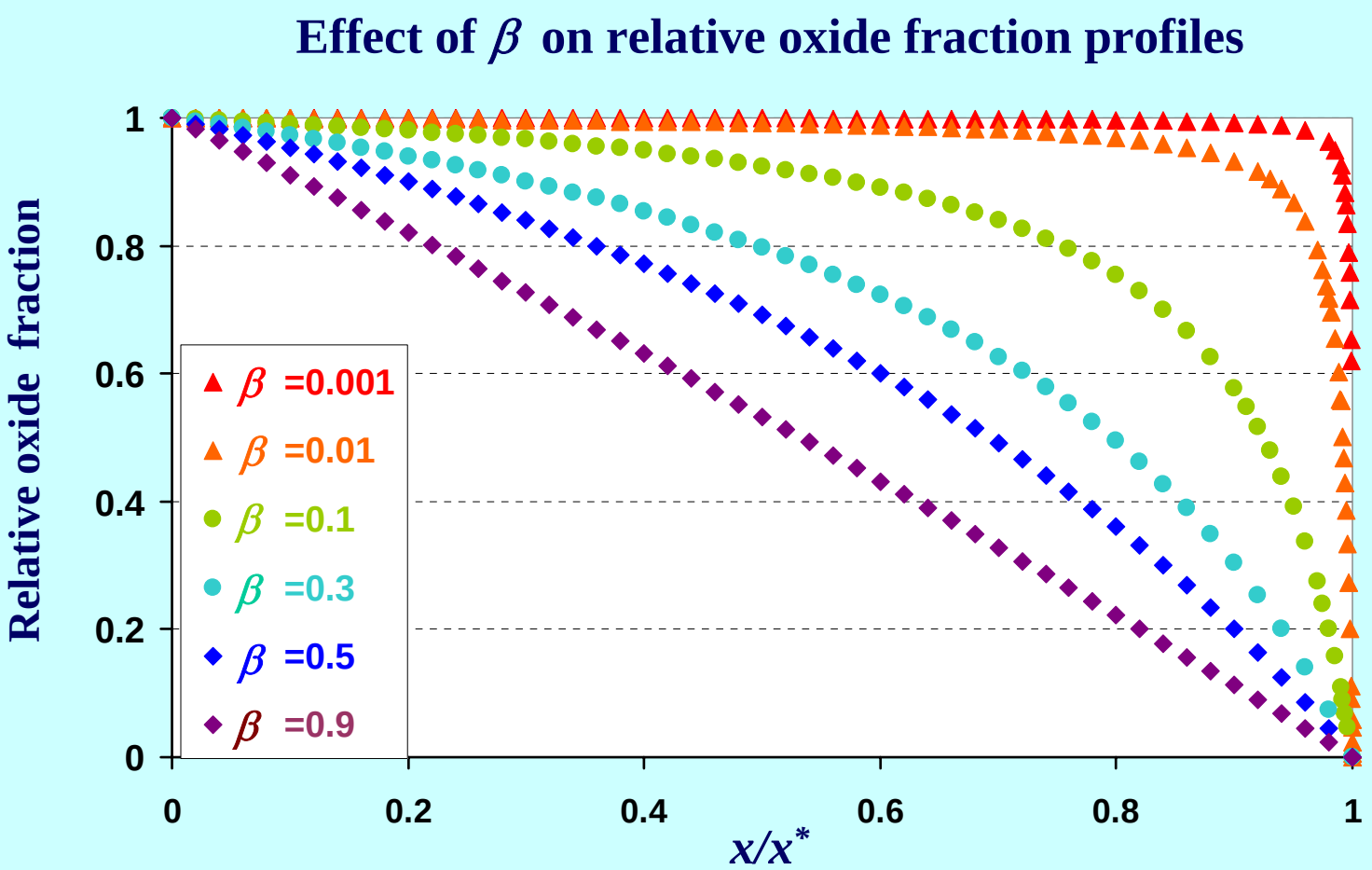
Simulation results: saturated case





Oxide Fraction Profile

Simulation results: unsaturated case



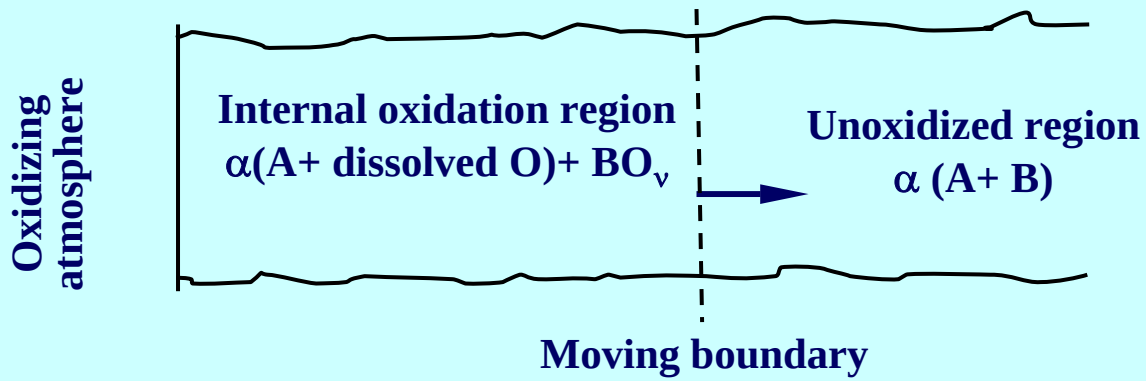
Oxide Fraction Profile

Summary:

- **When alloys are saturated with oxygen, oxide mole fraction decreases asymptotically to zero and the position of moving boundary cannot be defined.**
- **When alloys are unsaturated with oxygen, the moving boundary between internal oxidation region and unoxidized region is well defined.**

Concentration Profiles

The classic model:



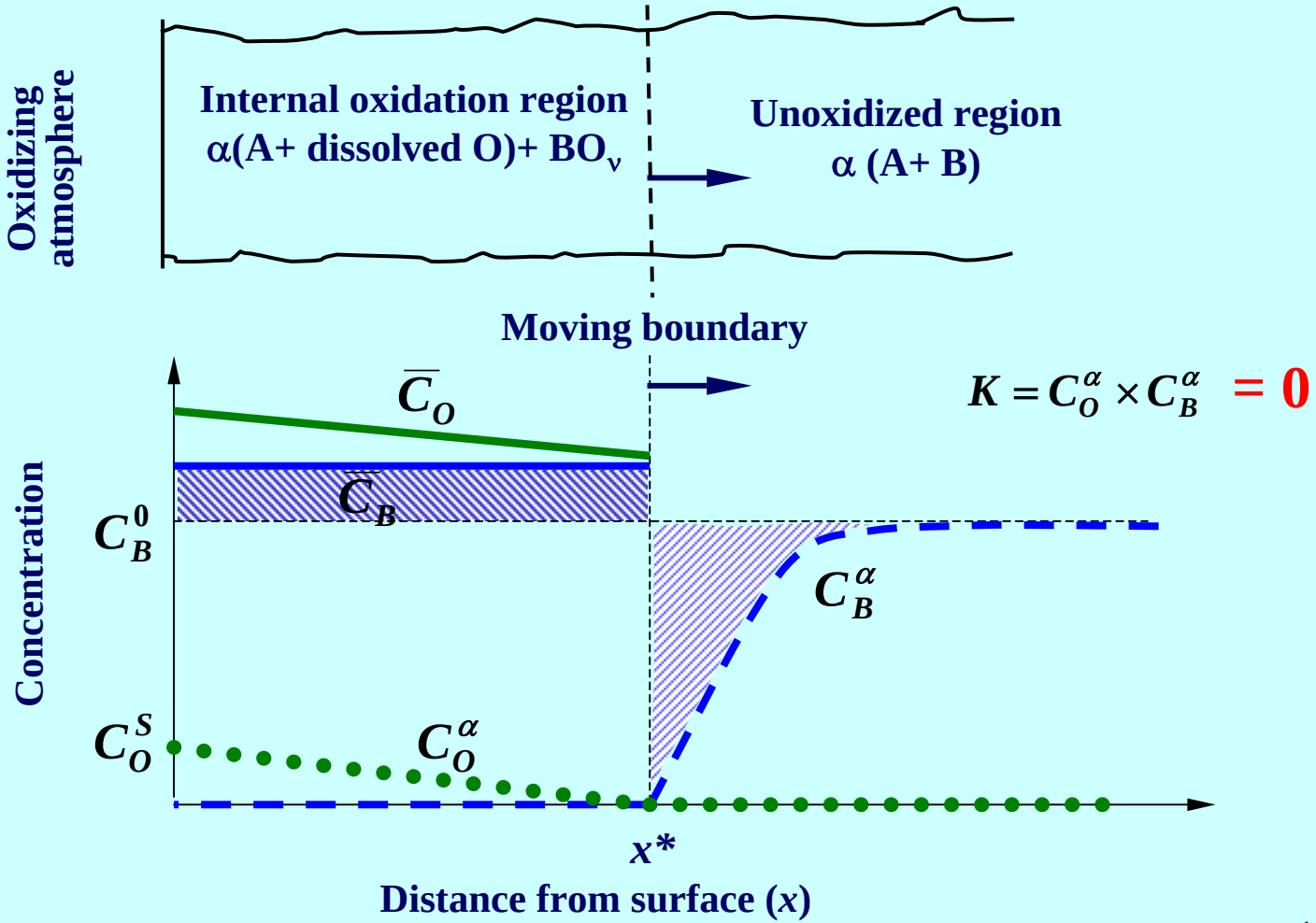
Assumptions:

- **All the solute B is consumed to form BO_v in the internal oxidation region.**
- **The concentrations of dissolved B and O at the moving boundary are zero.**

