Oxidation and Corrosion in High-Temperature Systems

G. H. Meier
Department of Materials Science & Engineering
University of Pittsburgh

ICMR Summer Program on
Advanced Thermostructural Materials

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Introduction

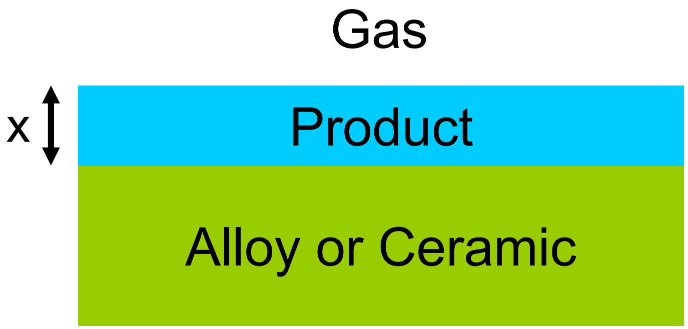
The rate of reaction between a reactive material and a gas is determined by the nature of the reaction product.

Thermodynamics

Reactive Potentials in Gas μ_{O2}, μ_{C}, μ_{S2}

Stable Product(s)

Vaporization



Thermomechanical Stability

PBR (V_{Prod}/V_{Alloy})

$X > 2E\Gamma/\sigma^2$

Diffusion

D's in Reaction Product

D's in Alloy, Ceramic

Film Properties

ASR = ρx

N. Birks, G. H. Meier, and F. S. Pettit, Introduction to High Temperature Oxidation of Metals, 2nd Edition, Cambridge University Press, Cambridge, 2006.

Oxidation and Corrosion of Metals and Alloys

a. Review of thermodynamic principles

b. Review of diffusion principles: point defects in metals and oxides

c. Principles of oxidation and corrosion

- Parabolic and transition from parabolic
- External vs. internal oxidation (Selective oxidation)
- Oxide adherence
- Environmental influences in real systems (Evaporation, H_2O content, dual-atmosphere, pressure, breakaway corrosion, corrosion in multi component gases)

d. Protective Coatings

Coating Fabrication

Coating Durability

Thermodynamic Principles

$$G' = H' - TS'$$

At constant temperature and pressure:

$\Delta G' < 0$ spontaneous reaction expected

$\Delta G' = 0$ equilibrium

$\Delta G' > 0$ thermodynamically impossible process

aA + bB = cC +dD

$$\Delta G' = c\mu_C + d\mu_D - a\mu_A - b\mu_B$$

$$\mu_i = \mu_i^o + RT \ln a_i$$

$$\Delta G' = \Delta G^\circ + RT \ln\left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right)$$

$$a_i \equiv \frac{f_i}{f_i^o} \cong \frac{p_i}{p_i^\circ}$$

$$\Delta G^o = c\Delta G_C^o + d\Delta G_D^o - a\Delta G_A^o - b\Delta G_B^o$$

At equilibrium:

$$\Delta G^\circ = -RT\ln\left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right)_{eq} = -RT\ln K$$

"Law of Mass Action"

Note: Free energy of formation data can be accessed either directly or as "Log $K_{P.}$ The latter allows direct calculation of the equilibrium constant for the overall reaction.

Calculation of Activities in a Gaseous Environment

Problem A gas consisting of 60 vol % H_2 and 40 vol% CO_2 is let into a reaction chamber and heated to 1200K at a total pressure of 1 atm. Calculate the oxygen partial pressure and carbon activity in this gas when it comes to equilibrium.

Solution The common species which can form in such a gas mixture and their log K_P values at 1200K are listed in the following table.

Species	log K_P
CO_2	17.243
CO	9.479
H_2O	7.899
H_2	0.00

$$H_2(g) + CO_2(g) = H_2O(g) + CO(g)$$

$$\log K_R = \log K_P^{H_2O} + \log K_P^{CO} - \log K_P^{CO_2} = 0.135$$

$$K_R = 1.365 = \frac{p_{H_2O}\, p_{CO}}{p_{H_2}\, p_{CO_2}}$$

$$p_i = \frac{n_i}{n_{tot}} P_{tot}$$

$$K_R = 1.365 = \frac{n_{H_2O} n_{CO}}{n_{H_2} n_{CO_2}}$$

Species	Initial Comp. (moles)	Final Comp. (moles)
H_2	0.6	0.6-λ
CO_2	0.4	0.4-λ
CO	0	λ
H_2O	0	λ

$$K_R = 1.365 = \frac{\lambda\lambda}{(0.6-\lambda)(0.4-\lambda)}$$

λ = 0.2575 moles.

