Theories and Computational Models for Internal Oxidation

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Outline

- **Objective**
- **Definition and Significance of β**
- **Classical Theory (β=0)**
- **Classical vs. Local Equilibrium theory**
- **Local Equilibrium Theory**
  - **β→1**
  - **β =0.5**
- **Conclusions**

Objective:

Simulate the Internal Oxidation behavior between two extremes in the parameter 'β' defined as [1]
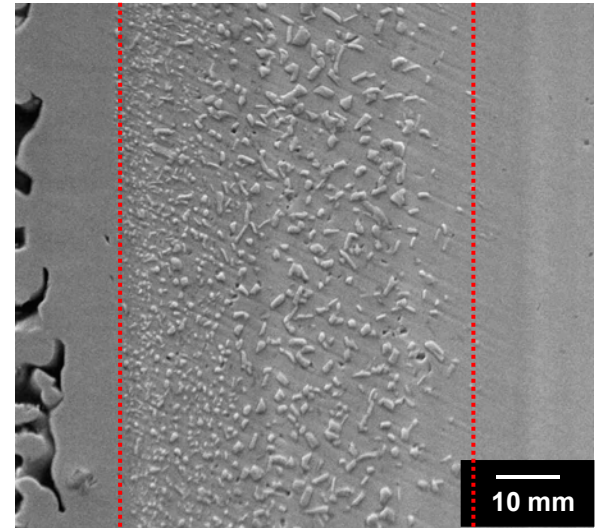
$$\beta = \frac{KS}{C_O^s C_B^o}$$

where,

KS solubility product,

C_O^s concentration of oxygen at surface, and

C_B^o concentration of alloying element in the original alloy

SEM image of Cu-7wt%Ni heated at 950 ºC for 1 hour in Rhines pack.[2]

Oxidized zone

10 mm

Significance of β

- Precipitate distribution can be expressed as a function of two dimensionless parameters for the following conditions [1]
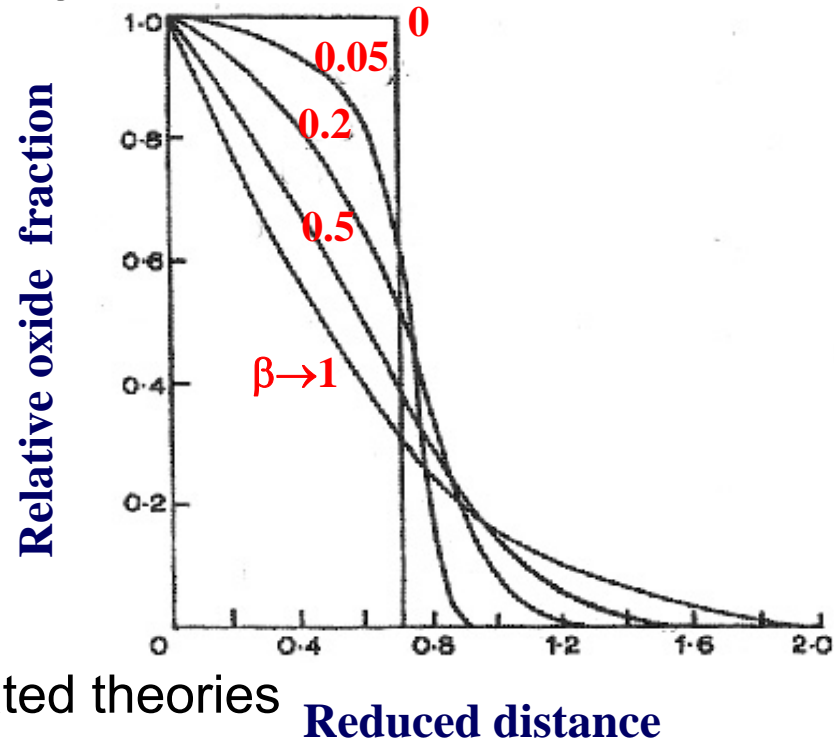 - $D_O \gg D_B$
  - $C_s \ll B^o$

