Internal Displacement Reactions in multi-component Oxides.

S.N.S.Reddy[1], D.Leonard[1,2], L.B.Wiggins[1] and K.T.Jacob[3]

[1] IBM Corporation
Systems & Technology group
Hopewell Junction, NY 12533

[2] Dept. of Materials Science
North Carolina State University
Raleigh, NC 27695

[3] Dept. of Metallurgy
Indian Institute of Science
Bangalore – 5600 12 , India

Introduction:

Internal displacement reactions in multi-component Oxides:

► Redox reaction inside an oxide matrix.

$$\text{A}_{\text{(metal)}} + \text{(B,C,…)O}_{\text{(oxide)}} = \text{“B”}_{\text{(metal)}} + \text{“(A,C,…)O”}_{\text{(oxide)}}$$

(No published studies)

► Internal displacement reaction inside a metal matrix

Nickel matrix: $3\,MoO_2 + 4\,\underline{Cr} = 2\,Cr_2O_3 + 3\,\underline{Mo}$

(Shook, Rapp & Hirth, Met.Trans., v.16A, 1985)

Related internal reactions:

► Internal Oxidation / Reduction in a matrix

- **Metal matrix:** $(A,B) \xrightarrow{\text{oxidation}} A$ (matrix) + BO (ppt)

  (Well known in literature)

- **Oxide matrix :** $(A,B)O \xrightarrow{\text{oxidation}} AO$ (matrix) + B_2O_3 (ppt)

  $(A,C)_2O_3 \xrightarrow{\text{reduction}} A_2O_3$ (matrix) + CO (ppt)

  $(A,C)O \xrightarrow{\text{reduction}} AO$ (matrix) + C (ppt)

H.Schmalzried & M.Backhaus-Riccoult,
Prog.Solid St.Chem., v.22, 1993

Internal displacement reactions:

OXIDE MATRIX :

(a) Oxide "line" compounds of narrow composition width:

$$A + BCO_{m+n} = \text{“}B\text{”} + \text{“}ACO_{m+n}\text{”}$$

[Oxide line Compound ⇒ Ratio, (B:C) = (A:C) = {(A+B):C} = constant]

(b) Oxide solid solutions of wide composition range:

$$x\,A + (B_xC_{1-x})O = x\,\text{“}B\text{”} + \text{“}(A_xC_{1-x})O\text{”}$$

[x ⇒ wide range of values]

……

Common features:

- ► Cation exchange reaction (B → A) and precipitation of B in oxide matrix.
- ► C is "inert" for cation exchange reaction.
- ► No change in Oxide crystal structure.
- ► Concentration gradients in product phases
- ► Oxygen sub-lattice is rigid: $\mathcal{D}_{cation} >> \mathcal{D}_O$

(Oxide is an electronic conductor ⇒ $t_e \approx 1$)

Reactions in an oxide “line” compound

A (metal) + BCO_{m+n} (oxide) = “B” (metal) + “ACO_{m+n}” (oxide)

“line” compound → (A:C) = (B:C) = {(A+B):C} =constant}
→ separate sublattice for (A,B) & C

$$\Delta G^0(\mathbf{CO}_n) << \Delta G^0(\mathbf{AO}_m) < \Delta G^0(\mathbf{BO}_m)$$

$$\Delta G^0(\mathbf{ACO}_{m+n}) < \Delta G^0(\mathbf{BCO}_{m+n})$$

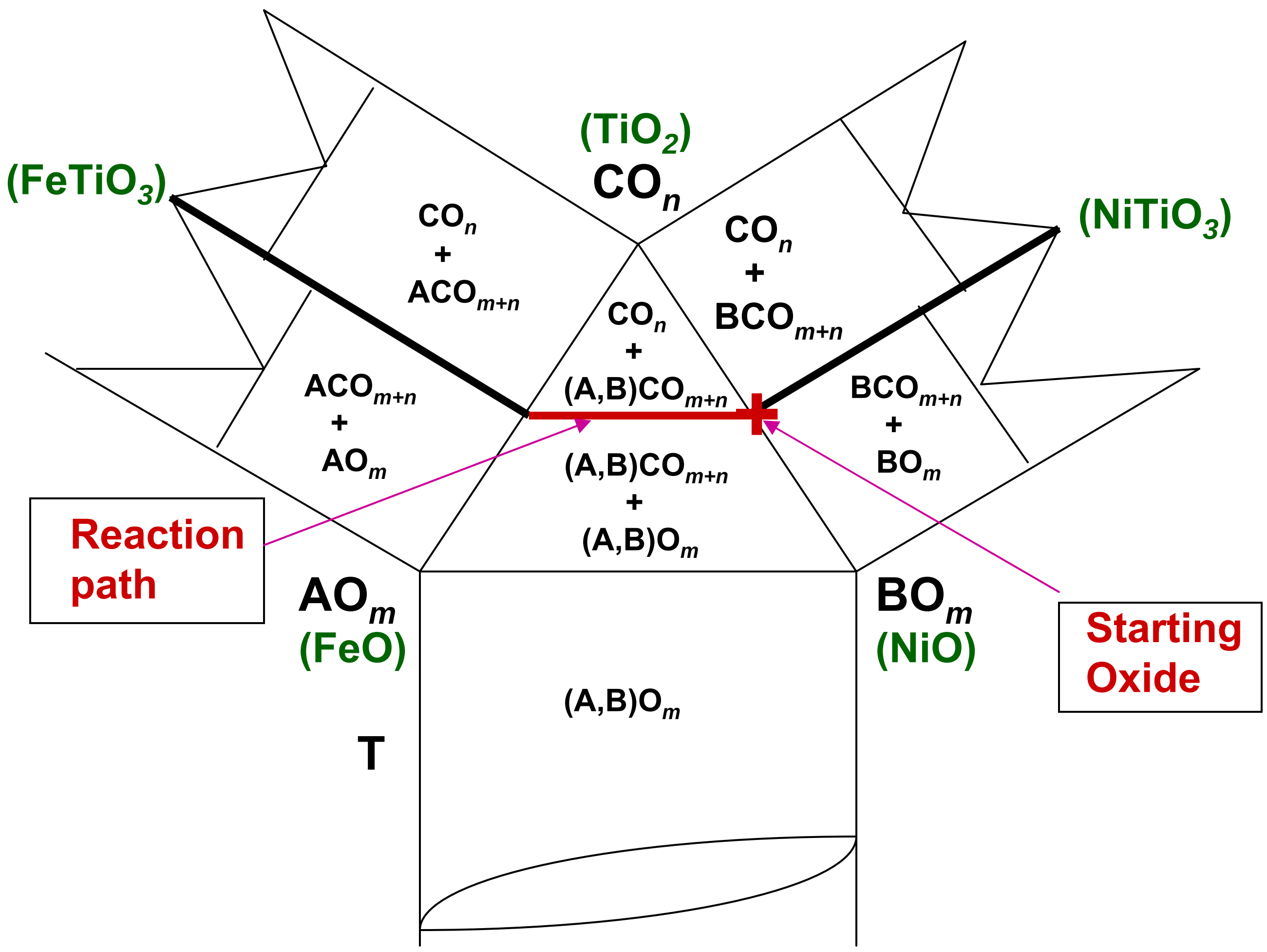


Fig.1. Oxides system for internal displacement reaction between a metal and an oxide “line” compound.

