

Diffusion and Interface Stability during Solid-State Displacement Reactions.

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Solid State Displacement Reaction: (Redox Reaction)



(A,B = metal ; X = non-metal.)

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Product Phases:

“B” → pure B or A-B alloy.

“AX” → pure AX or
(A,B)X solid solution or
(A_aB_b)X_x compound.

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Kinetic and Microstructural Control :

- Thermodynamics of product phases, “B” and “AX”
 - Solubility of X in “B” , if any.
 - Point defect chemistry of “AX”

* Diffusion in product phases, “B” and “AX”

Displacement Reaction between a metal and an oxide:



Product Phases, \mathbf{A} (metal) and \mathbf{BO} (oxide) :

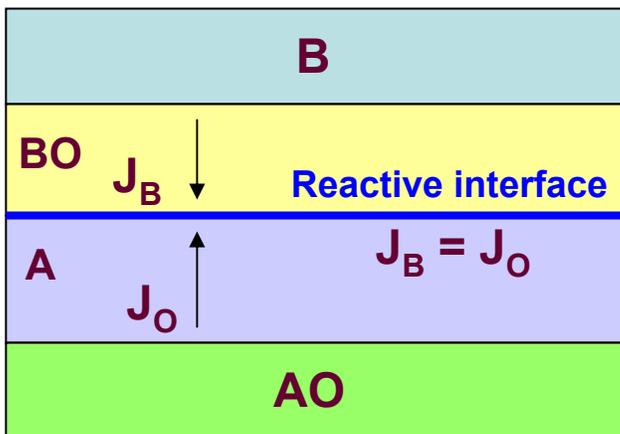
\mathbf{A} – Significant Solubility, $\mathbf{N}_\mathbf{O}(\mathbf{A})$ and Diffusivity, $\mathcal{D}_\mathbf{O}(\mathbf{A})$ of Oxygen.

-- Flux $\mathbf{J}_\mathbf{O}(\mathbf{A})$ contributes to kinetics.

\mathbf{BO} – Point defects in *Cation sublattice* only.

-- Flux $\mathbf{J}_\mathbf{B}(\mathbf{BO})$ contributes to kinetics.

-- *Oxygen is essentially immobile* $\{ \mathcal{D}_\mathbf{B}(\mathbf{BO}) \gg \mathcal{D}_\mathbf{O}(\mathbf{BO}) \}$



Two Limiting Cases:

(i) $\mathbf{J}_\mathbf{B}(\mathbf{BO})$ is rate limiting.

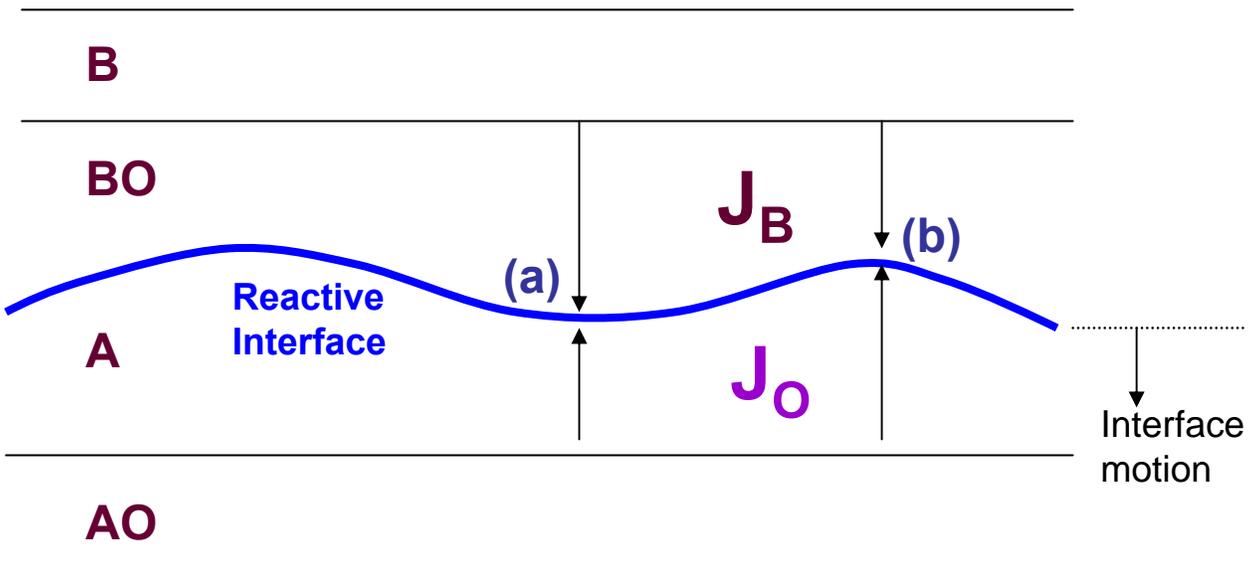
(ii) $\mathbf{J}_\mathbf{O}(\mathbf{A})$ is rate limiting.