- $R = F(\beta, y)$ [1]
  - Where R is relative oxide fraction
  - β is solubility parameter
  - y is reduced distance
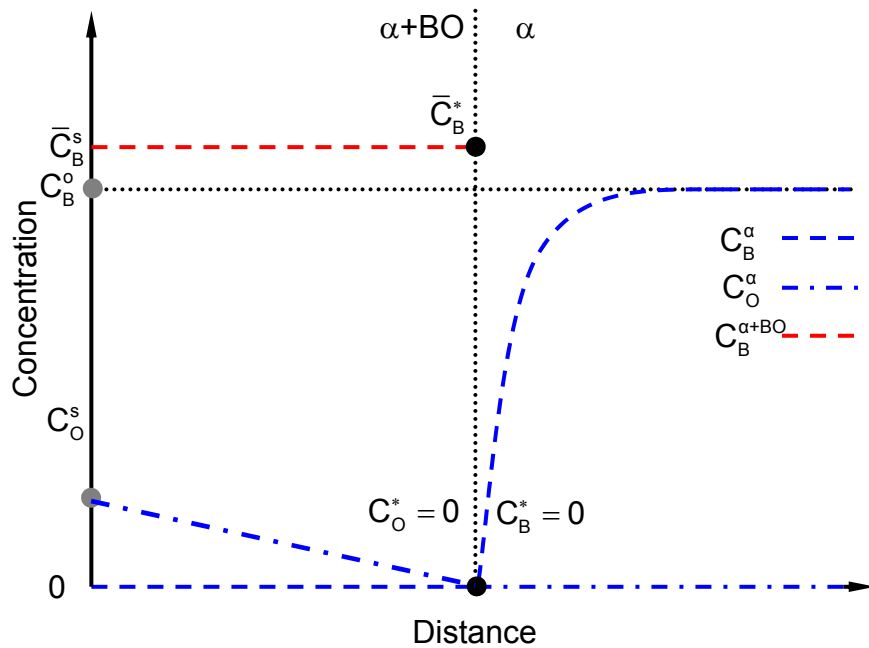
- Limiting Cases of β and accepted related theories
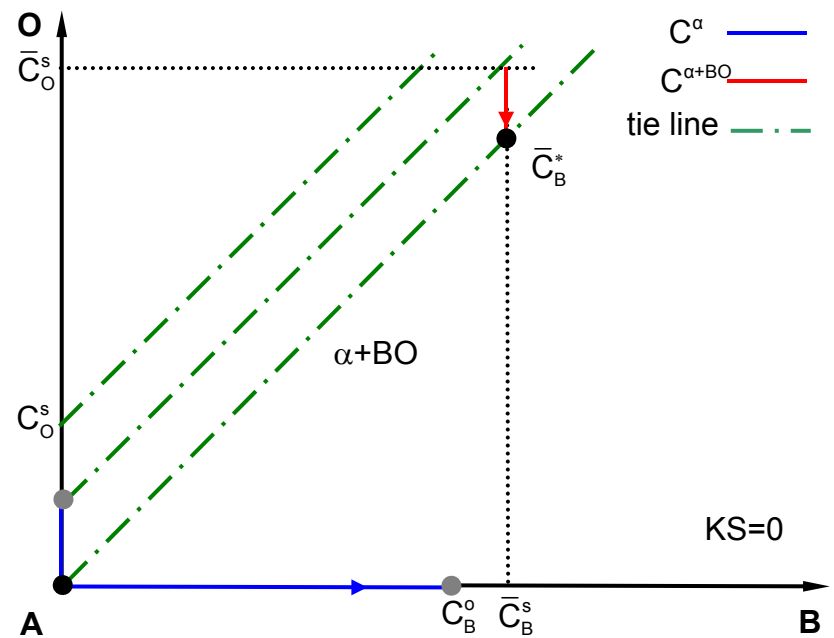 - β = 0   (Classical Theory)
  - β → 1   (Local Equilibrium Theory)

Classical Theory

β = 0 (KS = 0)

Concentration Profile

Diffusion Path

C. Wagner, Z. Electrochem, 63, (1965), p.772

- Diffusion path for KS>0, but approaching zero.
    - Linear in the two-phase region[3,4,5,6]
    - Path in α is tangent to the solvus at the reaction boundary[6]
- No concentration jump at the reaction boundary[6]