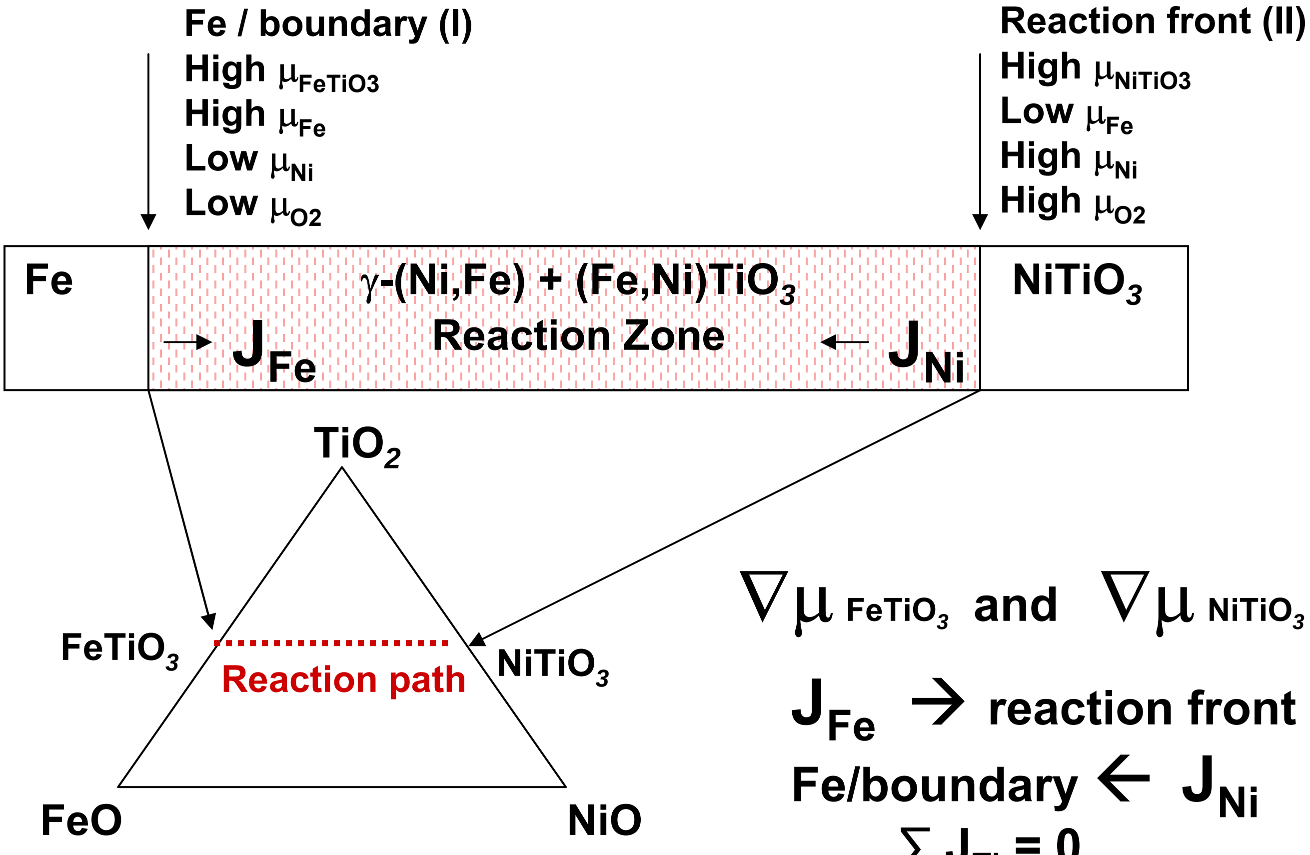
Displacement reaction in ilmenite structure:

$Fe + NiTiO_3 = \text{“}Ni\text{”} + \text{“}FeTiO_3\text{”}$

$\Delta G^0_{1273K} \approx -66$ kJ /mole

OXIDE: **Ilmenite Structure – derivative of Corundum ;**
Alternating sheets of Ni^{2+}/Fe^{2+} and Ti^{4+}
(two seperate cation sublattice)
$(Ni,Fe)TiO_3$ Solid Solution; Ratio, (Ni+Fe):Ti = 1:1

(Point defects & Diffusion in Ilmenite at reaction T: No data)