Ref : R.A.Rapp, A.Ezis and G.J.Yurek

Metallurgical Transactions, 4 , 1973, pp. 1283-92

- **Stability of Reactive Interface.**
- **Product Zone Microstructure.**

Stability of Reactive Interface -- C. Wagner's Criterion :



Limiting Cases:

Case (i) : J_B (BO) is rate limiting.

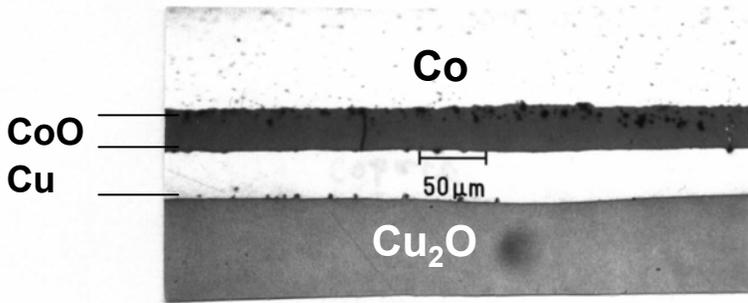
J_B at location (b) $>$ J_B at location (a)
 \Rightarrow Interface becomes **planar** with time.

Case (ii): J_O (A) is rate limiting.

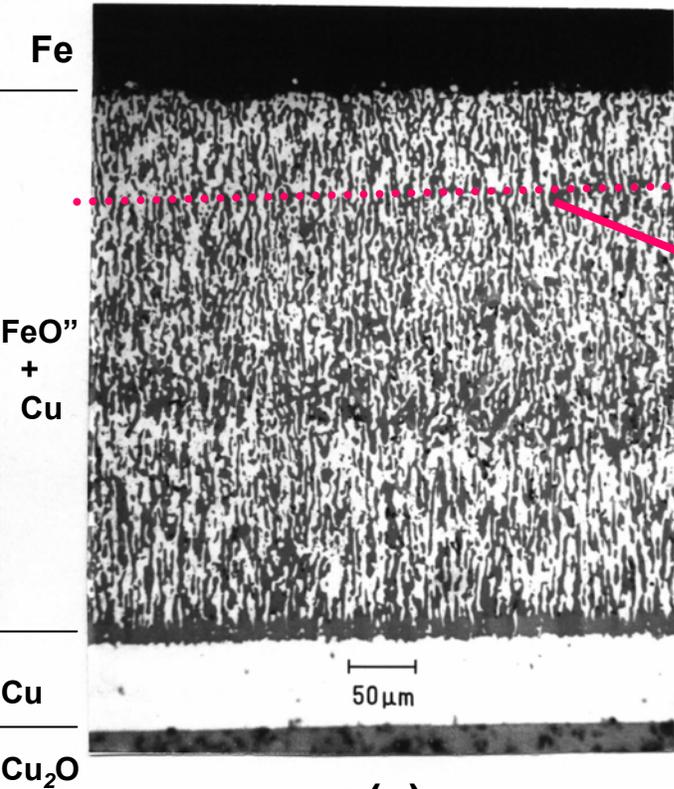
J_O at location (a) $>$ J_O at location (b)
 \Rightarrow Interface **instability** increases with time.

Reactive interface is morphologically unstable when it moves against the flux of the rate determining component

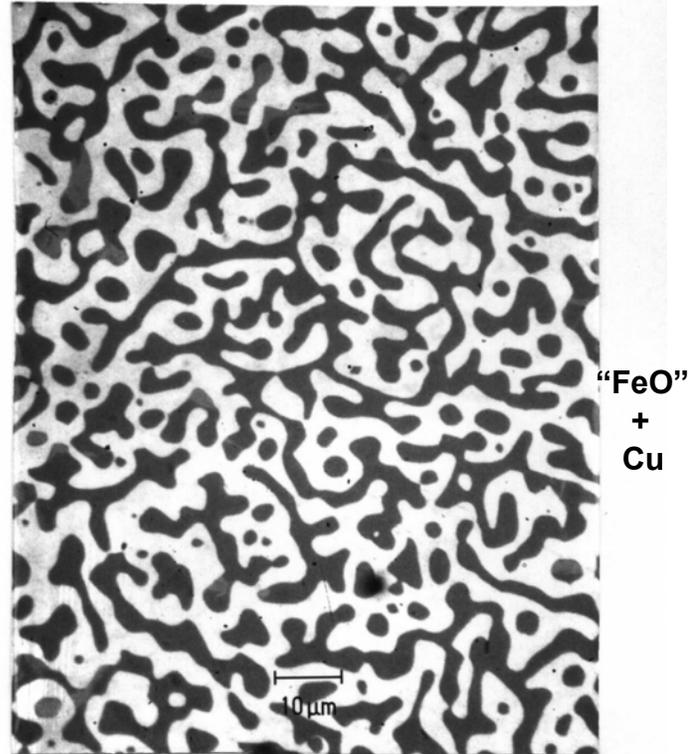
H. Schmalzried, Chemical Kinetics of Solids,
VCH Weinheim, 1995