- Path is inconsistent with the "classical theory"[7] for when KS = 0
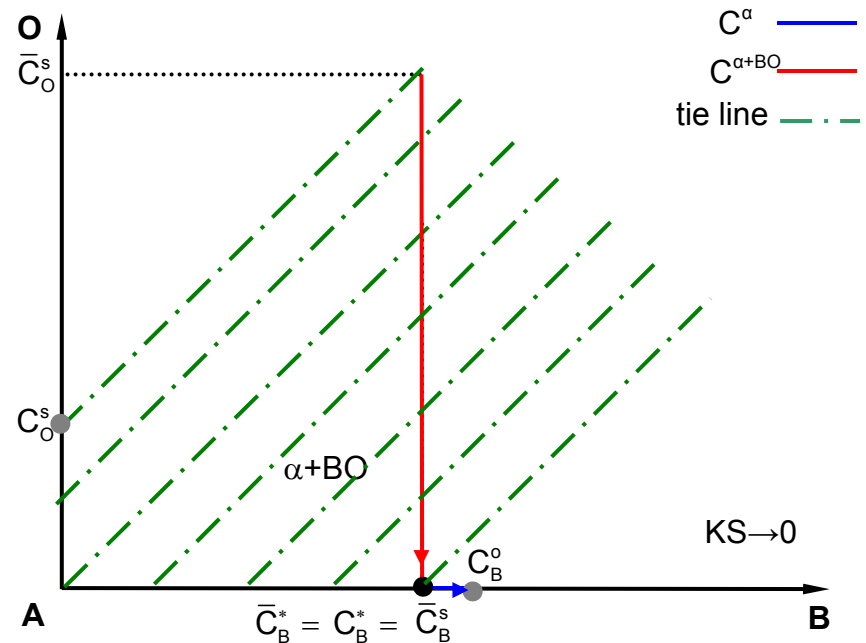
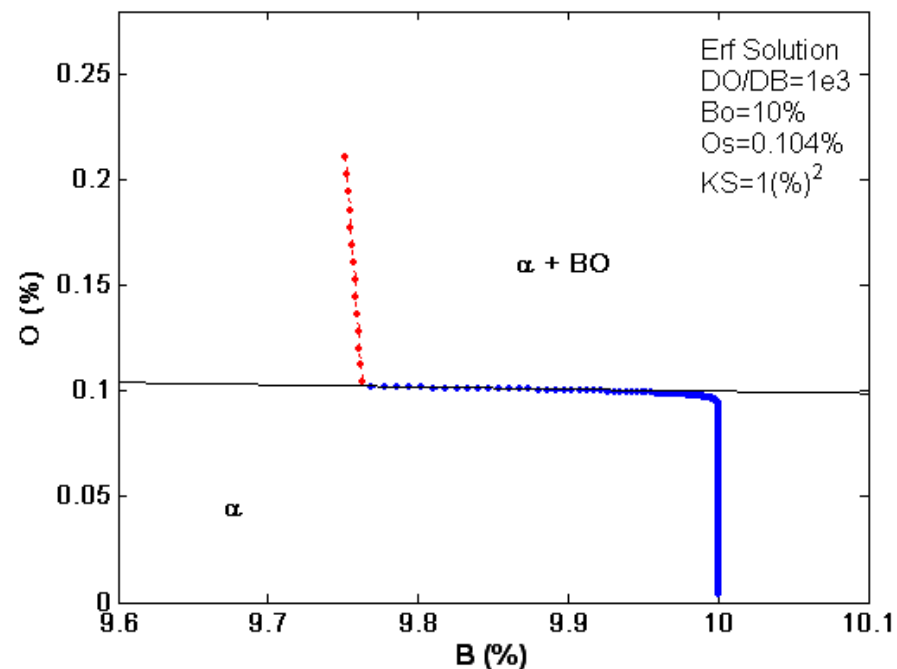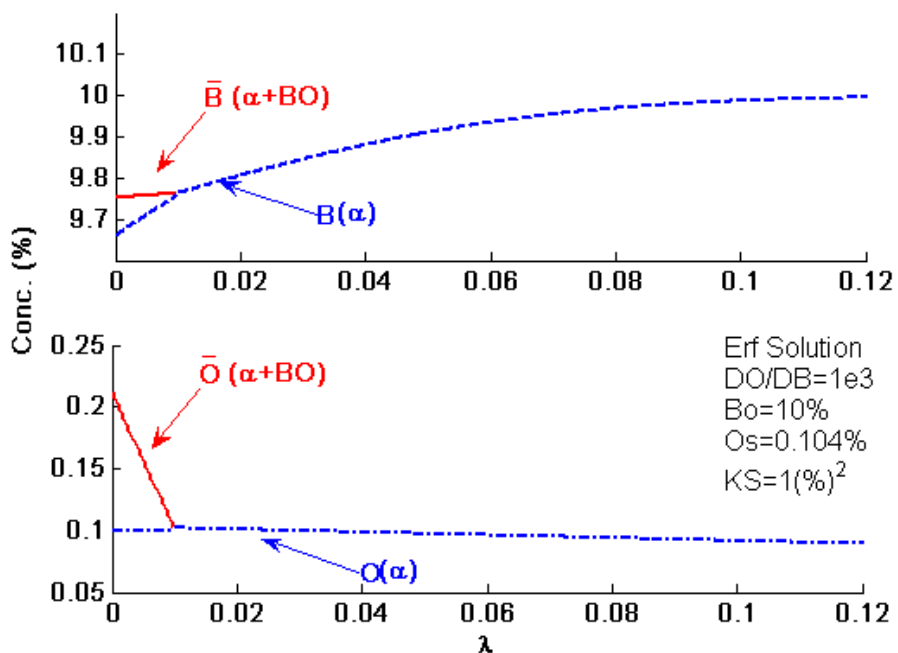# Local Equilibrium Theory (Const. $[D_{eff}]\alpha+BO$)