Fe / boundary (I)
High μ_{FeTiO3}
High μ_{Fe}
Low μ_{Ni}
Low μ_{O2}

Reaction front (II)
High μ_{NiTiO3}
Low μ_{Fe}
High μ_{Ni}
High μ_{O2}

$\nabla\mu_{FeTiO_3}$ and $\nabla\mu_{NiTiO_3}$

$J_{Fe} \rightarrow$ reaction front

Fe/boundary $\leftarrow J_{Ni}$

$\sum J_{Ti} = 0$

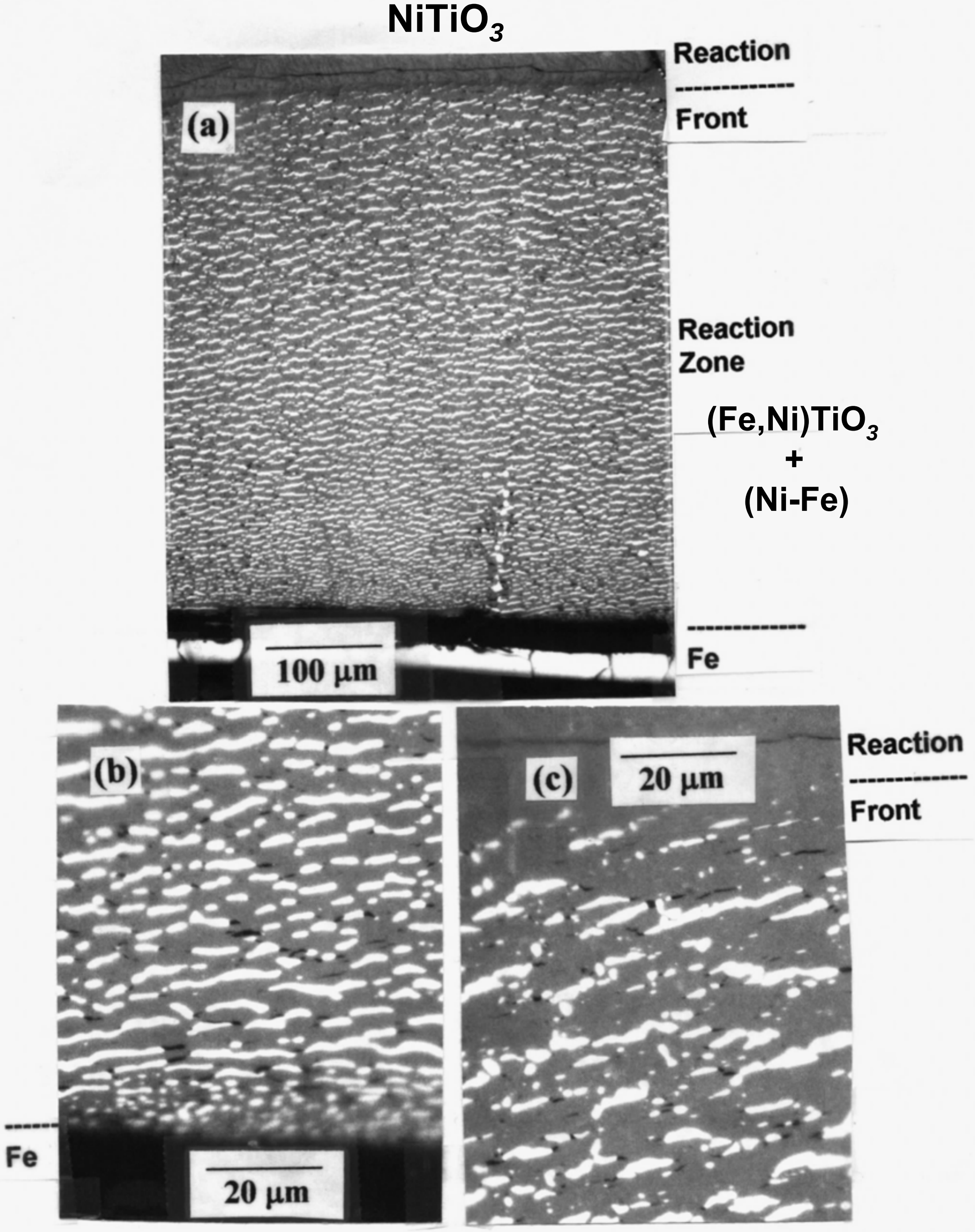


Fig.8. Reaction between Fe and single crystal NiTiO$_3$ at 1273 K and 25 hours; bright phase: γ-(Ni,Fe)alloy; gray phase: (Fe,Ni)TiO$_3$; dark spots: porosity. (a) complete reaction zone; (b) region near Fe / boundary; (c) region near reaction front.

Periodic precipitation of γ – (Ni,Fe) alloy ;

Liesegang phenomenon $\{(x_n+\Delta x_n)/x_n = x_{n+1}/x_n = k\}$?

⇒ Linear increase of spacing with band number ?