*** C. Wagner, Z. Electrochem, 63 (1959) 772.**

Concentration Profiles

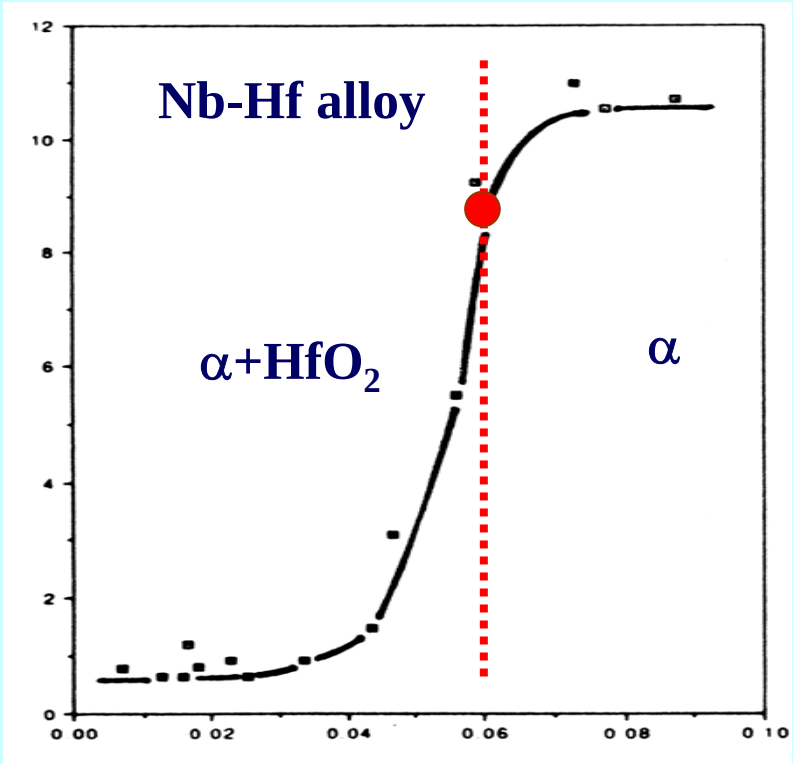
The classic model:



* C. Wagner, Z. Electrochem, 63 (1959) 772.

Concentration Profiles

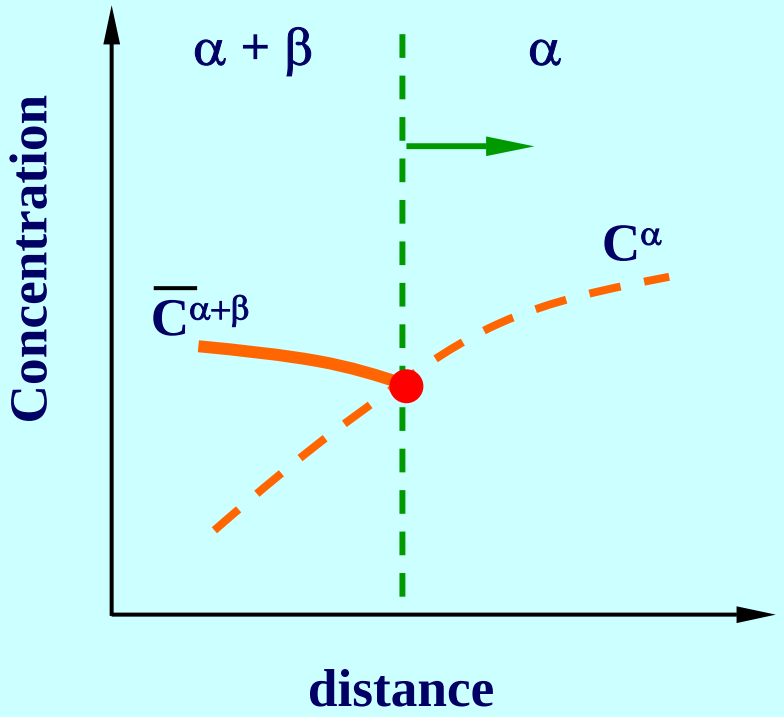
Experimental results in literature:



* D. L. Corn *et al.* Oxidation of Metals, 35 (1991) 139

Concentration Profiles

Concentration profiles under local equilibrium conditions

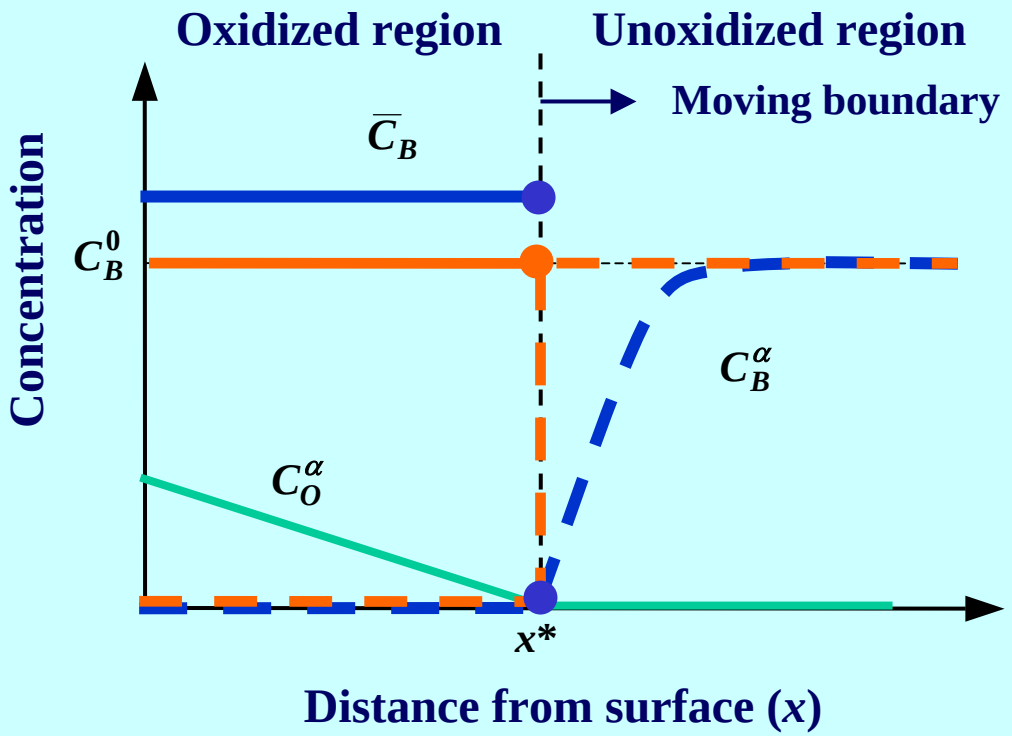


- **Matrix concentration profile, C^{a}, is continuous in slope and value.**
- **Average profile, $\overline{C}^{\alpha+\beta}$, and matrix profile, C^{α}, meet at the moving boundary.**

*** W.J. Boettinger *et al.* Acta Metall.Mater. 48 (2000) 481-492.**
*** J. E. Morral and H. Chen, Scripta Mater. 43 (2000) 699-703.**