Reaction:
 $\text{Cu}_2\text{O} + \text{Co} = 2\text{Cu} + \text{CoO}$
 Rate Control: $J_{\text{Co}}(\text{CoO})$



(a)



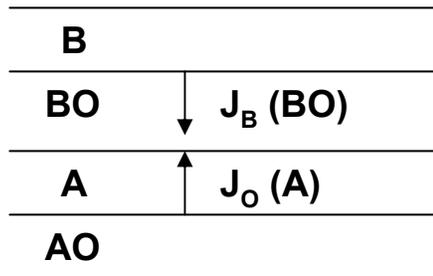
(b)

Reaction: $\text{Cu}_2\text{O} + \text{Fe} = 2\text{Cu} + \text{“FeO”}$
 (a) Cross-sectional view ; (b) transverse view
 Rate Control: $J_{\text{O}}(\text{Cu})$

(bright phase: metal ; dark phase: Oxide)

(Reproduction of work by Rapp, Ezis and Yurek at 1223 K)

Interface Stability as a function of \mathcal{D}_B in BO :

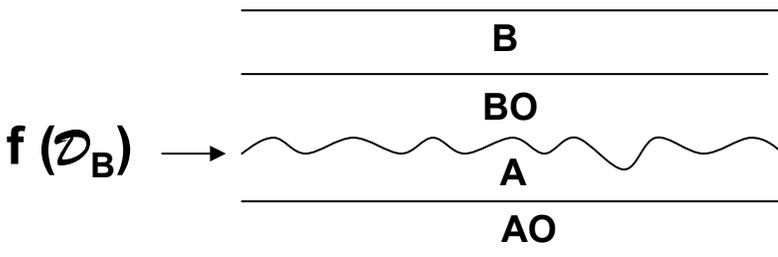


Rate Control : $J_B(BO)$

(examples: Cu_2O/Ni or Co)

* Maintain constant $N_O(A)$ and $\mathcal{D}_O(A)$

• Increase $\mathcal{D}_B(BO)$ → ↓↓



Mixed Control



Rate Control : $J_O(A)$
(unstable interface)

Strategy:



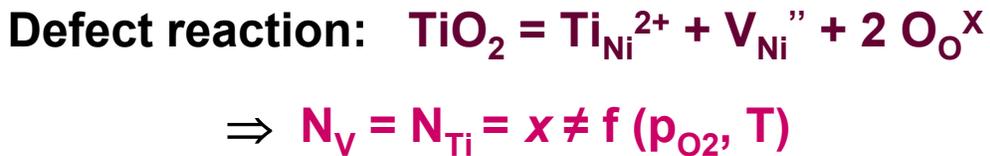
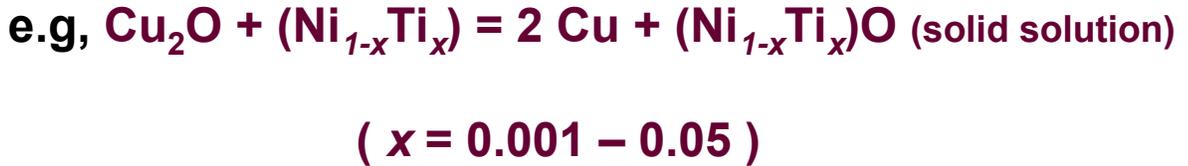
(D = "dopant")

Dopant function : $N_V \text{ in } (B,D)O > N_V \text{ in } (BO)$
 $\mathcal{D}_B \text{ in } (B,D)O > \mathcal{D}_B \text{ in } (BO)$

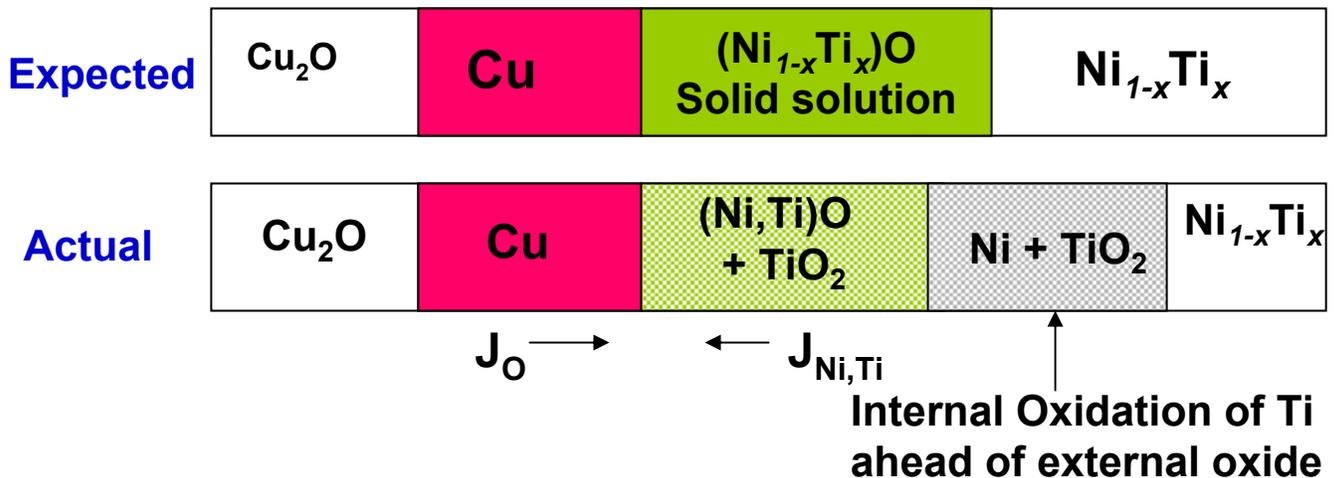
(N_V = Cation Vacancy concentration)