$$\beta \rightarrow 1 \ (KS \rightarrow C_O^s C_B^o)$$

Concentration Profile

Diffusion Path

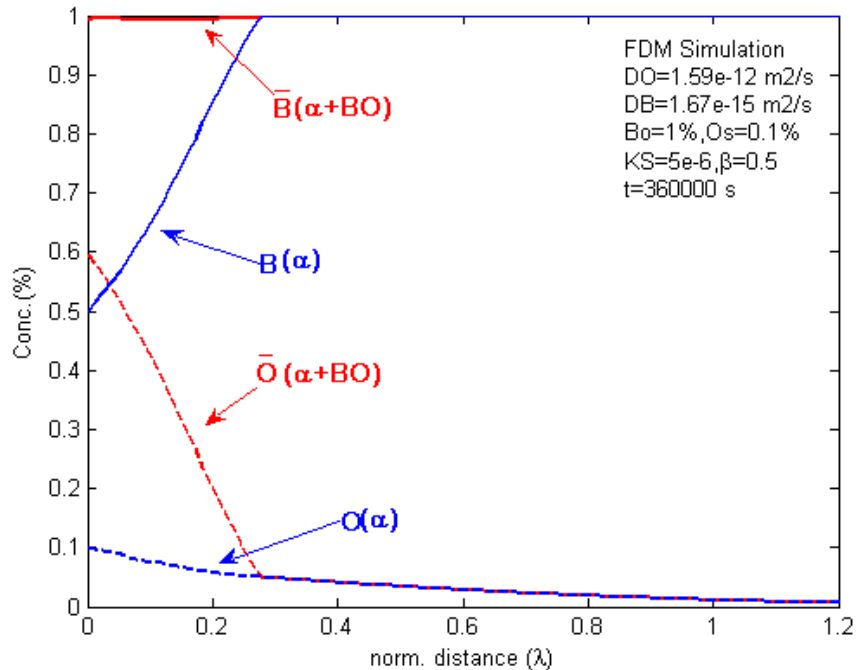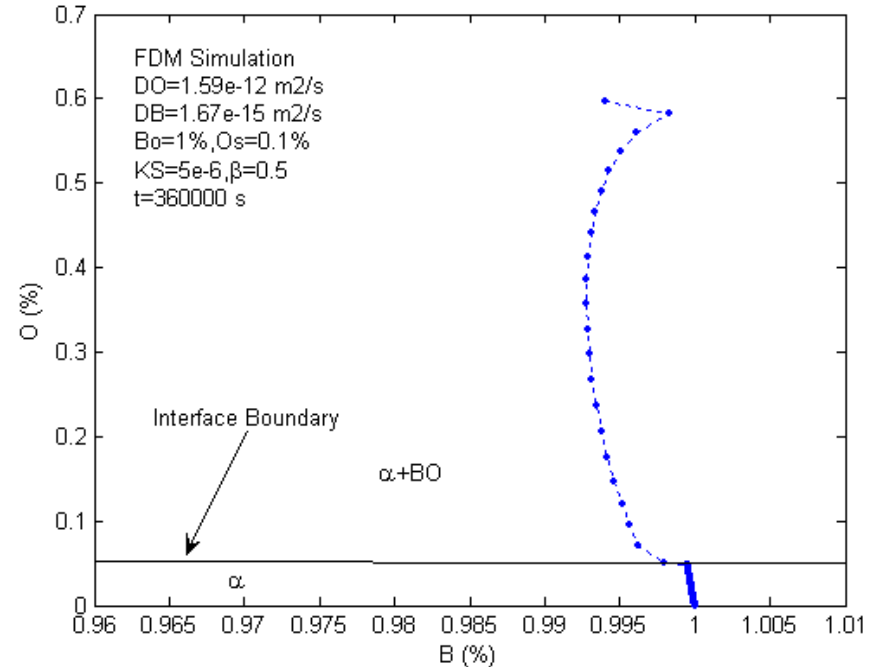*Y. Li, J. E. Morral, Acta Materialia, 50, (2002), p.3683*