Concentration Profiles

The classic model versus Local equilibrium model



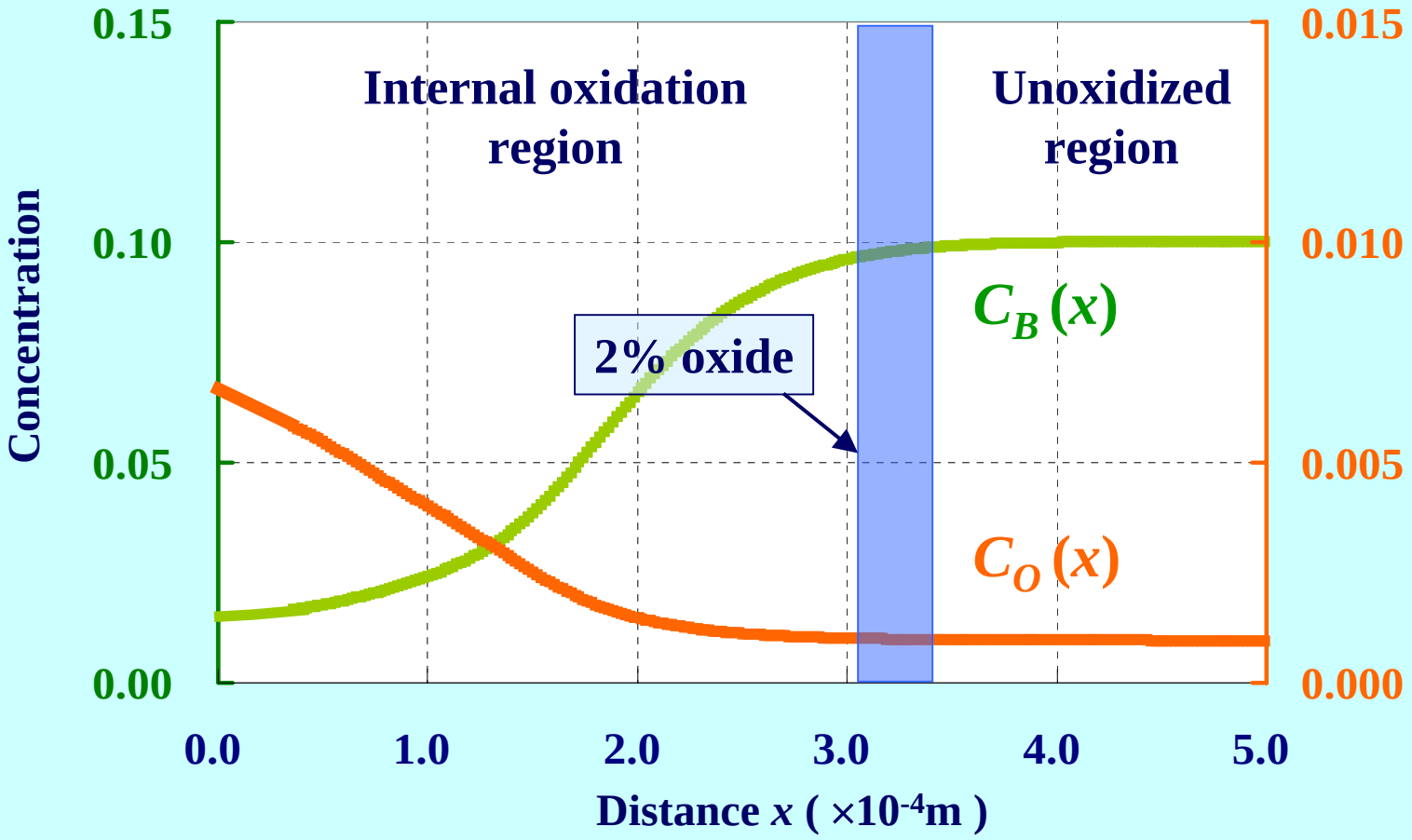
K = 0

The classic model: $\overline{C}_B$ C_B^α

Local equilibrium model: $\overline{C}_B$ C_B^α

Concentration Profiles

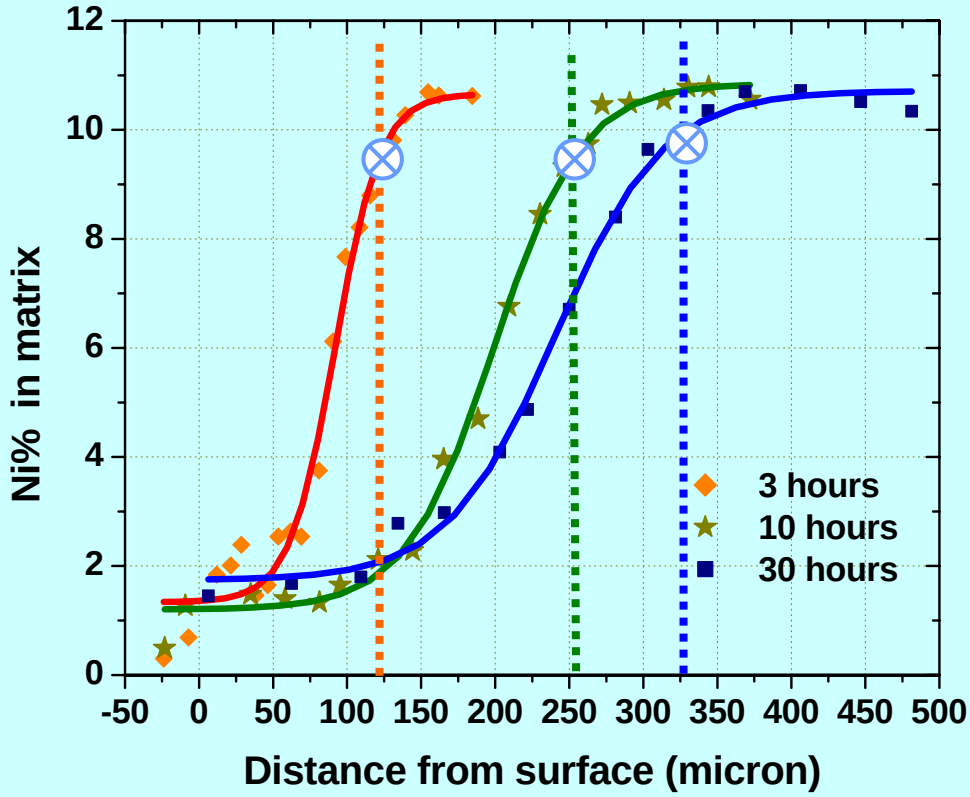
DICTRA simulation results: saturated case



Simulation conditions: β=0.96, $D_B/D_O=10^{-3}$

Concentration Profiles

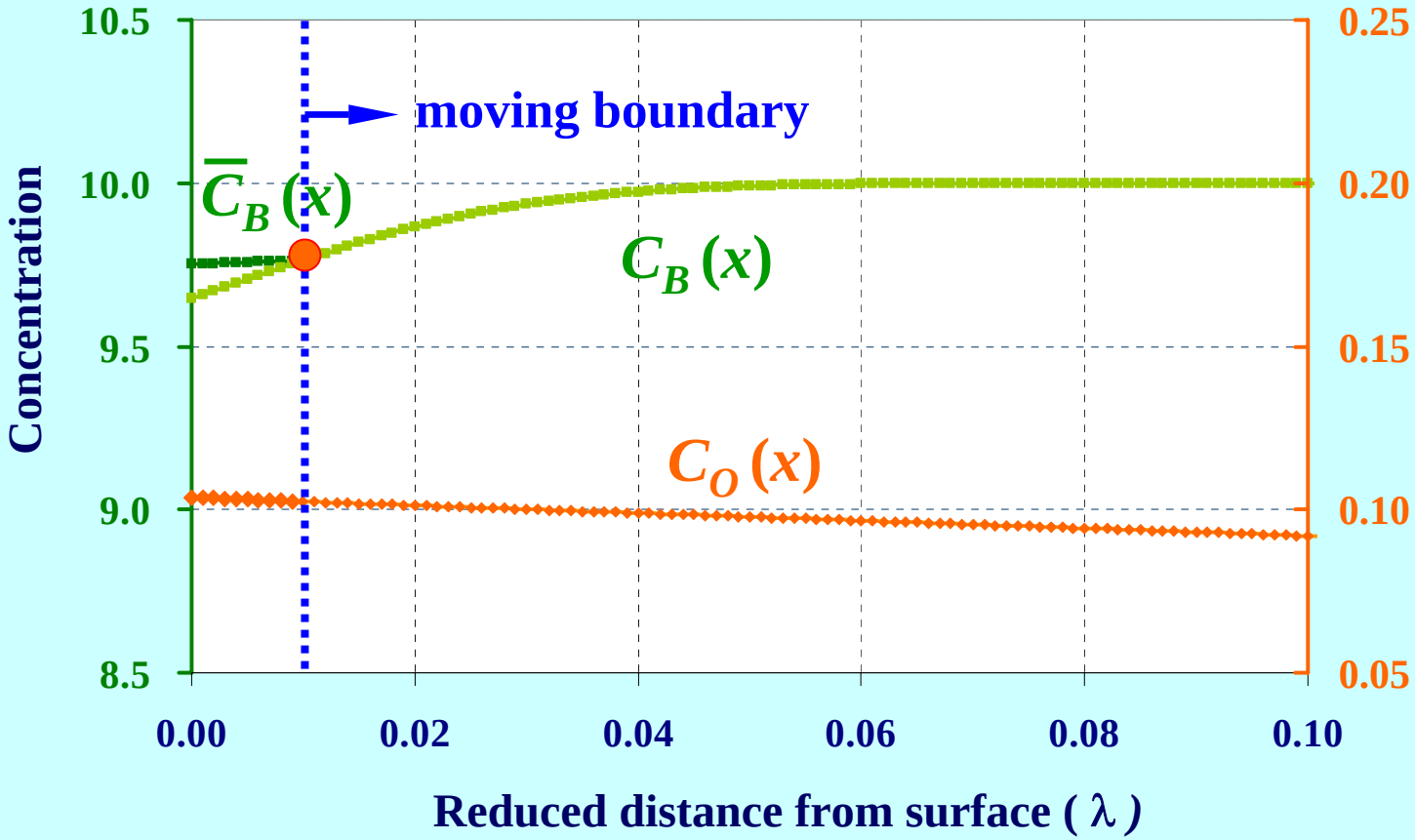
Concentration profiles of Cu-10% Ni alloys oxidized at 950 °C