Species	Final Comp. (moles)	Partial Pressures (atm)
H_2	0.3425	0.3425
CO_2	0.1425	0.1425
CO	0.2575	0.2575
H_2O	0.2575	0.2575

Calculation of Activities

Oxygen Partial Pressure

$$H_2(g) + 1/2O_2(g) = H_2O(g)$$

$$K_P = 7.924x10^7 = \frac{p_{H_2O}}{p_{H_2}\,p_{O_2}^{1/2}} = \frac{0.2575}{0.3425\,p_{O_2}^{1/2}}$$

$$p_{O_2} = 9.0x10^{-18}\,atm$$

Carbon Activity

$$2CO(g) = CO_2(g) + C(s)$$

$$\log K_R = \log K_P^{CO_2} - 2\log K_P^{CO} = -1.715$$

$$K_R = 0.193 = \frac{p_{CO_2}a_C}{p_{CO}^2} = \frac{0.1425a_C}{(0.2575)^2}$$

$$a_C = 0.009$$

Will this gas with $p_{O_2} = 9.0x10^{-18}\,atm$ oxidize Ni or Cr?

$$Ni(s) + \tfrac{1}{2}O_2(g) = NiO(s)$$

Log K_P = 5.75

$$K_P = \frac{1}{p_{O_2}^{\frac{1}{2}}} = 5.6x10^5$$

$$p_{O_2}^{eq} = 3.2x10^{-12}\,atm$$

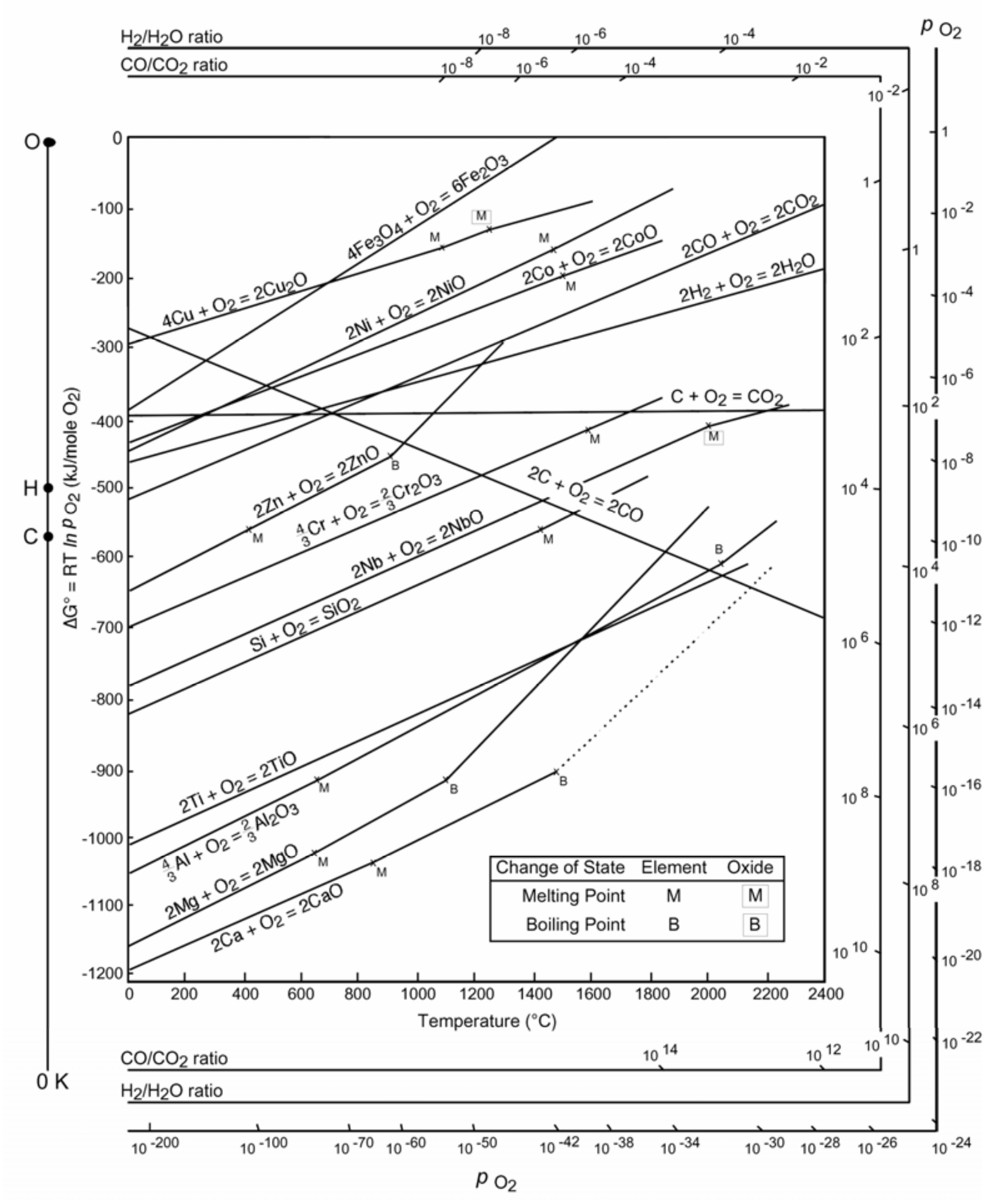
Ni cannot oxidize

$$2Cr(s) + \tfrac{3}{2}O_2(g) = Cr_2O_3(s)$$