Local Equilibrium Theory, Intermediate Case of β

$$\beta = 0.5 \quad (KS = C_O^s C_B^o /2)$$

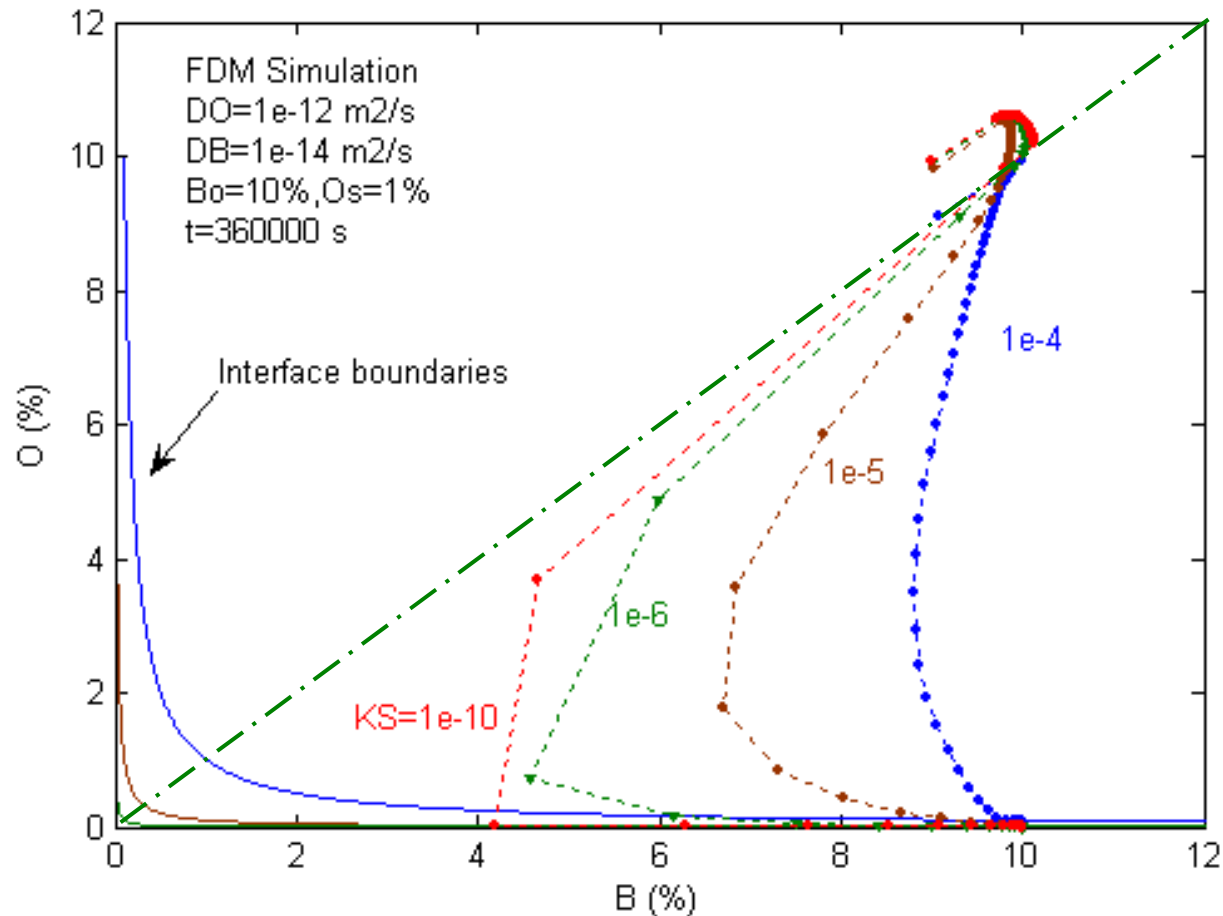**Concentration Profile**   **Diffusion Path**