⊗ **Estimated position of oxidation frontier**

Concentration Profiles

Error Function Model simulation results: unsaturated case



Simulation conditions: β=0.96, $D_B/D_O=10^{-3}$

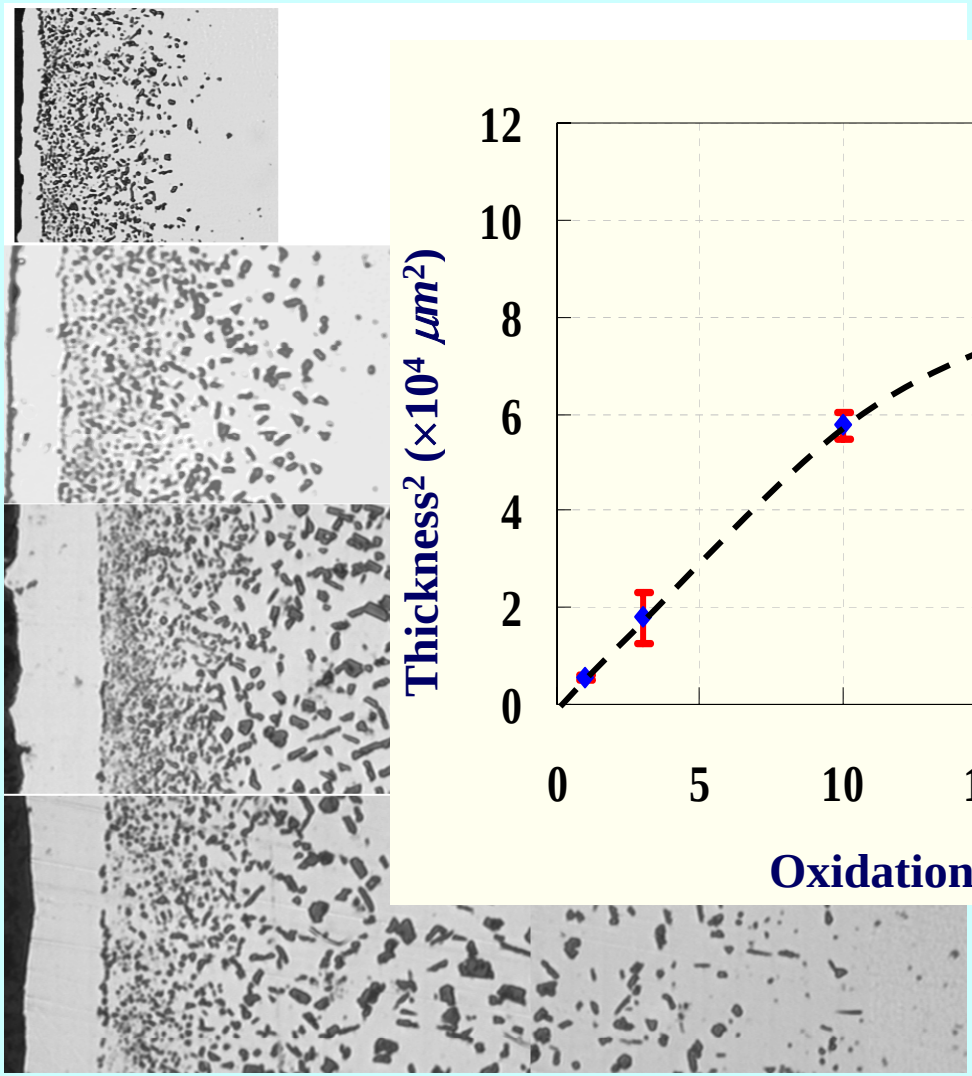
Concentration Profiles

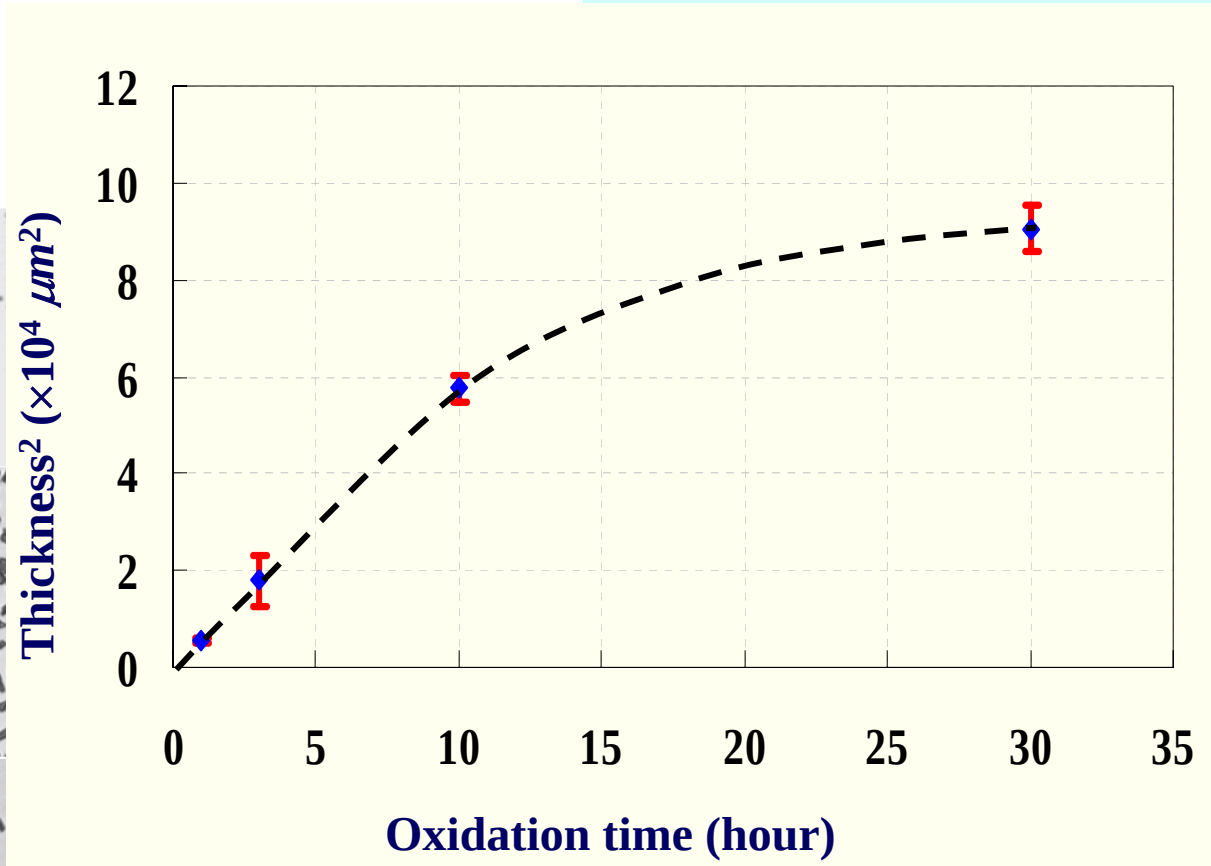
Summary:

- **Concentration profiles in the classic model are in error because they are not supported by experimental results in the literature or in this study and have no theoretic basis.**
- **When K = 0, there is no long-range diffusion of solute B, thus the enrichment phenomena proposed by the classic model doesn't occur.**
- **Near the boundary between oxidized and unoxidized region, matrix solute concentration approaches initial solute concentration rather than zero as assumed by the classic model.**

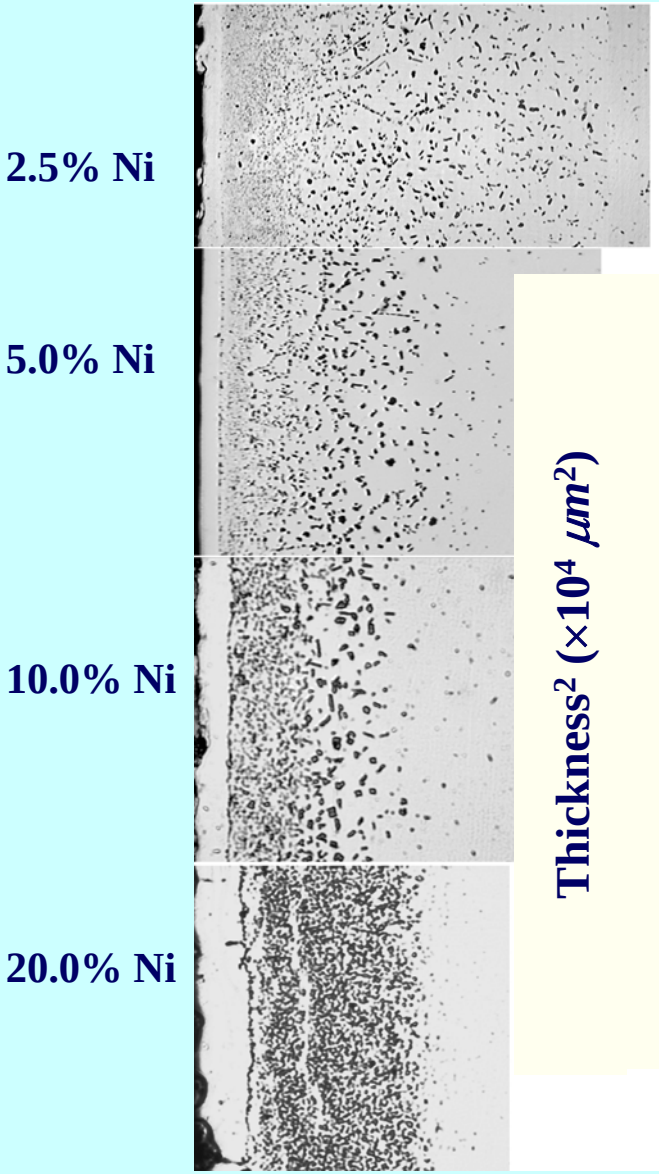
Thickness of Internal Oxidation Region

Cu-10%Ni alloys oxidized at 950 °C



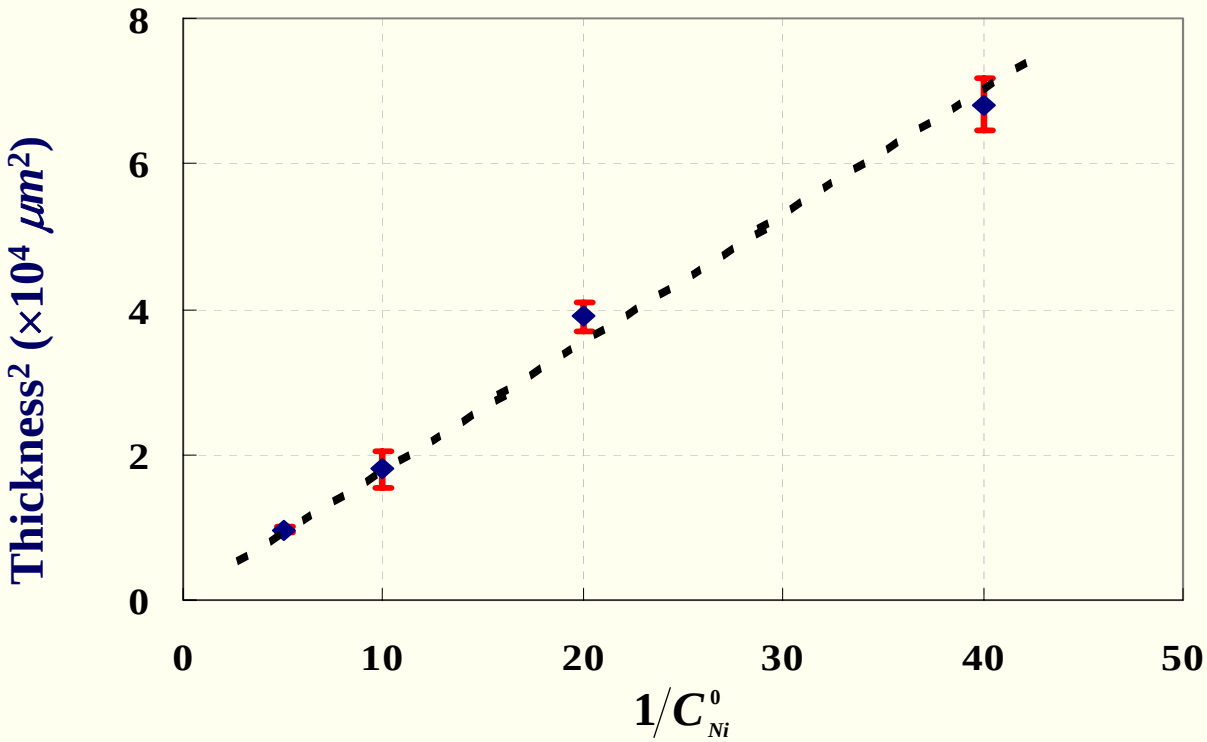


Thickness of Internal Oxidation Region



Cu-Ni alloys oxidized

at 950 °C for 3 hours



Conclusions (1)

For saturated cases:

(a) Because oxide fraction decreased asymptotically to zero, there was no distinct boundary between the oxidized and unoxidized regions.

(b) For $D_O >> D_B$, when oxide fraction approaches zero, matrix solute concentration is close to initial solute concentration.

(c) DICTRA predicted internal oxidation under local equilibrium for $0.03 < \beta < 0.22$ for alloys saturated with oxygen.

Conclusions (2)

For unsaturated cases:

(a) The moving boundary between internal oxidation region and unoxidized region is well defined.

(b) For $D_O >> D_B$, solute concentration in matrix at the moving boundary is close to initial solute concentration.

(c) When $\beta \rightarrow 1$, Error Function Model can be used to model internal oxidation for unsaturated alloys.