Doping Mechanism to increase N_V in (B,D)O :

(a) **Charge compensation: (Valence of D > Valence of B)**



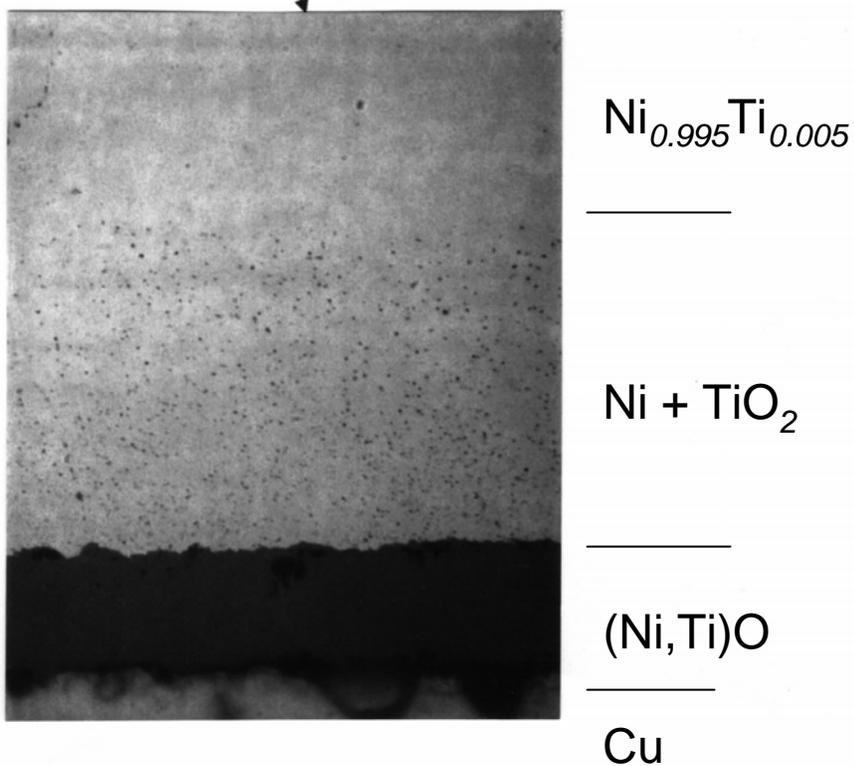
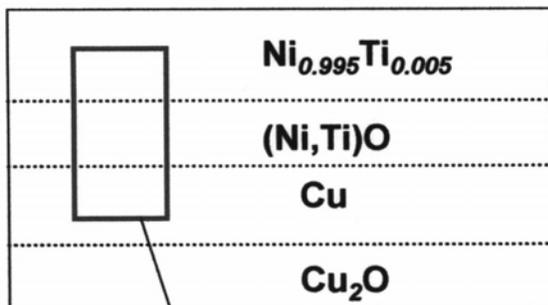
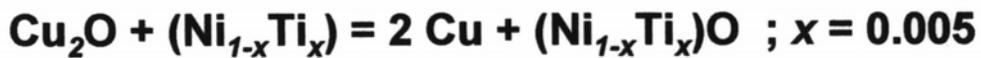
Assumption: Homogenous (Ni,Ti)O solid solution.



Consequence of Internal Oxidation:

- **Inhomogenous (Ni,Ti)O phase.**
- $N_{\text{Ti}} (= N_V) < x$ in (Ni,Ti)O oxide solid solution.
- **Rate control transition, $J_{\text{Ni}} (\text{Ni,Ti})\text{O} \rightarrow J_{\text{O}} (\text{Cu})$ was not possible.**

Reaction:



Product zone microstructure for the reaction between Cu_2O and (Ni,Ti) alloy.