Finite Difference Simulation
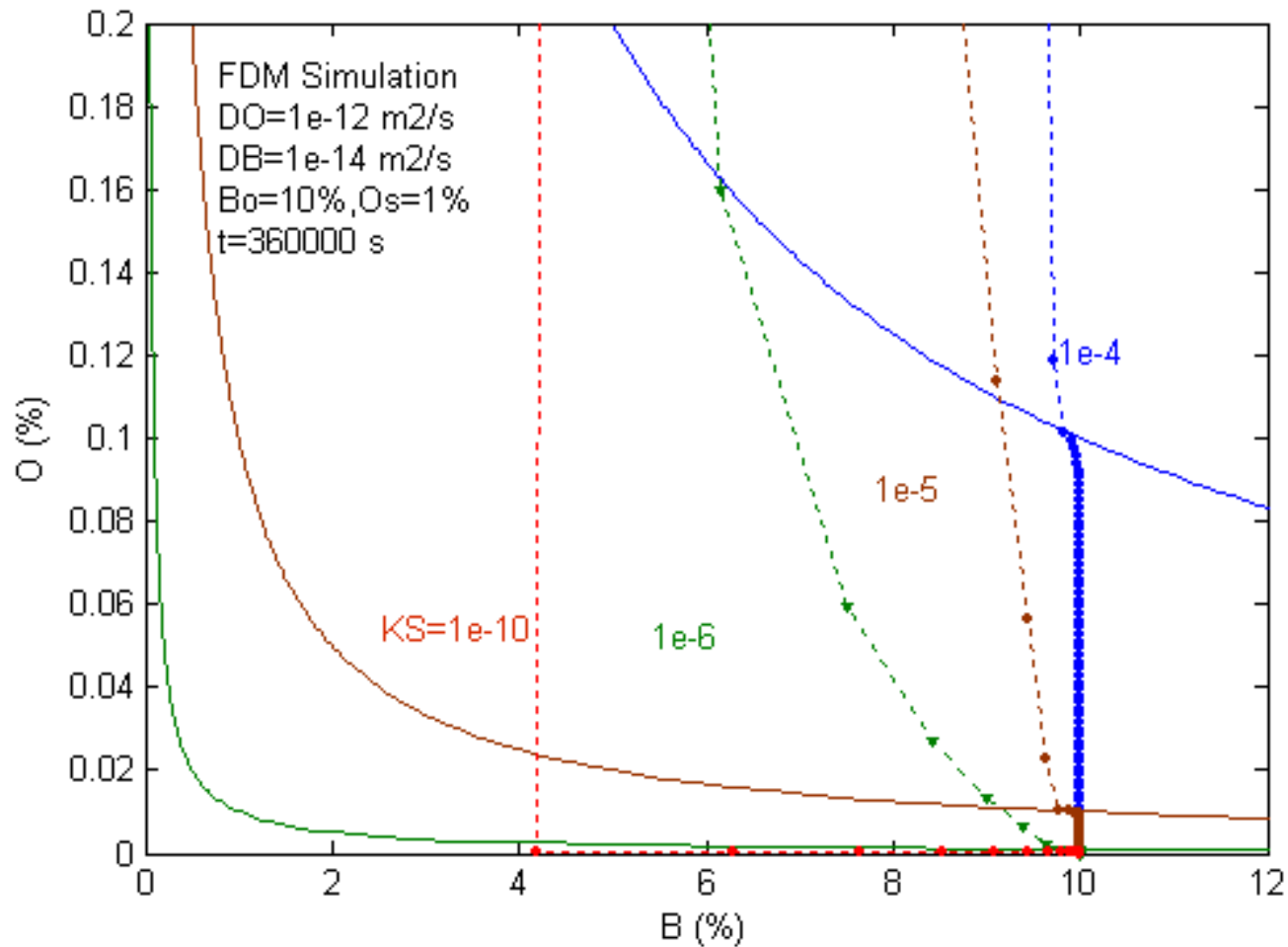
Finite Difference Simulations for Variable KS (β)