Acknowledgements

- Major advisor: Dr. John E. Morral
- Dr. Ronald N. Caron at Olin Corporation
- Dr. Carelyn E. Campbell at NIST
- Dr. Caian Qiu at Ques Tek
- UConn staff: Mary Anton, Fred Massicotte
- All members of UConn diffusion group
- National Science Foundation

Applications

- **Design alloys with improved oxidation resistant**
- **Design intermetallic alloys capable of protective scale formation (e. g. Al_2O_3, Cr_2O_3 and SiO_2)***
- **Synthesize functional ceramic surface structures (e.g. nitride and carbide catalysts Co_3Mo_3N or Co_3Mo_3C) by gas-metal reactions (oxidation, nitridation, carburization, etc.)***

*** M. P. Brady and P.F. Tortorelli, Intermetallics, 12(2004) 779-789**

Approach: Experimental studies

Rhines Pack: Cu (shot) + Cu_2O (powder) in a stainless steel tube

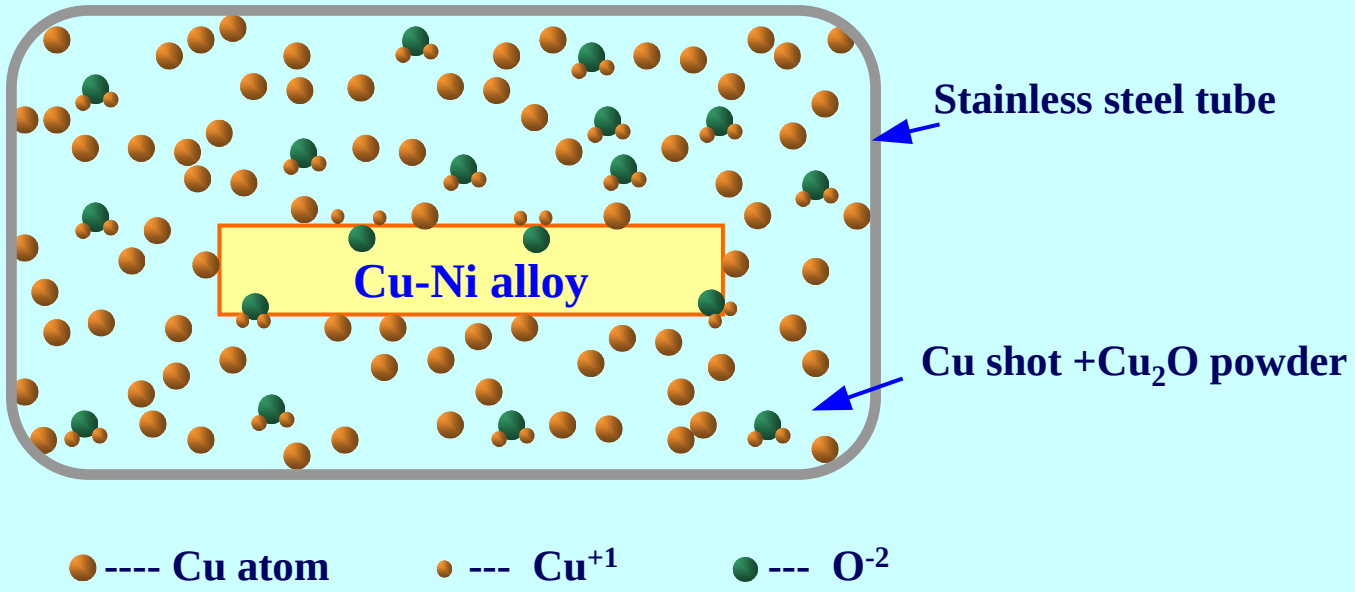
Sample size : 10×10 ×20 (mm)

The tube was welded at the ends in argon atmosphere

Experimental results: Optical microstructures

Two Cu sources for the new Cu layer:

(1) The mixture of Cu and Cu_2O in a Rhines Pack

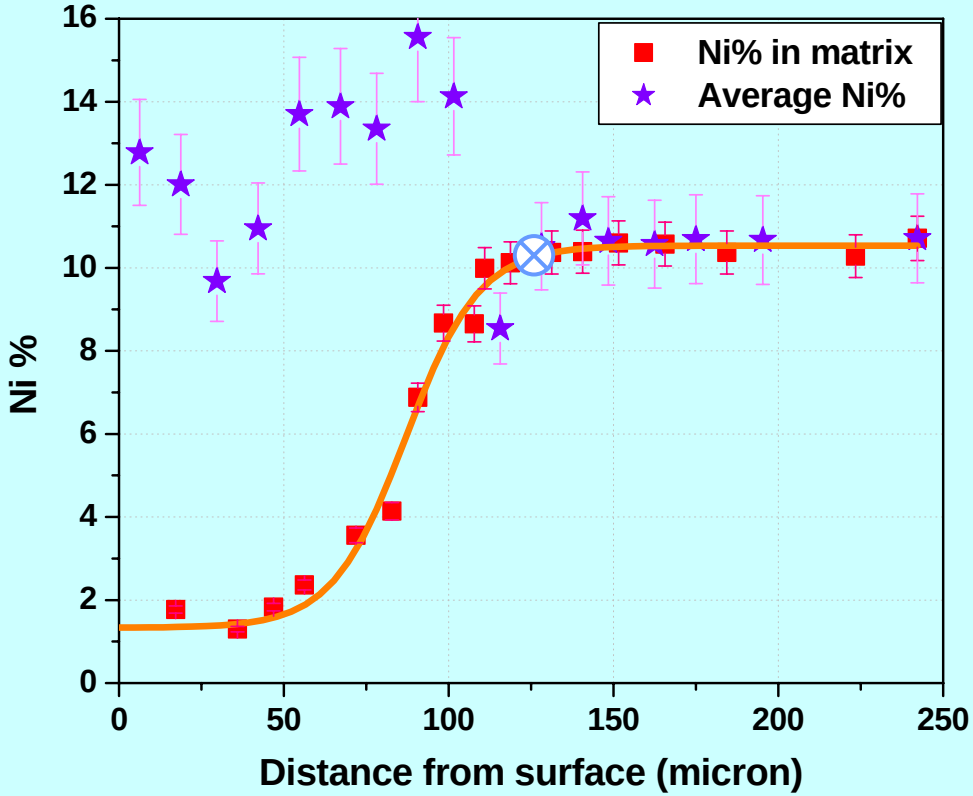


(2) Internally oxidized Cu-Ni alloys

Ni : 6.59 cm^3/mole **NiO: 11.15 cm^3/mole**

Experimental results: EDX

Concentration profiles of Cu-10% Ni alloys oxidized at 950° C



⊗ Estimated position of oxidation frontier

Experimental results: EDX

New Cu layer at the surface:

4500
4000

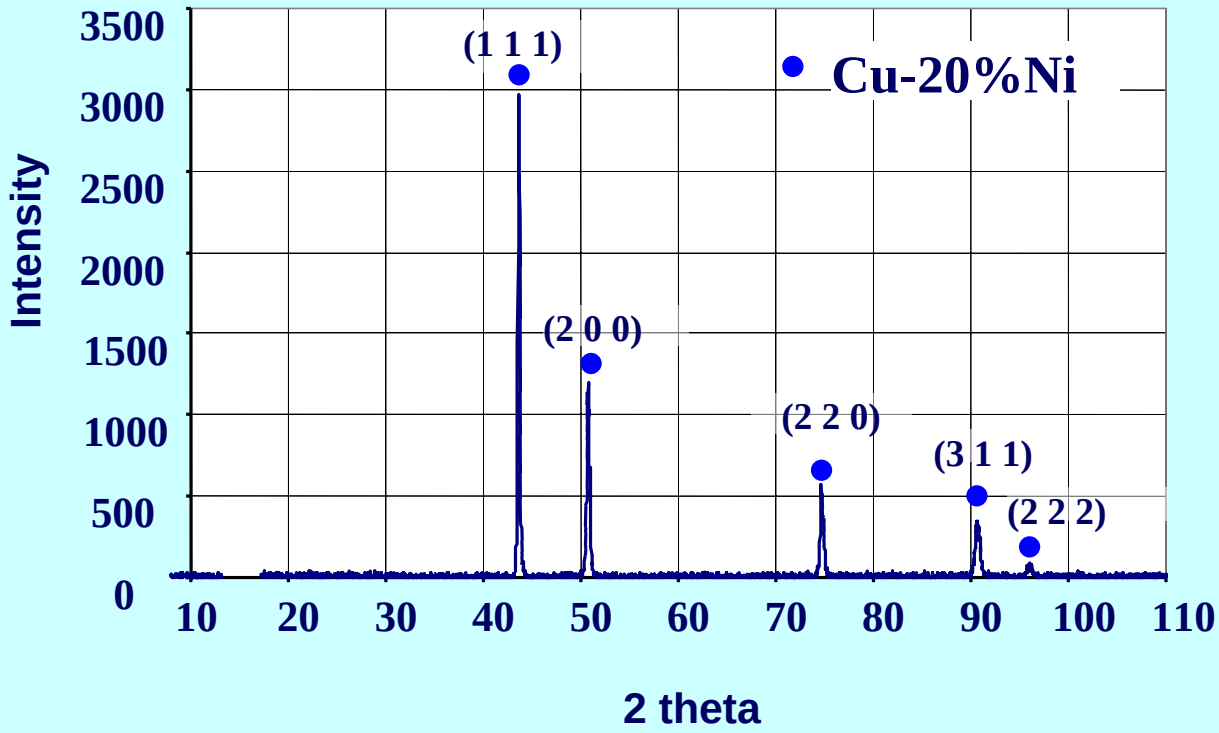
	$K\alpha_1$	$K\beta_1$	$L\alpha_1$	$L\beta_1$
Cu	8.046	8.904	0.93	0.95
Ni	7.477	8.263	0.851	0.863

Quantitative results:

Cu --- 99.69 wt%
Ni --- 0.31 wt%

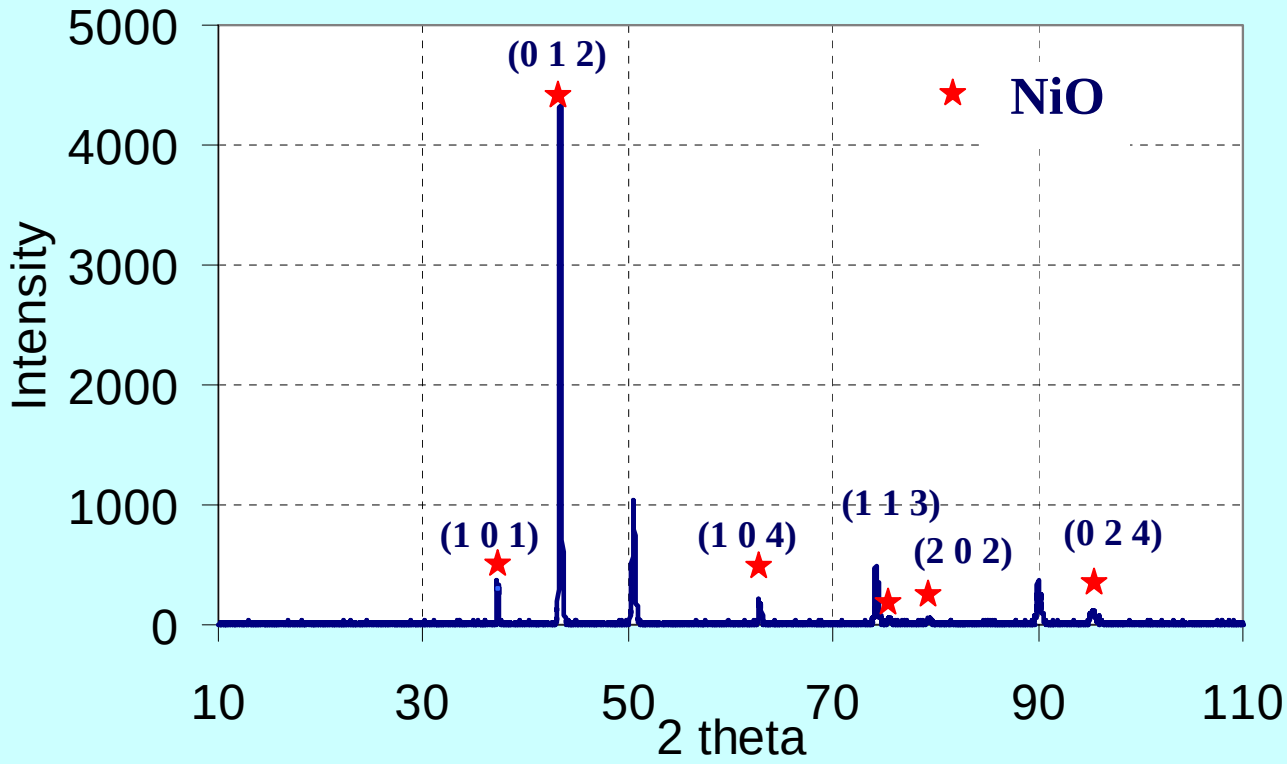
Experimental results: Phase identification (XRD)

XRD patterns of Cu-20%Ni – before oxidation



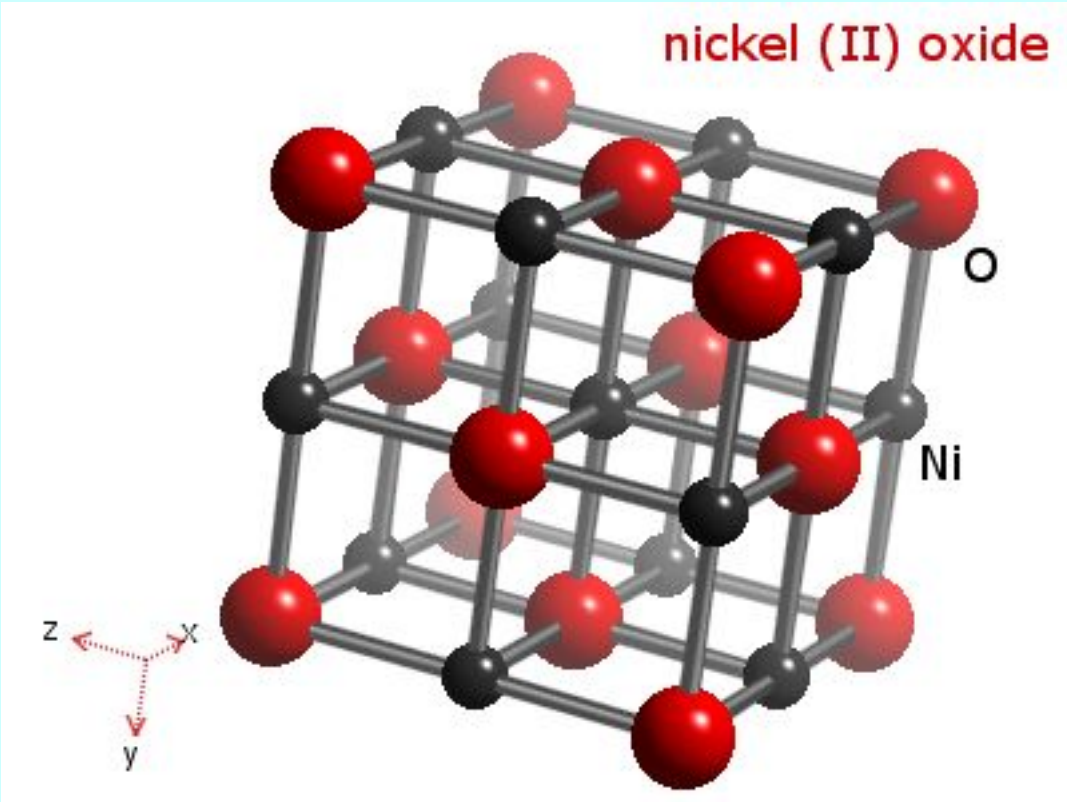
Experimental results: Phase identification (XRD)

XRD patterns of Cu-20%Ni – after oxidation



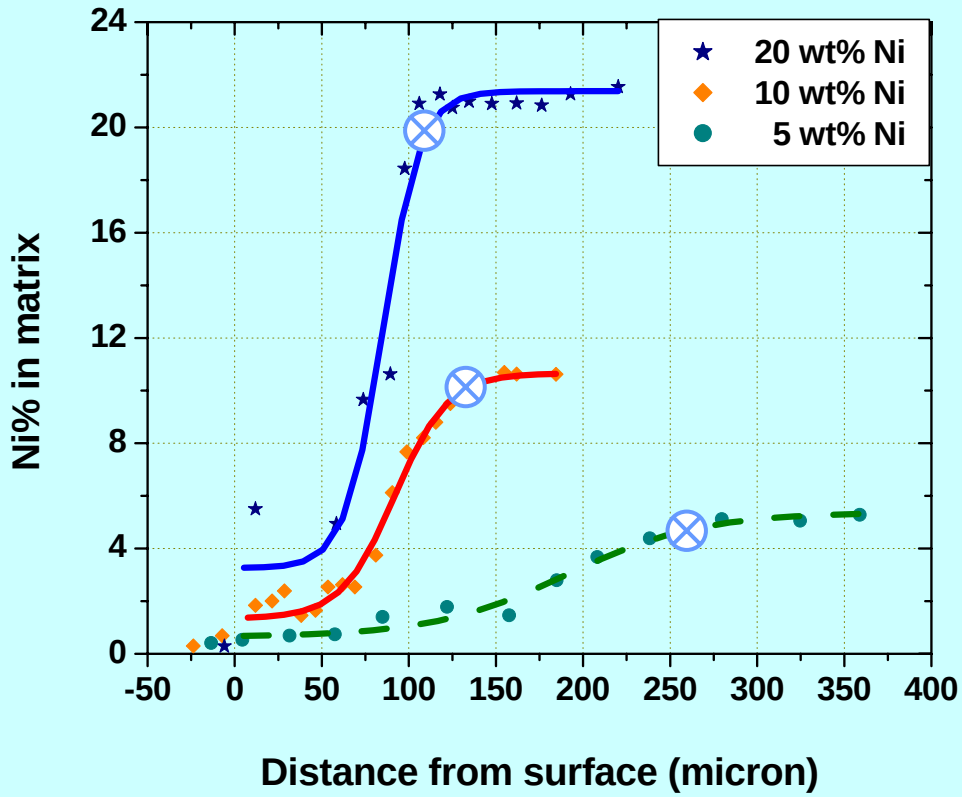
Experimental results: Phase identification (XRD)

NiO crystal structure:



Experimental results: EDX

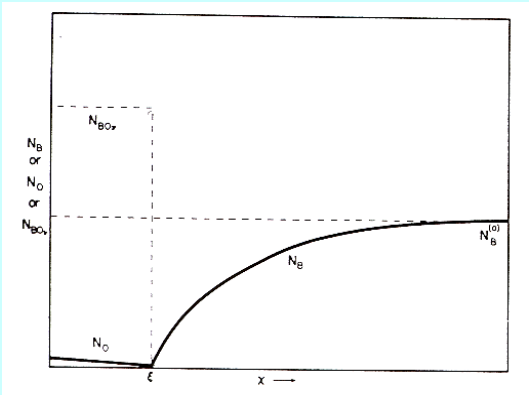
Concentration profiles of Cu-Ni alloys oxidized at 950° C for 3 hours



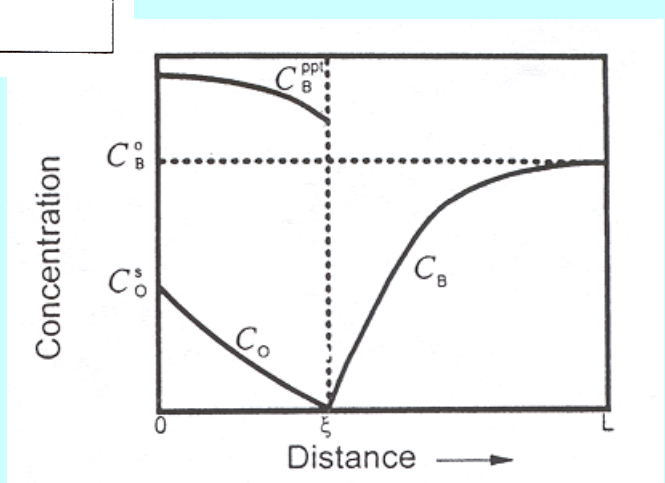
⊗ Estimated position of oxidation frontier