$$p_{O_2}^{eq} = 1.2x10^{-24}\,atm$$

Cr will tend to oxidize

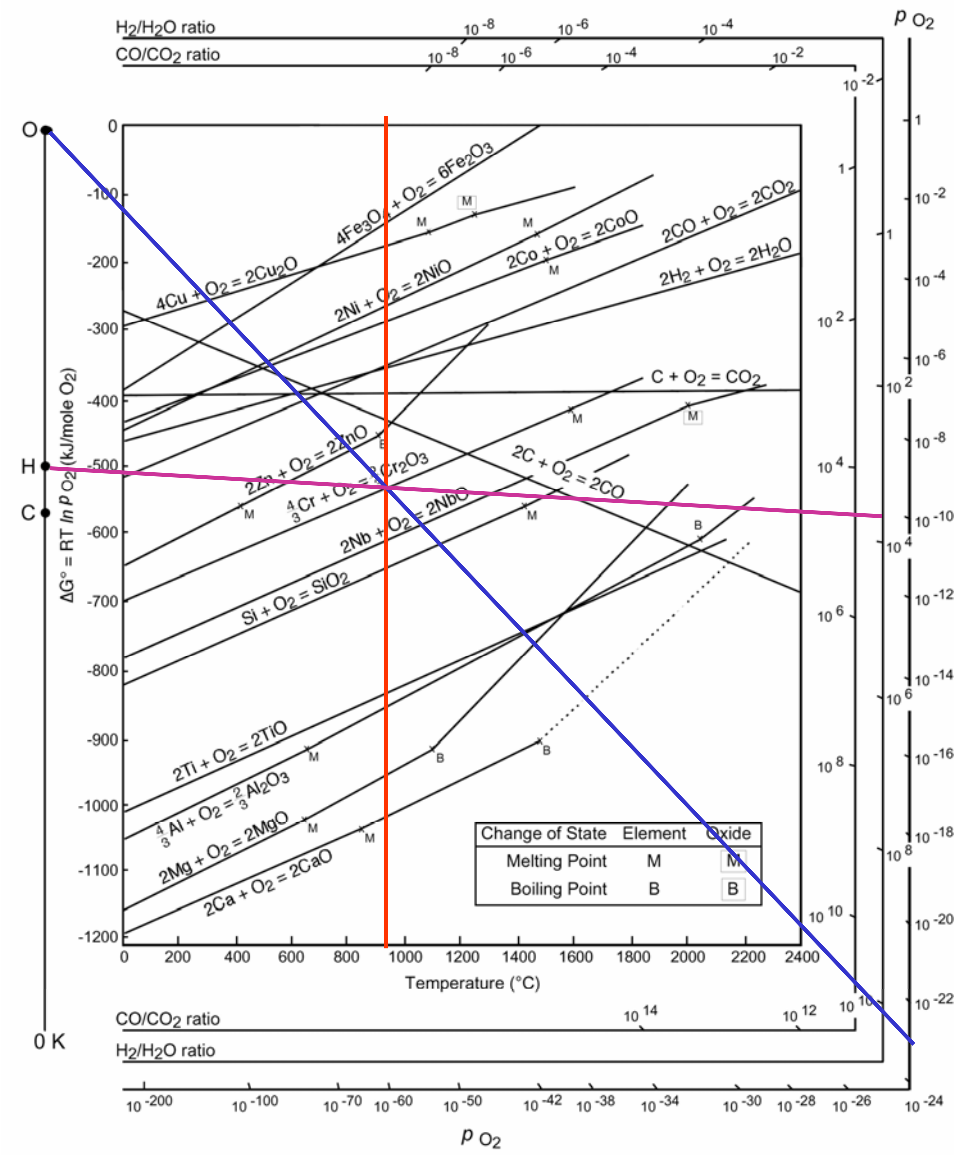
Ellingham (Richardson) Diagram



Ellingham (Richardson) Diagram

$$p_{O_2} = 9.0x10^{-18}\,atm$$

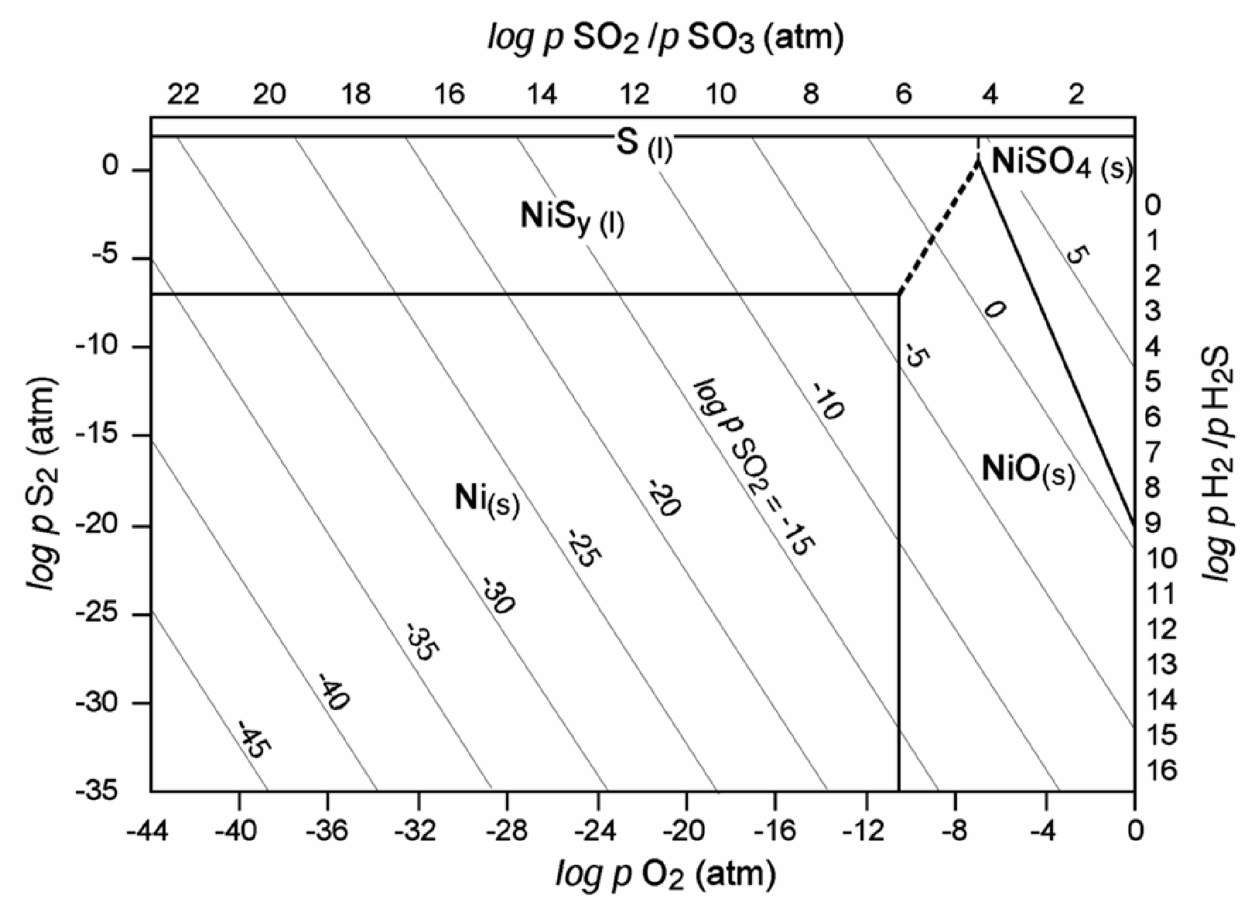
$$\frac{p_{H_2}}{p_{H_2O}} = 1.33$$



Isothermal Stability (Ellingham) Diagram

Ni-S-O System, 1250K

Ternary – Type 1 Diagram



Generalized “Phase Diagrams”