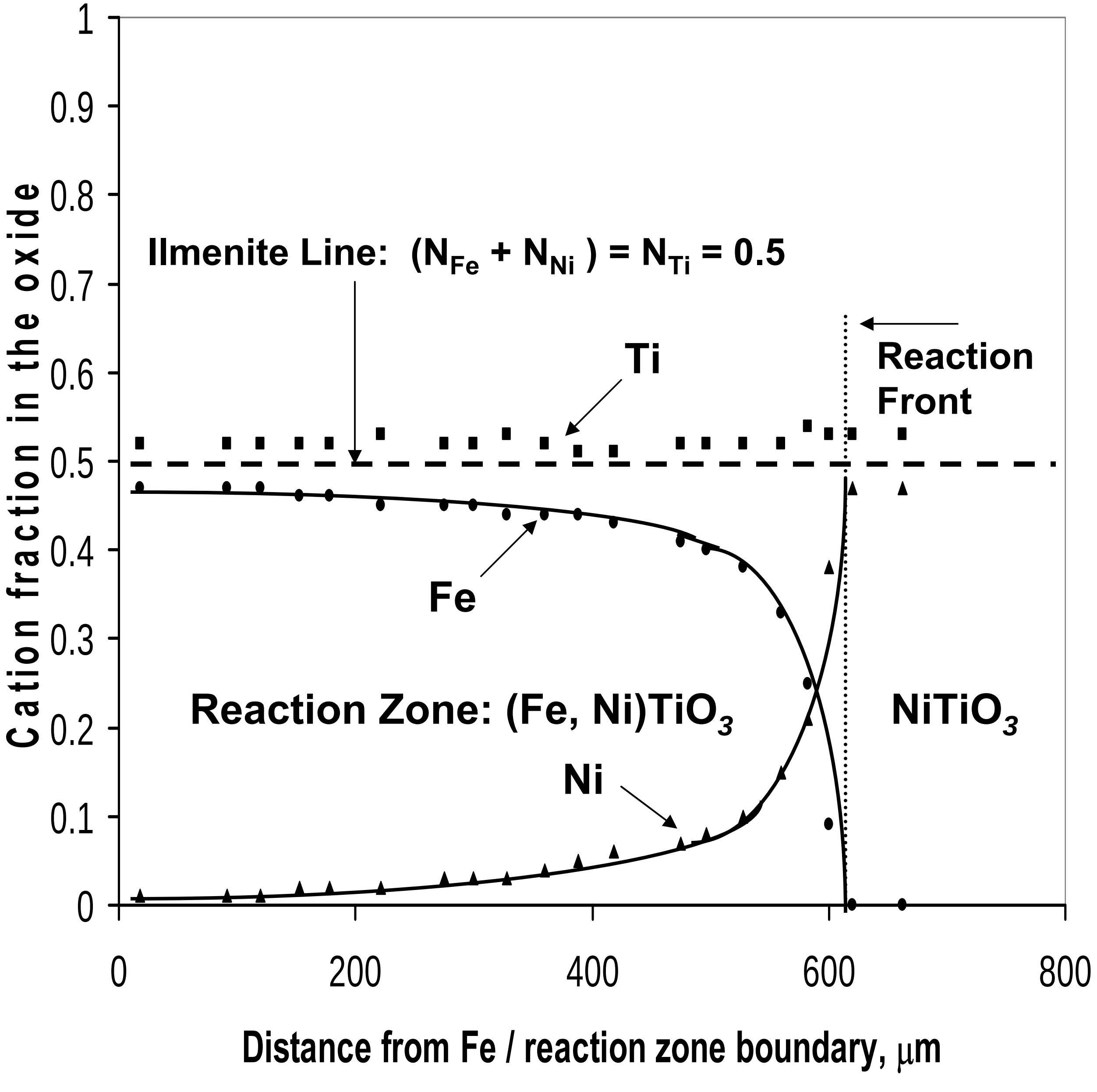


Fig.10. EPMA analysis of Oxide Composition in the product zone for the reaction between Fe and single crystal $NiTiO_3$ at 1273 K ; time = 49 hrs.(Note: EPMA points deviate from ilmenite composition by about 6% --due to machine calibration; the lines are drawn for eye recognition purpose only)

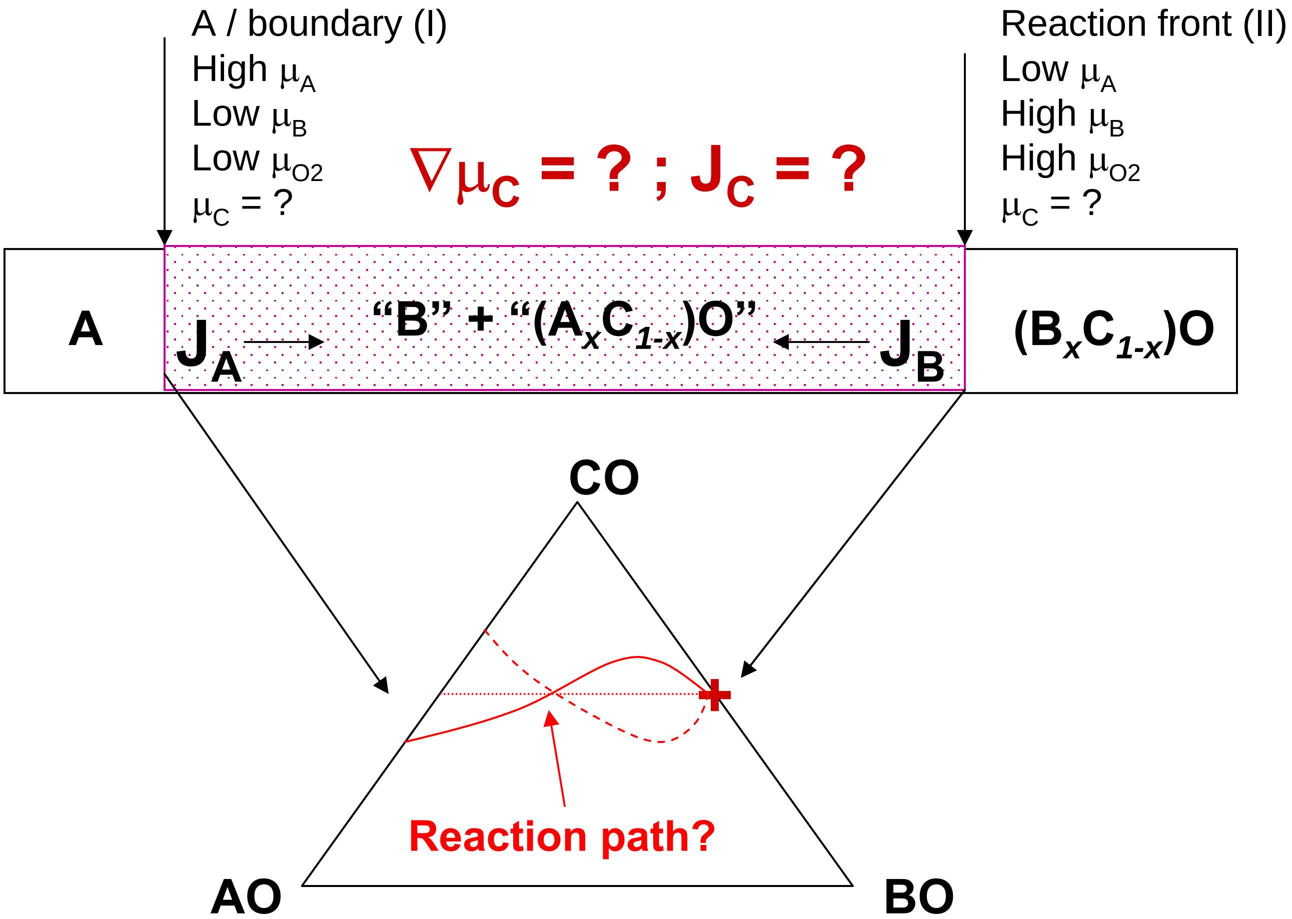
Internal displacement reaction in an oxide solid solution:

x A (metal) + $(B_xC_{1-x})O$ (oxide) = x "B" (metal) + "$(A_xC_{1-x})O$" (oxide)

(A,B,C)O --- solid solution in the entire composition range.

A,B,C --- Occupy the *same cation sub-lattice.*

C --- "Inert" for cation exchange ; $\Delta G^0_{CO} \ll \Delta G^0_{AO} < \Delta G^0_{BO}$



A / boundary (I)
High μ_A
Low μ_B
Low μ_{O2}
μ_C = ?

$\nabla\mu_C$ = ? ; J_C = ?