- Results
  - The diffusion path bends towards the classical theory diffusion path, but unlike the classical theory the concentration at the reaction boundary remains near the initial alloy concentration in these simulations.
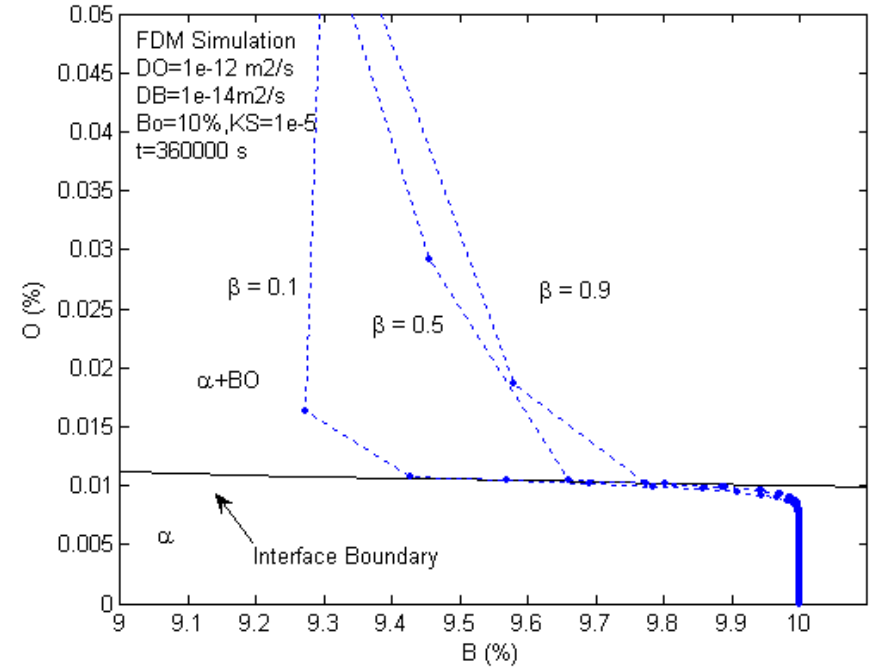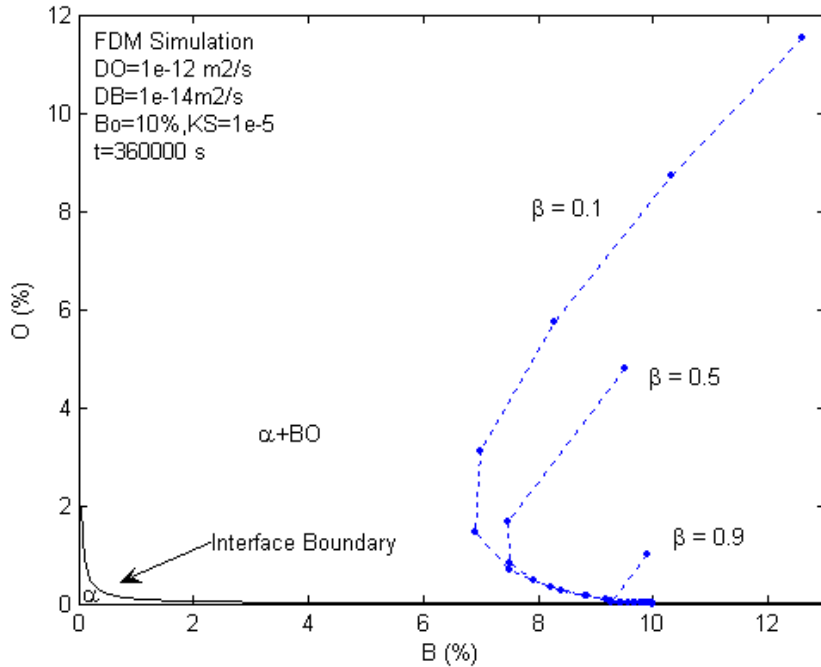