Doping mechanism to increase N_V :

(b) Increase in non-stoichiometry of product oxide, (B,D)O:

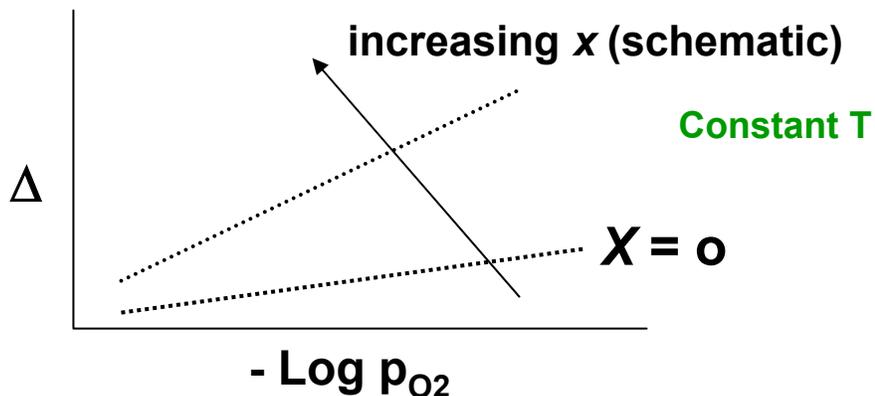


Δ in (B,D)O > Δ in BO

$\Rightarrow N_V = f(N_D, p_{\text{O}_2}, T)$



Cu_2O	Cu	$(\text{Co}_{1-x}\text{Fe}_x)\text{O}$	$\text{Co}_{1-x}\text{Fe}_x$
	$\longrightarrow J_\text{O}$	$\longleftarrow J_{\text{Co,Fe}}$	



Ref: Aukrust, Muan, 1964

Subramanian, Tinkler, Dieckmann, 1994

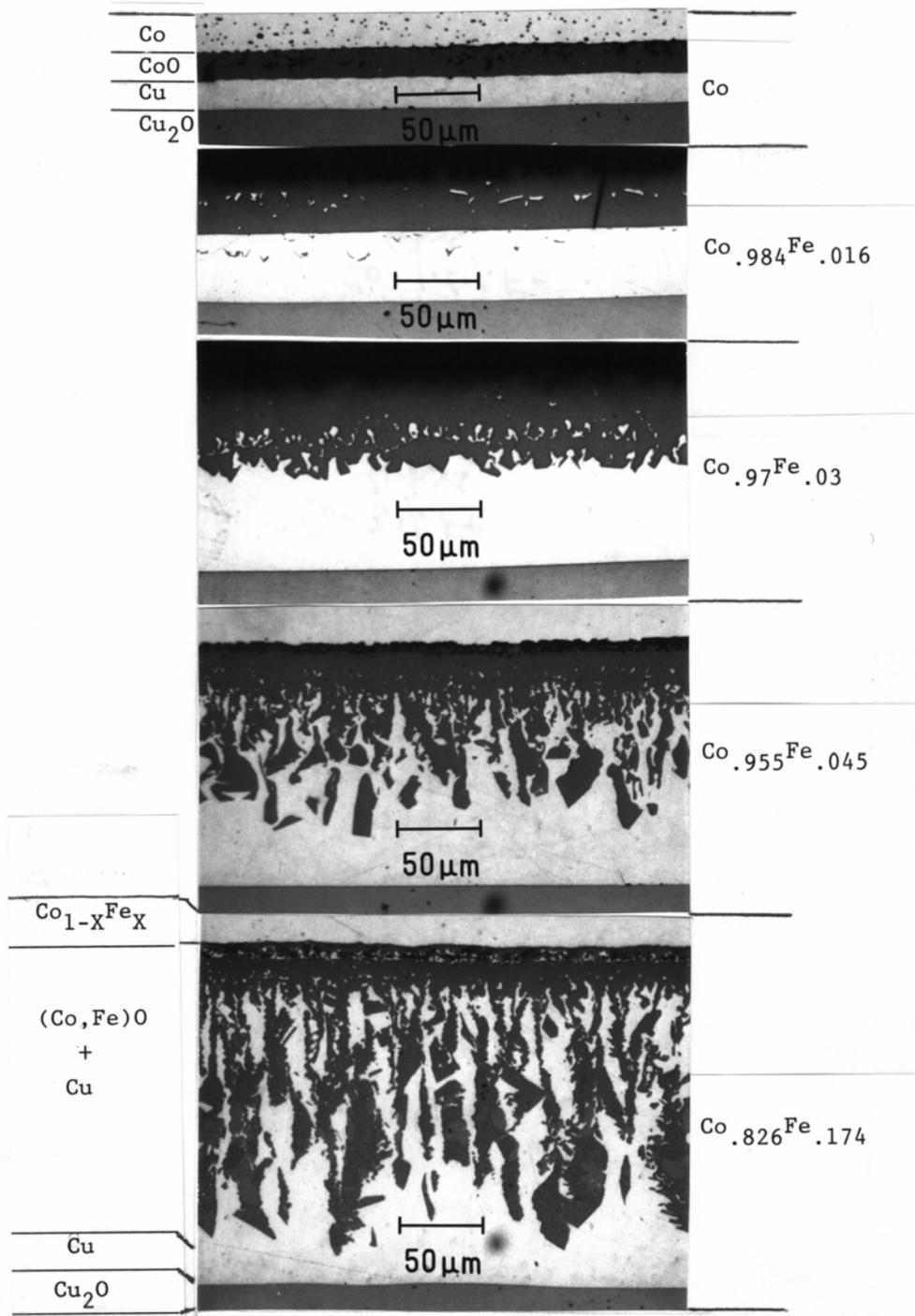


Fig. Displacement reaction between Cu_2O and $\text{Co}_{1-x}\text{Fe}_x$ alloys at 1223K. Product phase morphology after 4 hours.