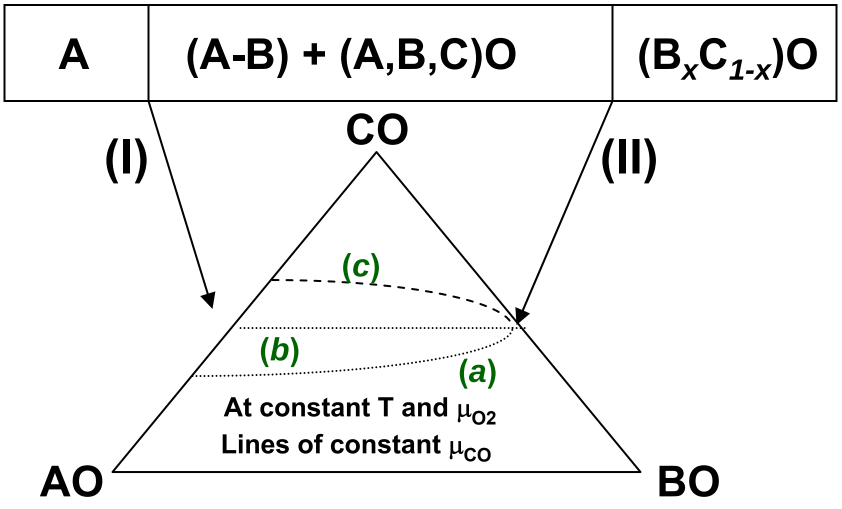
Reaction front (II)
Low μ_A
High μ_B
High μ_{O2}
μ_C = ?

Reaction path?

$$J_A = -L_{AA}\nabla\mu_A - L_{AB}\nabla\mu_B - L_{AC}\nabla\mu_C$$
$$J_B = -L_{AB}\nabla\mu_A - L_{BB}\nabla\mu_B - L_{BC}\nabla\mu_C$$
$$J_C = -L_{AC}\nabla\mu_A - L_{BC}\nabla\mu_B - L_{CC}\nabla\mu_C$$

At boundaries (I) & (II):

$\mu_C = \mu_{CO} - \mu_{O2}$; μ_{O2} (I) $<$ μ_{O2} (II)



<u>For a given *x* in the starting oxide:</u>

(a) and (*b*) : μ_{CO} (I) $\geq$ μ_{CO} (II)

$\Rightarrow$ μ_C (I) $>$ μ_C (II)

(*C*) : μ_{CO} (I) $<$ μ_{CO} (II)

however, in most cases: $|\Delta\mu_{O2}| > |\Delta\mu_{CO}|$

and μ_C (I) $>$ μ_C (II)

Net result : J_C → **Reaction front {boundary (II)}**
("up-hill" diffusion of C)

<u>After time t</u> : N_{CO} **at boundary (I)** $<$ **(1-** ***x*****)** ;

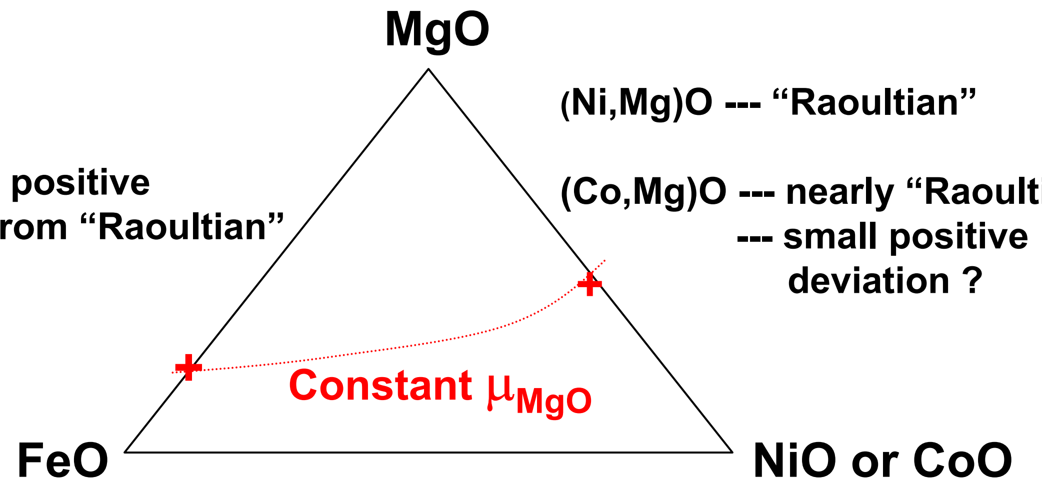
N_{CO} **at boundary (II)** $>$ **(1-** ***x*****)**

Model reactions in oxide solid solutions:

$$x\,\text{Fe} + (\text{Ni}_x\,\text{Mg}_{1-x})\text{O} = x\,\text{“Ni”} + \text{“}(\text{Fe}_x\,\text{Mg}_{1-x})\text{O”}$$

$$x\,\text{Fe} + (\text{Co}_x\,\text{Mg}_{1-x})\text{O} = x\,\text{“Co”} + \text{“}(\text{Fe}_x\text{Mg}_{1-x})\text{O”}$$

Point defect structure in Oxide: Cation Vacancies, $V_M = f\,(x\,,\,p_{o2},\,T)$

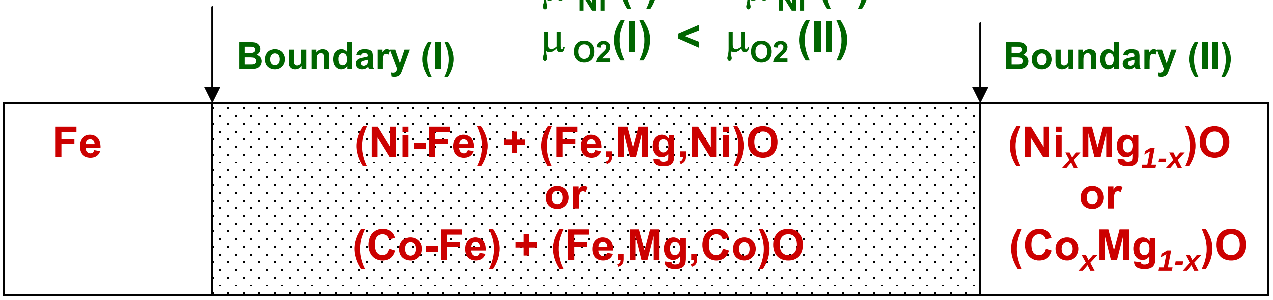


(Fe,Mg)O – positive
Deviation from “Raoultian”

(Ni,Mg)O --- “Raoultian”

(Co,Mg)O --- nearly “Raoultian”
--- small positive
deviation ?