Background: Existing models of internal oxidation

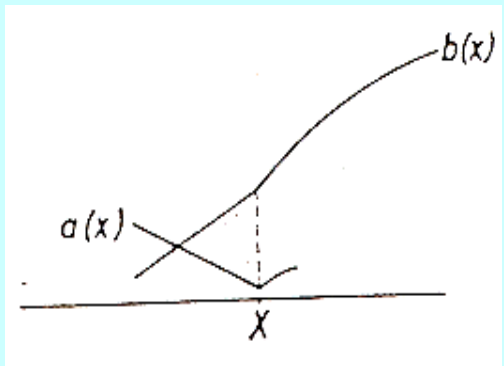
(a)



(b)

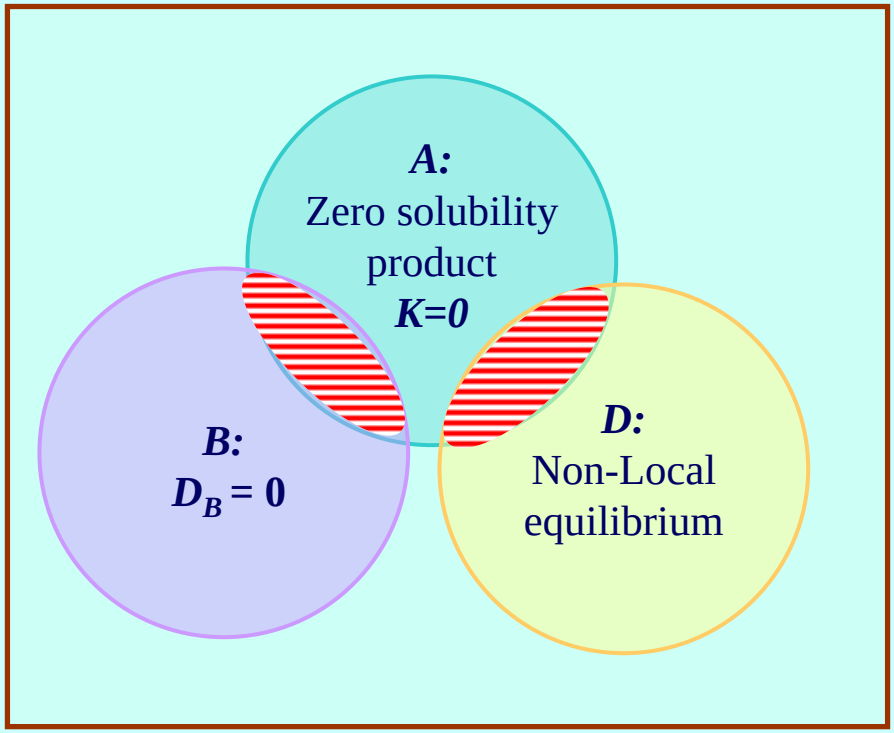


(c)



(a) C. Wagner, Z. Electrochem, 63 (1959) 772.
(b) J. A. Nesbitt, Oxidation of Metals, 44 (1995) 309.
(c) G. Bohm *et al.* Acta Metall.,12 (1964) 641

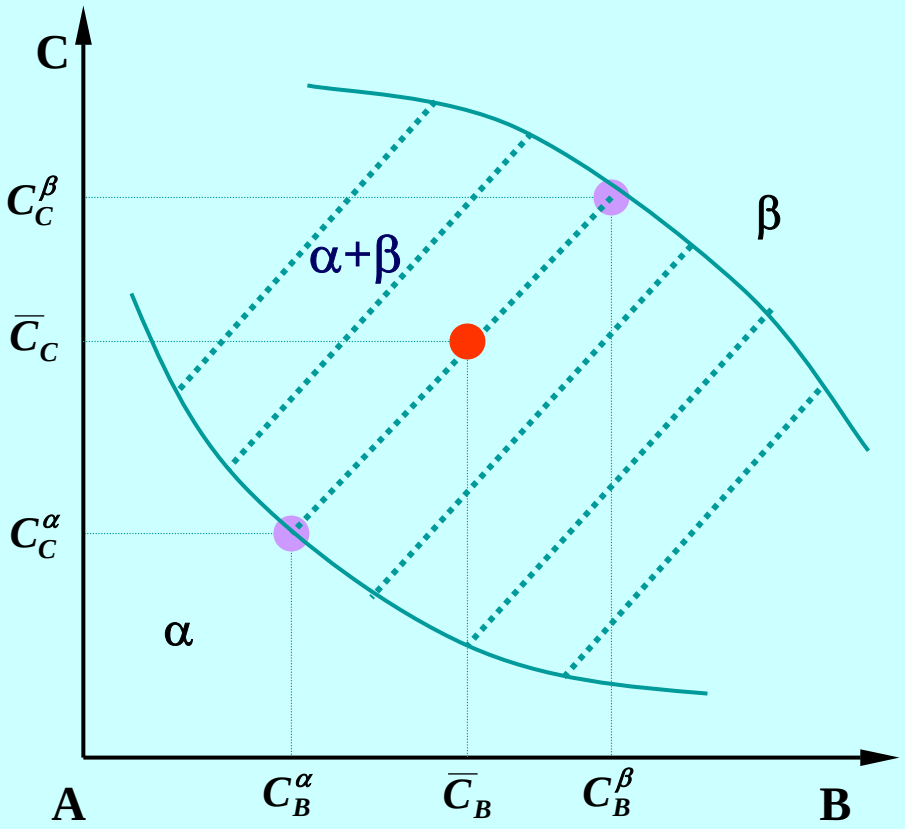
Background: Venn diagram



The classic mode = $(A \cap D) \cup (A \cap B)$

Local equilibrium model = D^C

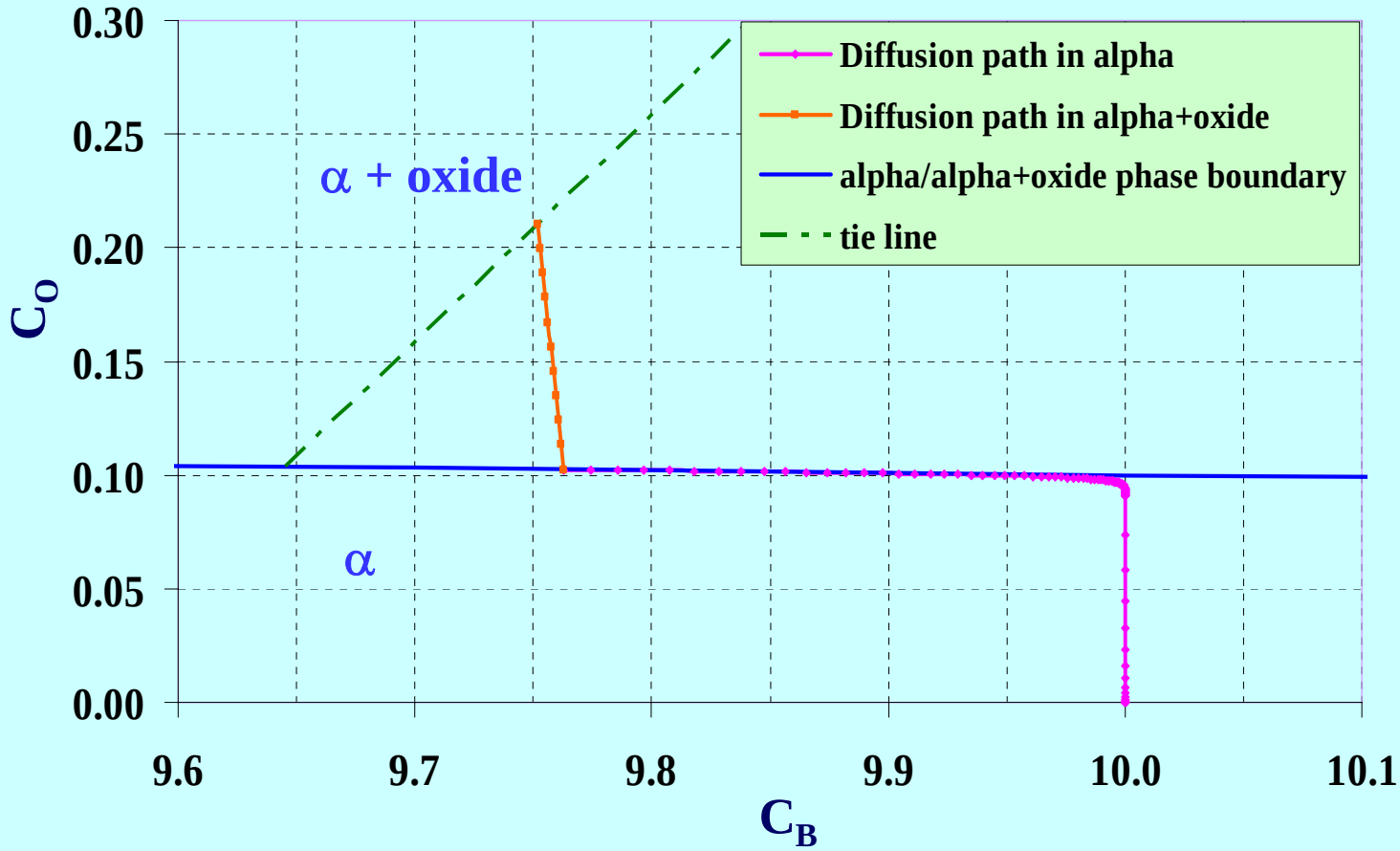
Background: Local equilibrium assumptions



- The compositions and amount of each phase are given by the local average composition, the phase diagram, and the lever rule.
- Nucleation and growth rate of precipitates are so rapid that only long range diffusion need be considered.