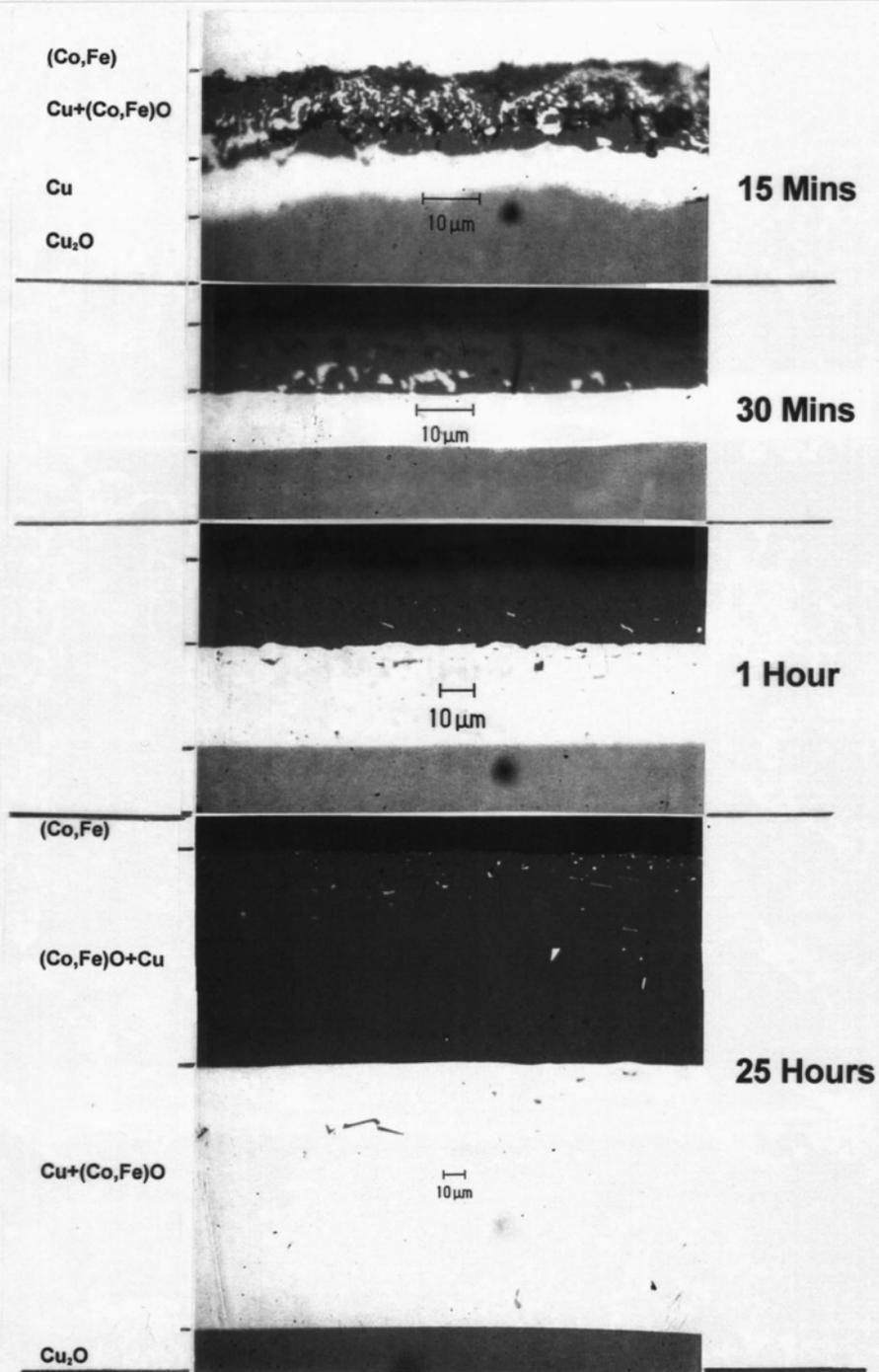


Fig.5. Evolution of the reactive interface morphology with time for the displacement reaction between Cu_2O and $\text{Co}_{0.984}\text{Fe}_{0.016}$ at 1223 K.