$\mu_{Fe}(I) > \mu_{Fe}(II)$
$\mu_{Mg}(I) > \mu_{Mg}(II)$
$\mu_{Ni}(I) < \mu_{Ni}(II)$
$\mu_{O2}(I) < \mu_{O2}(II)$



$J_{Fe}\,,\,J_{Mg} \rightarrow$ $\leftarrow J_{Ni}\,,\,J_{Co}$

“Up-hill” diffusion of Mg.

Gradient in (Fe^{2+} / Fe^{3+}) ratio $\Rightarrow$ effect on J_{Fe} ?

Fe + $(Ni_x\,Mg_{1-x})$O = “Ni” + “$(Fe_x\,Mg_{1-x})$O

T = 1273 K

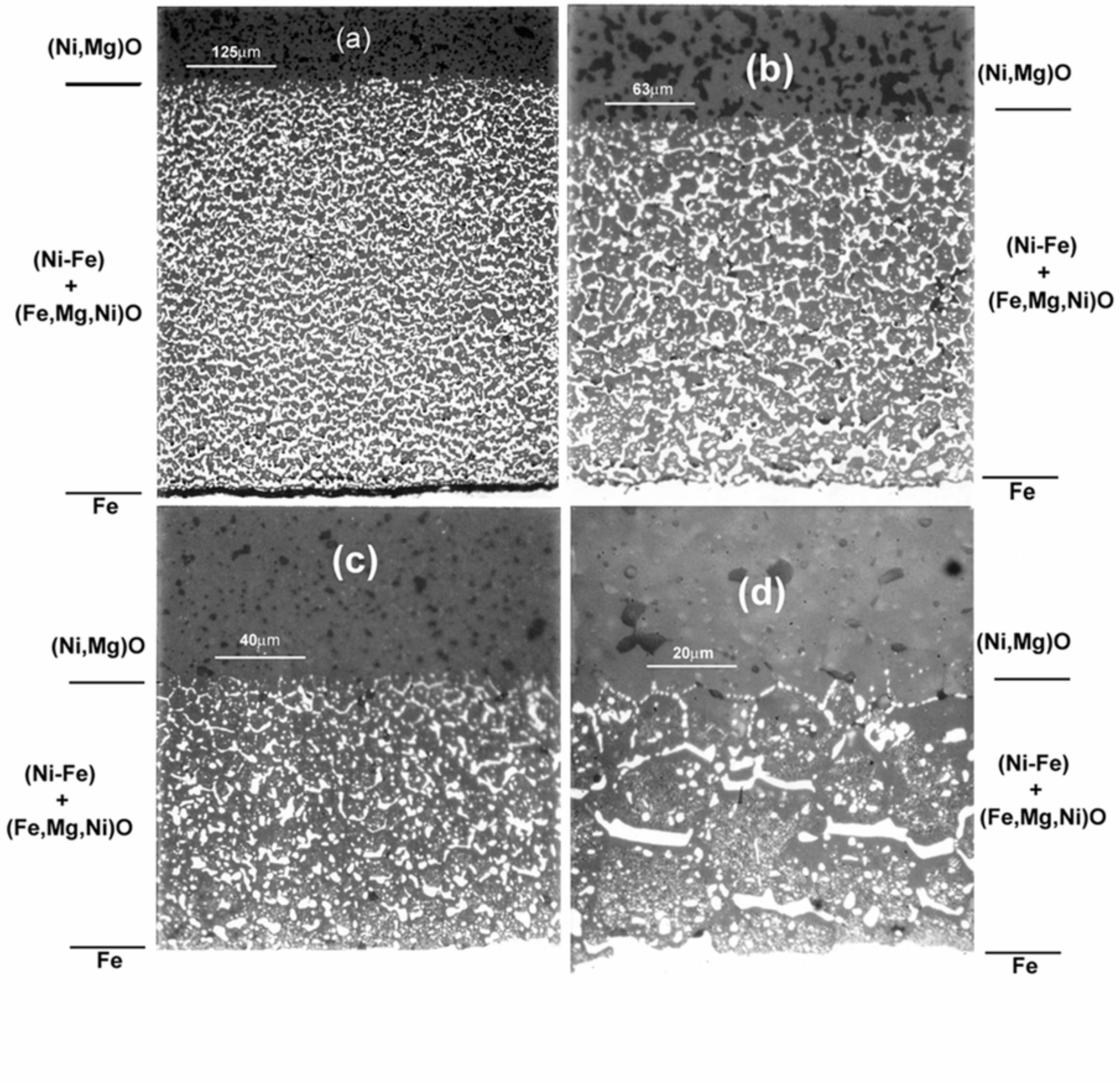


Fig.8. Cross sectional view of the reaction zone between Fe and (Ni_xMg_{1-x})O at 1273 K. (a) $x = 0.7$, t = 12 h; (b) $x = 0.5$, t = 9 h; (c) $x = 0.3$, t = 25 h; (d) $x = 0.2$, t = 49 h.

$Fe + (Co_{0.5}\,Mg_{0.5})O = \text{“}Co\text{”} + \text{“}(Fe_{0.5}\,Mg_{0.5})O$