Simulation results: EFM

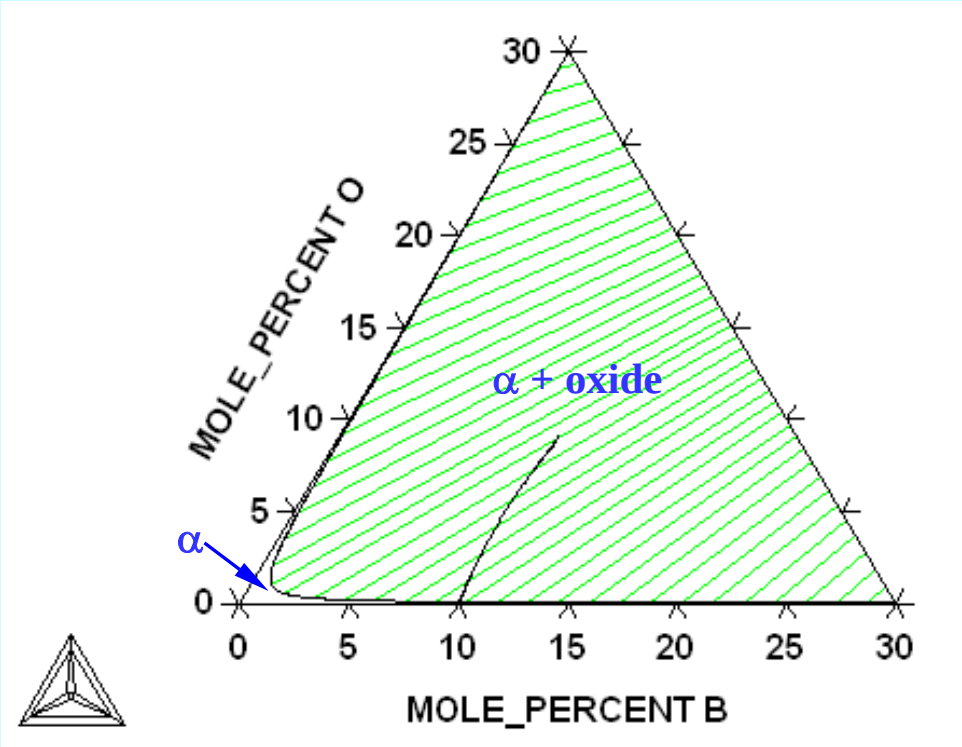
Diffusion paths:



Simulation conditions: $K = 9.6 \times 10^{-5}$, = $^{-}$, = , =

Simulation results: DICTRA

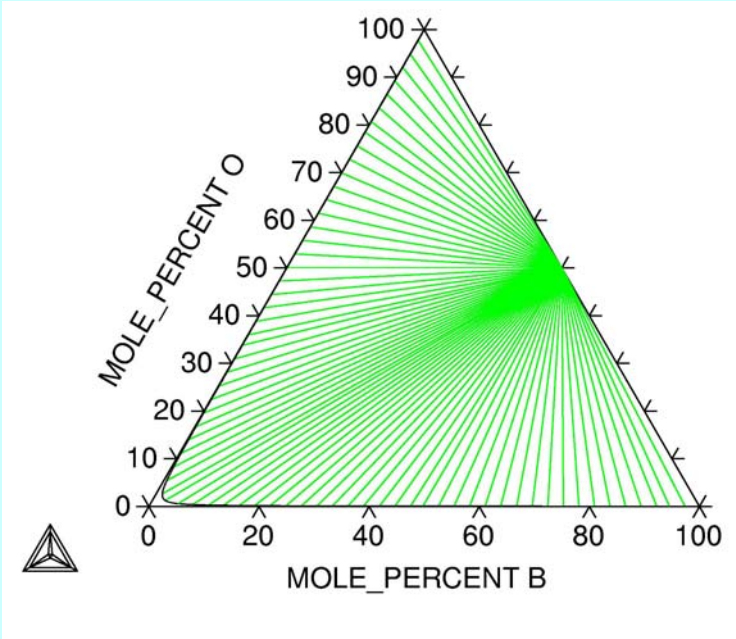
Diffusion path:



Simulation conditions: $K = 9.6 \times 10^{-5}$, = ⁻, = , =

DICTRA simulation

An ideal A-B-O solid solution system

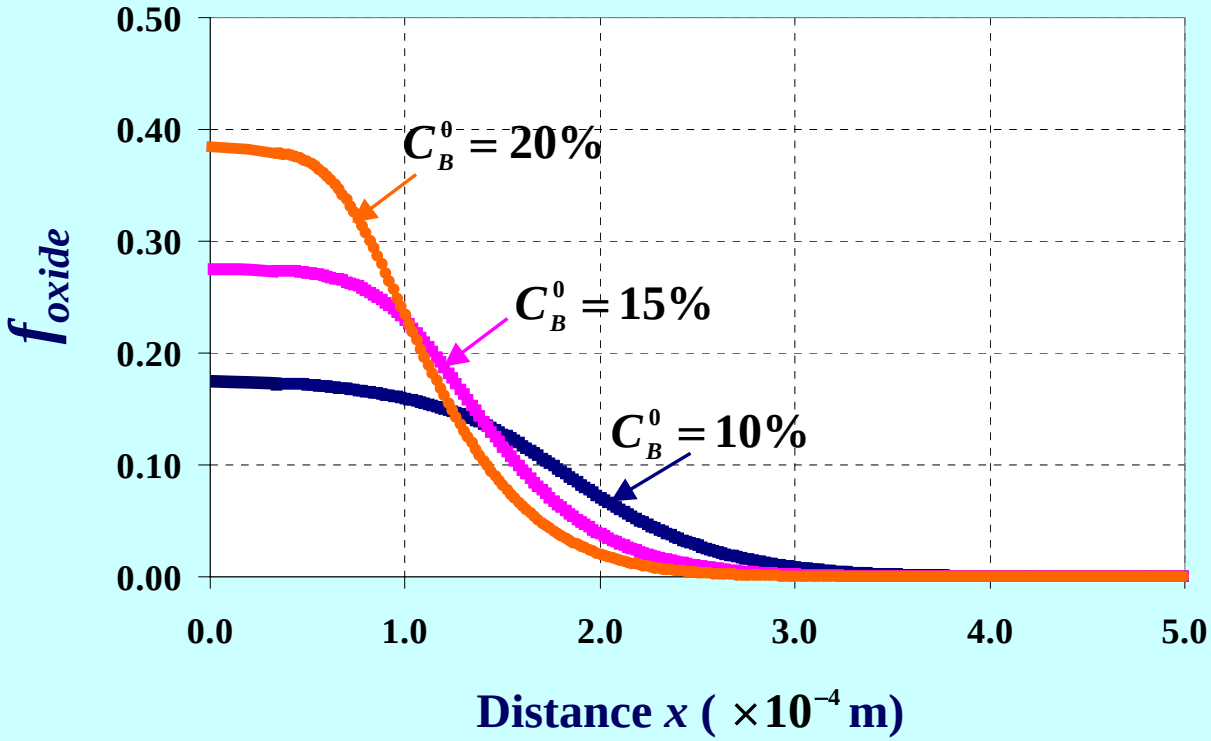


Three elements:
A - solvent
B - solute
O - fast diffuser ($D_O >> D_B$)

Two phases:
- **matrix phase**
- **line compound (BO)**

Simulation results: DICTRA

Effect of C_B^0 on oxide mole fraction:



Simulation conditions: $K = 9.6 \times 10^{-5}$, = ⁻ , =

Simulation results

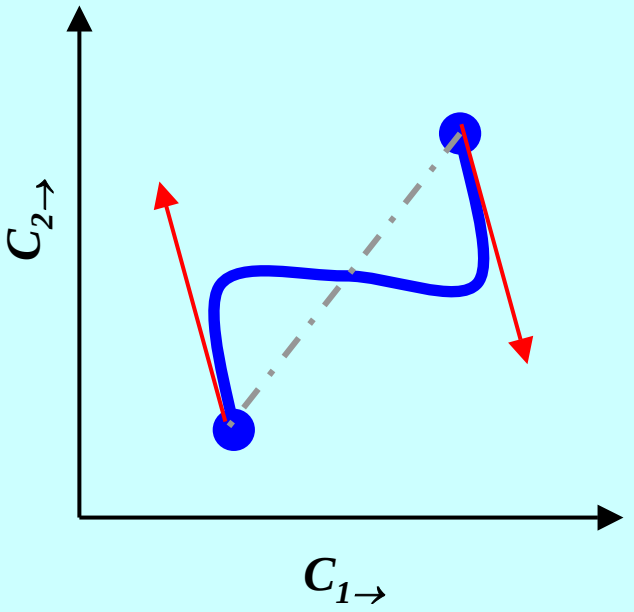
Comparison of EFM and DICTRA

	EFM	DICTRA
Application	Unsaturated case	Saturated case
Boundary conditions	C_o^s = Constant $J_B = -D_B \frac{\partial C_B}{\partial x}$	C_o^s = Constant $J_B = 0$
[D^{eff}]	Constant	Concentration dependent
Phase boundary	Linear	$C_B C_o = K$
β	$\beta \rightarrow 1$	$0.03 < \beta < 0.55$
Local equilibrium conditions	Satisfied	Satisfied

Interesting diffusion paths

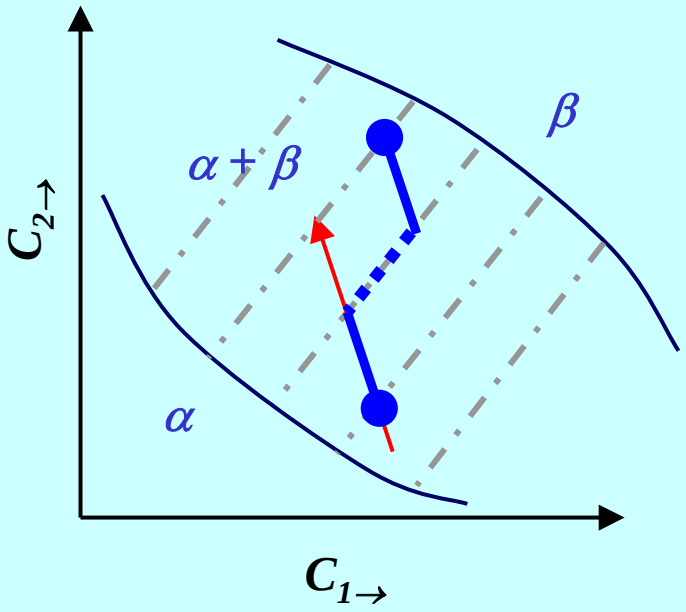
Single-phase region

Serpentine shape



two-phase region

Zigzag shape



$$\begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix}$$

Major eigen vector direction

Gibbs Phase law: $f = c - p + 2$