FDM Simulation
DO=1e-12 m2/s
DB=1e-14 m2/s
Bo=10%,Os=1%
t=360000 s

Interface boundaries

1e-4

1e-5

1e-6

KS=1e-10

• Result from the previous slide with expanded %O scale

FDM Simulation
DO=1e-12 m2/s
DB=1e-14 m2/s
Bo=10%,Os=1%
t=360000 s

KS=1e-10   1e-6   1e-5   1e-4

Finite Difference Simulations for Variable C_B^o
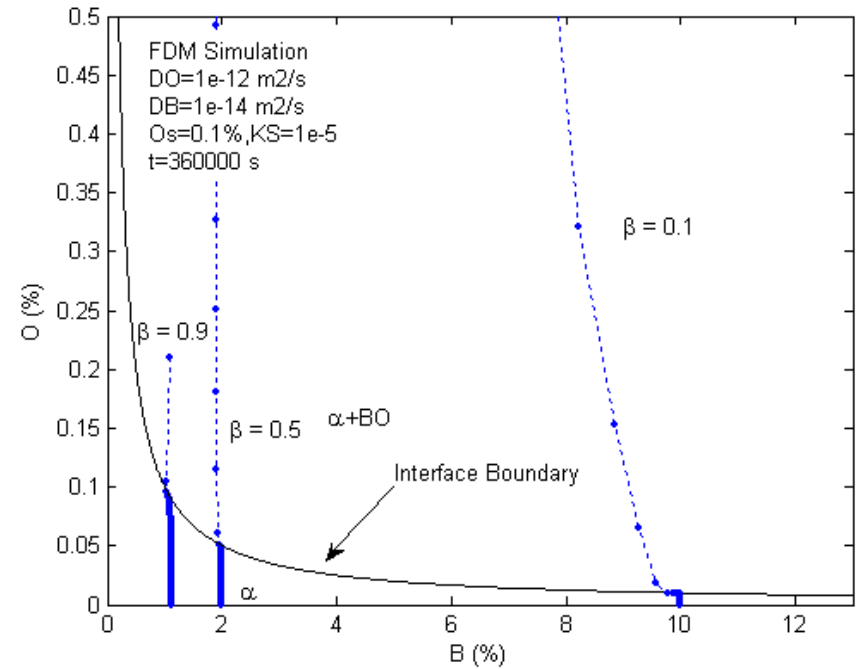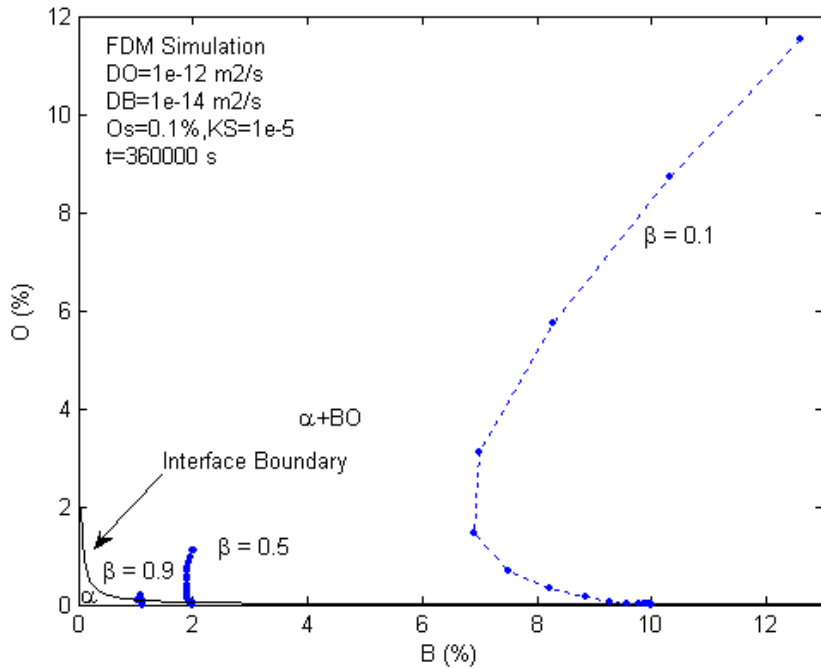
Conclusions

•Local equilibrium theory approaches the classical theory, but never has a discontinuity in concentration at the moving reaction boundary as does the classical theory.

•Concentrations of solute at the reaction boundary were near the initial alloy concentration for values of β down to 10^{-3}.

• It follows that carbides, nitrides, sulfides, and even less stable oxides should not be modeled by assuming that the concentration at the reaction boundary is zero.

•A concentration dependent effective diffusivity is the missing link between the local equilibrium and classical theory of internal oxidation

References:

1) E.K. Ohriner and J.E. Morral Scripta Metall, **13** (1979), p.9

2) Yali Li and J. E. Morral, Acta Mater., **50**, (2002), p.3683

3) P.K.Gupta and A. R. Cooper, Physica, **54**, (1971), p.29

4) W. D. Hopfe and J. E. Morral, Acta Mater., **32**, (1994), p.3887

5) H. Chen and J. E. Morral, Acta Mater., **47** , (1999), p.1175

6) W.J. Boettinger, S.R. Coriell, C.E. Campbell and G.B. McFadden. Acta mater. **48** (2000), p. 481.

7) C. Wagner, Z. Electrochem, **63**, (1965), p.772

Thank You