T = 1273 K

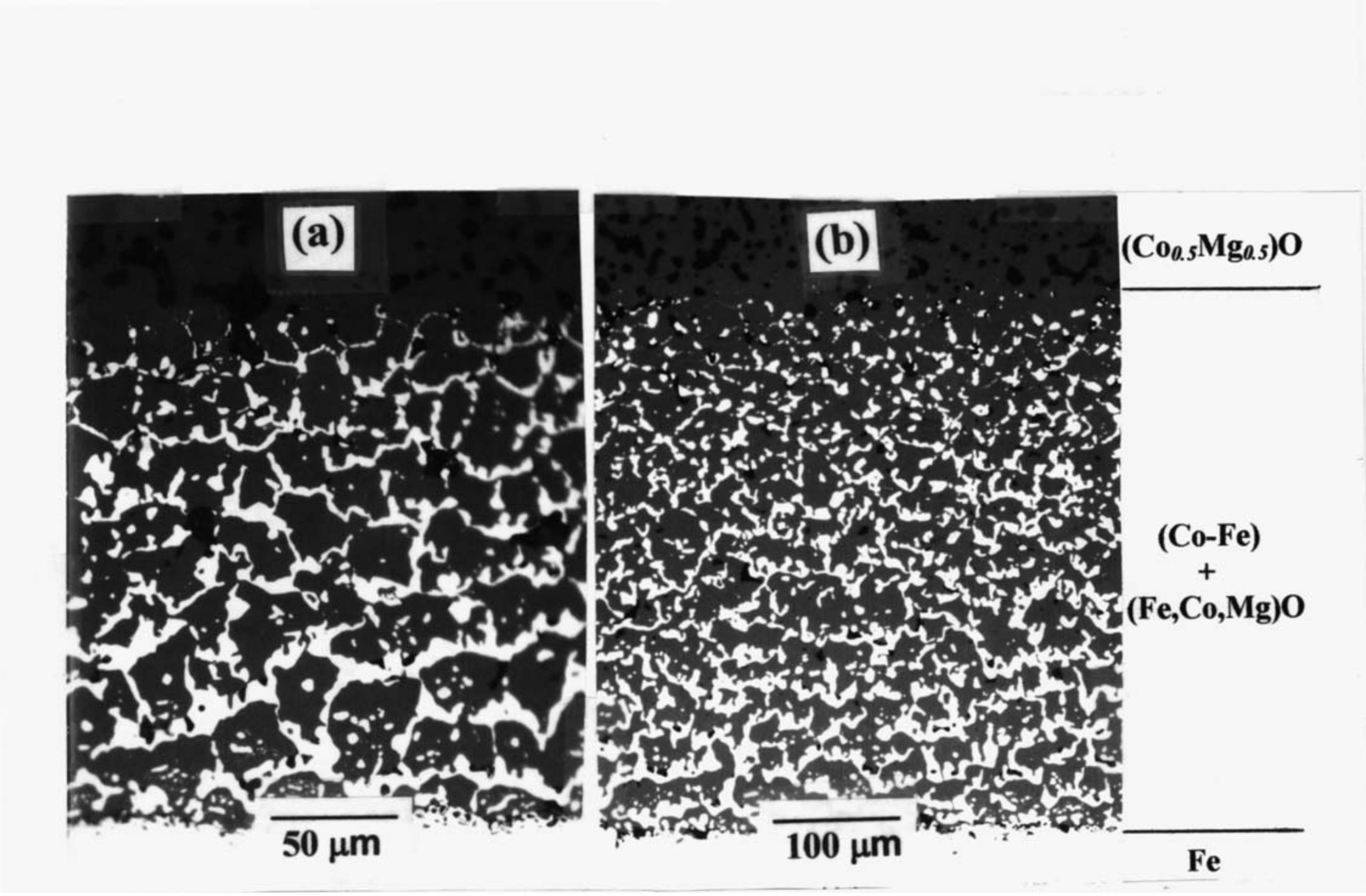


Fig 9. Displacement reaction between Fe and $(Co_{0.5}Mg_{0.5})O$ at 1273 K. (a) 16 hrs; (b) 62 hrs.

Is the precipitation *“periodic”* for reactions in Single Crystal Oxide Solid Solutions ?

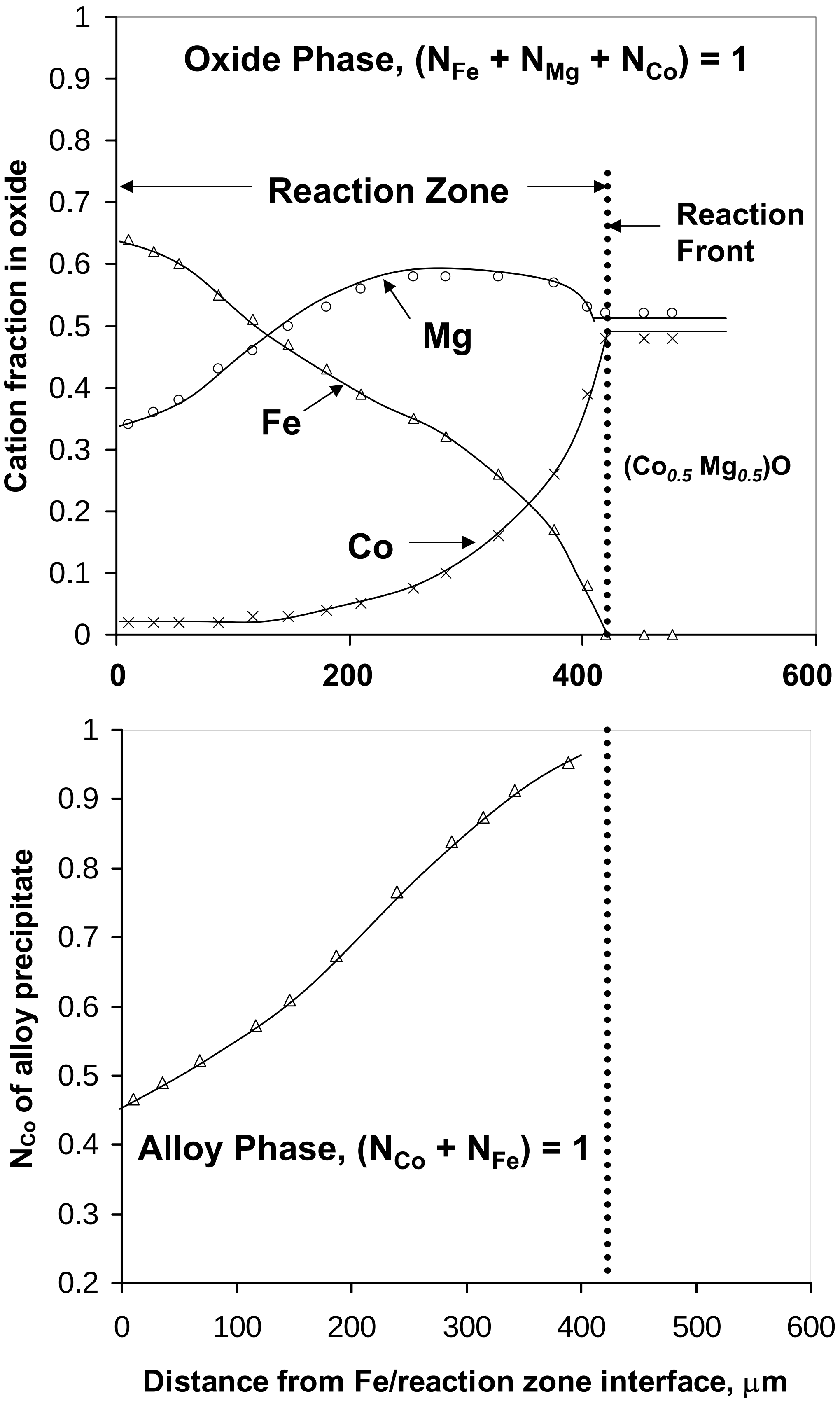


Fig.9. Composition of the product phases for the internal displacement reaction between Fe and $(Co_{0.5}Fe_{0.5})O$ at 1273 K and 62 hrs. (Lines are for eye-recognition only)