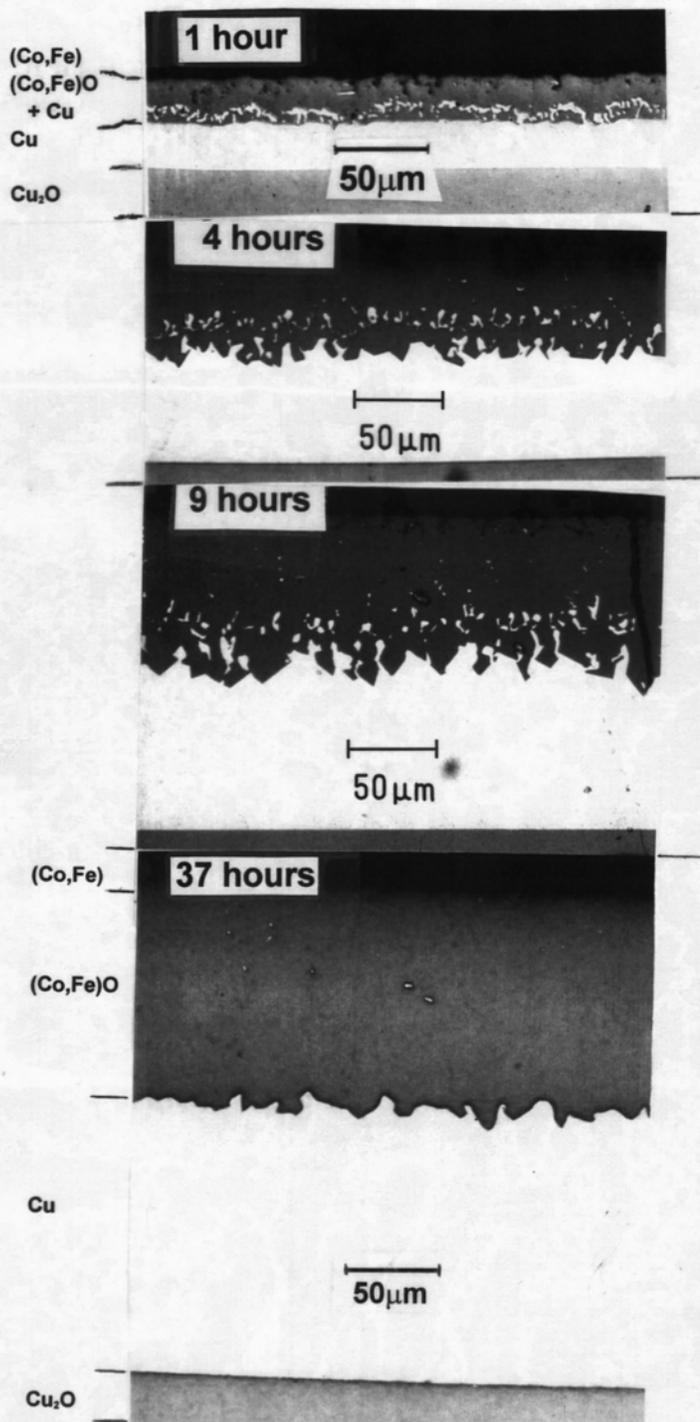


Fig.6. Reaction Zone Morphology between Cu_2O and $\text{Co}_{0.97}\text{Fe}_{0.03}$ as a function of time at 1223 K.

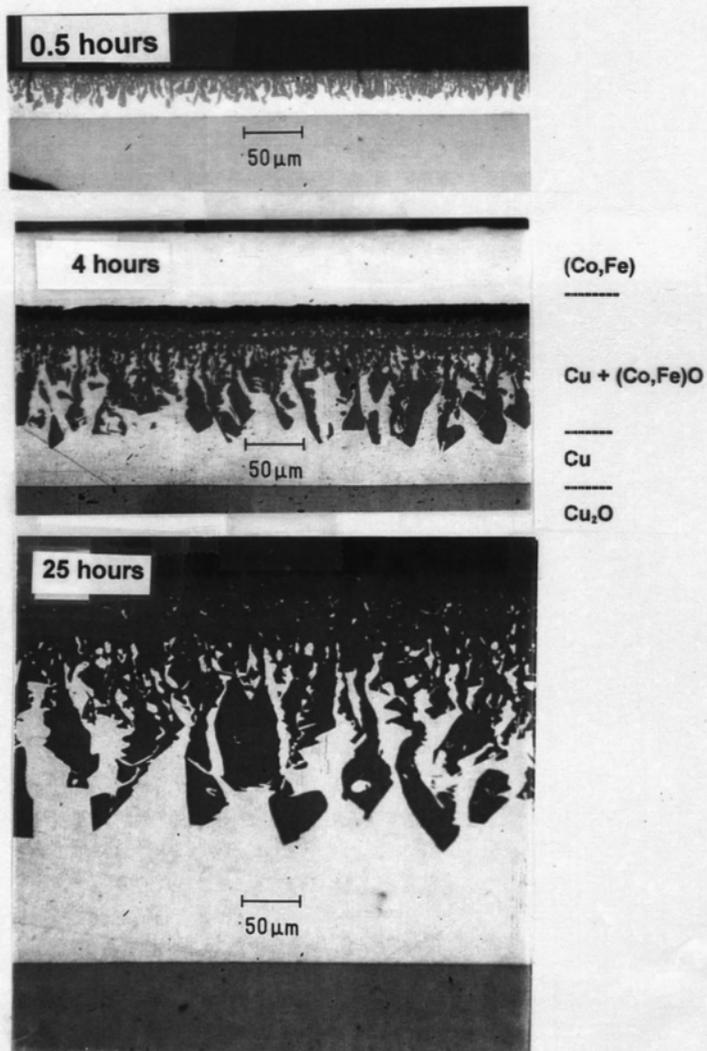
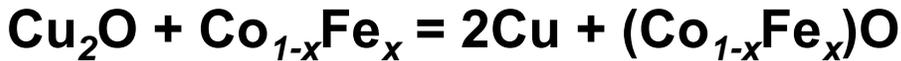