Reaction in solid solutions of “line” compounds:

$Fe + (Ni_{0.5}\,Mg_{0.5})TiO_3$ = “Ni” + “$(Fe_{0.5}\,Mg_{0.5})TiO_3$”

(“Inert” cations : Mg & Ti)

Cation sub-lattice(i) : Ni, Mg & Fe
Cation sub-lattice(ii) : Ti

} **Ilmenite structure**
(Fe+Ni+Mg):Ti = 1:1

Net Cation flux:

J_{Fe} , J_{Mg} → reaction front; J_{Ni} → Fe / boundary; J_{Ti} =0

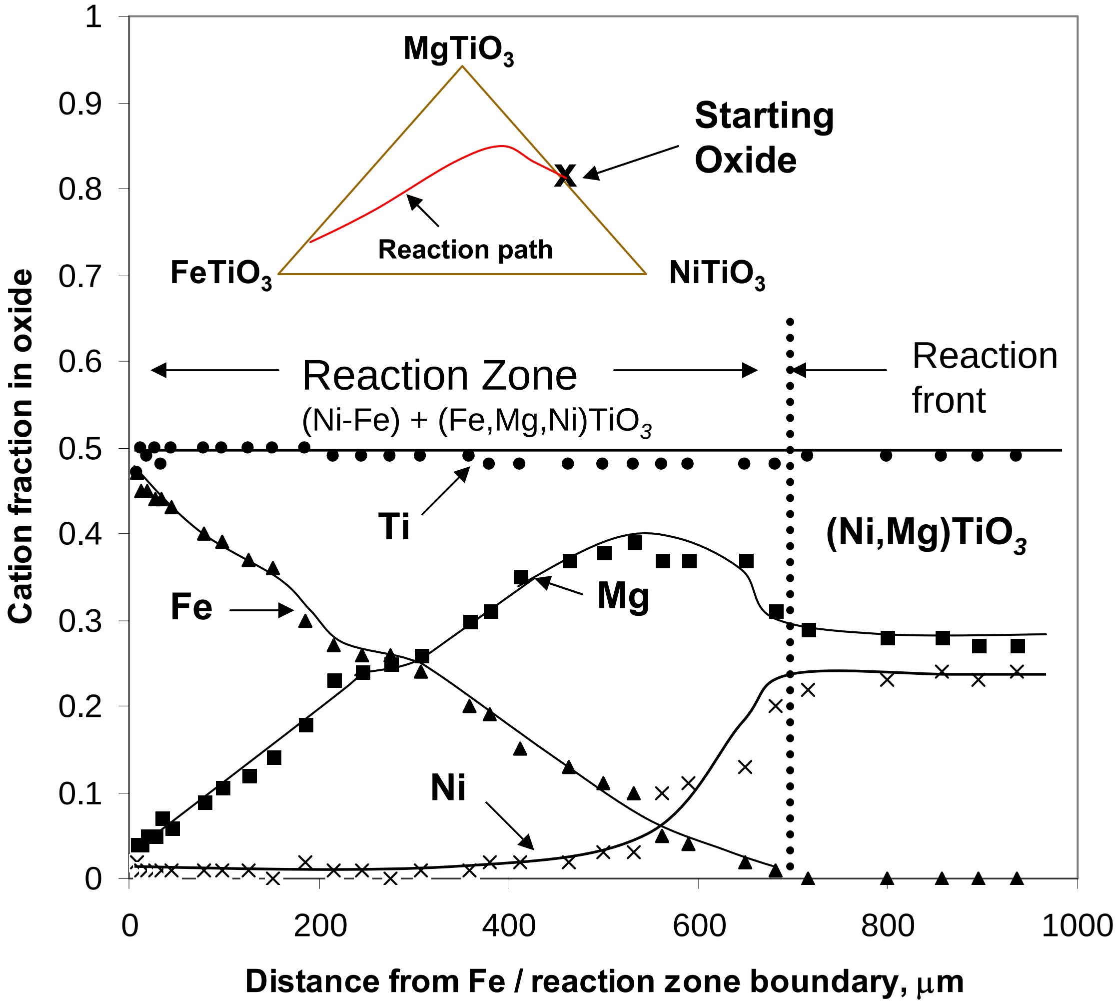


Fig.8. EPMA analysis of product oxide composition for the reaction between Fe and $(Ni_{0.5}Mg_{0.5})TiO_3$ .T = 1273 K ; time = 100 hrs.

(lines are for eye recognition only)

Summary

(i) Oxide "line" compounds of narrow composition width:

Model reaction: Fe + $NiTiO_3$ = "Ni" + "$FeTiO_3$"

--- periodic precipitate of (Ni-Fe) alloy ; Gradients in N_{Fe} & N_{Ni} .

--- Product oxide, "$FeTiO_3$" : ($FeTiO_3$ – $NiTiO_3$) solid solution.
Gradients in N_{Fe} & N_{Ni}. (Ni+Fe) : Ti = 1:1

--- Net cation flux in product oxide:

J_{Fe} → reaction front ; J_{Ni} → Fe / boundary ; J_{Ti} = 0.

……

(ii) Oxide solid solutions of wide composition range:

Model Reactions: Fe + $(Ni_xMg_{1-x})O$ = "Ni" + "$(Fe_xMg_{1-x})O$"
Fe + $(Co_xMg_{1-x})O$ = "Co" + "$(Fe_xMg_{1-x})O$

--- "Ni" = (Ni-Fe) ; "Co" = (Co-Fe) ; Composition gradients.

--- "$(Fe_x Mg_{1-x})O$" : (Fe,Mg,Ni or Co)O solid solution.

--- Net Cation Flux: J_{Fe} , J_{Mg} → reaction front ;
$J_{Ni\ or\ Co}$ → Fe / boundary ;

……

- ***Internal displacement reactions are useful to synthesize Metal-ceramic composites with unique structures.***

- ***Only qualitative nature of diffusion in oxides can be obtained from a study of these reactions.***