Fig. 7. Reaction Zone Morphology as a function of time for the reaction between Cu_2O and $\text{Co}_{0.965}\text{Fe}_{0.045}$.

Kinetics (T = 1223 K):



$x = 0, 0.015$ and $0.03 \rightarrow$ planar interface at long times.

$J_{\text{Co, Fe}}$ in $(\text{Co}_{1-x}\text{Fe}_x)\text{O}$ -- Rate limiting ?

Parabolic rate Constant for Cu phase, $k_p^{\text{Cu}}(x)$

X	$k_p^{\text{Cu}}, \text{m}^2\text{s}^{-1}$		$k_p^{\text{Cu}}(x) / k_p^{\text{Cu}}(x=0)$ (experimental)
	experimental from reaction	calculated from D_{Cation}	
0	6.0×10^{-15}	# 8.5×10^{-15}	-----
0.015	6.6×10^{-14}	-----	11
0.03	1.1×10^{-13}	-----	18

D_{Co}^{T} in CoO from Dieckmann, 1977.

Other Cation diffusion data in (Co,Fe)O at 1473 K:

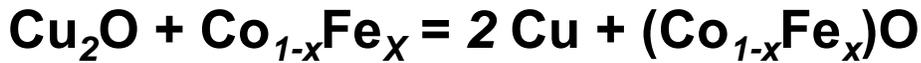
$$\{D_{\text{Co, Fe}} \text{ in } (\text{Co}_{0.984}\text{Fe}_{0.016})\text{O}\} / \{D_{\text{Co}} \text{ in CoO}\} = 7 - 9$$

Hoshino, Peterson, 1985

$$\{D_{\text{Co, Fe}} \text{ in } (\text{Co}_{0.97}\text{Fe}_{0.03})\text{O}\} / \{D_{\text{Co}} \text{ in CoO}\} = 21 - 25$$

Tinkler, Subramanian, Dieckmann, 1994

Transition in reactive interface Stability:



Experimental observation: (1223 K)

$x = 0.03 \Rightarrow$ stable, planar interface at long times

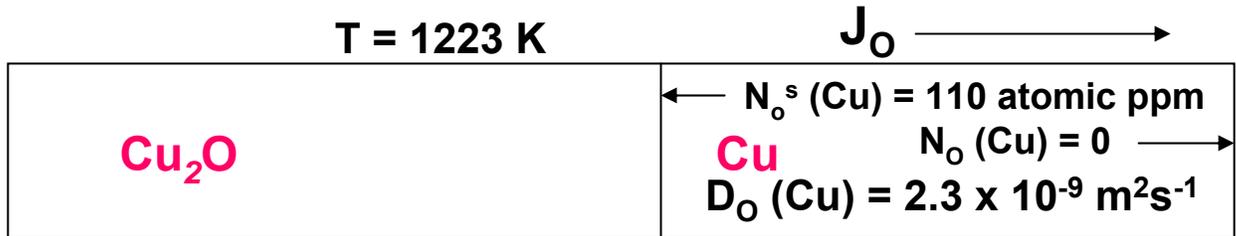
$x = 0.045 \Rightarrow$ non-planar interface at long times

$x = 0.03 + \varepsilon \Rightarrow$ stability transition ($\varepsilon = 0.005 - 0.01$)

$$k_p^{\text{Cu}} (x = 0.03) = 1.1 \times 10^{-13} \text{ m}^2\text{s}^{-1} \text{ (corresponds to } J_{\text{cation}}^{\text{max}})$$

$$k_p^{\text{Cu}} (x = 0.03 + \varepsilon) = (1.1 + \delta) \times 10^{-13} \text{ m}^2\text{s}^{-1} \text{ (---- ditto -----)}$$

What is k_p^{Cu} maximum when $J_{\text{O}}(\text{Cu})$ is rate limiting ?



$$k_p^{\text{Cu}} (\text{maximum}) = 5.0 \times 10^{-13} \text{ m}^2\text{s}^{-1} \text{ \{corresponds to } J_{\text{O}}^{\text{max}}(\text{Cu})$$

$$= (1.1 + 3.9) \times 10^{-13} \text{ m}^2\text{s}^{-1}$$

↑
 δ

Summary:

Transition of interface stability occurs when:

$$J_{\text{O}}^{\text{max}} (\text{metal}) \approx J_{\text{cation}}^{\text{max}} (\text{oxide})$$

> stable

< unstable