Gibbs Phase Rule: $F = C - P + 2$

Combined 1st and 2nd Laws

$$dU' = TdS' - PdV' + \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3$$

$$\mu_i \equiv \left(\frac{\partial U'}{\partial n_i} \right)_{S', V', n_j} = \overline{G}_i$$

T, P, μ_i = potentials (φ)

S', V', n_i = conjugate extensive variables (q)

Type 1: φ_i vs φ_j Invariant Equilibria = “point”

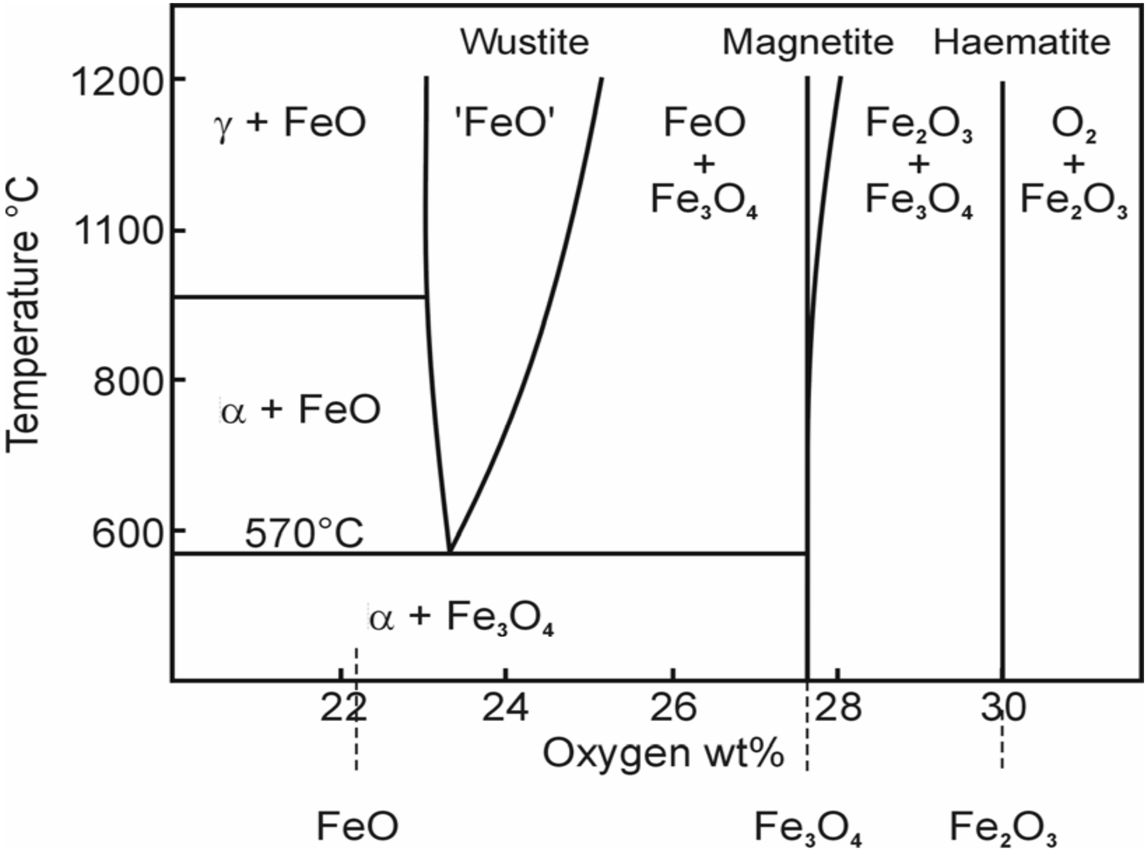
Type 2: φ vs q_i/q_j Invariant Equilibria = “line”

Type 3: q_i/q_k vs q_j/q_k Invariant Equilibria = “area”

Pelton, A. D. and Schmalzried, H., *Met. Trans.*, **4**, (1973) 1395.

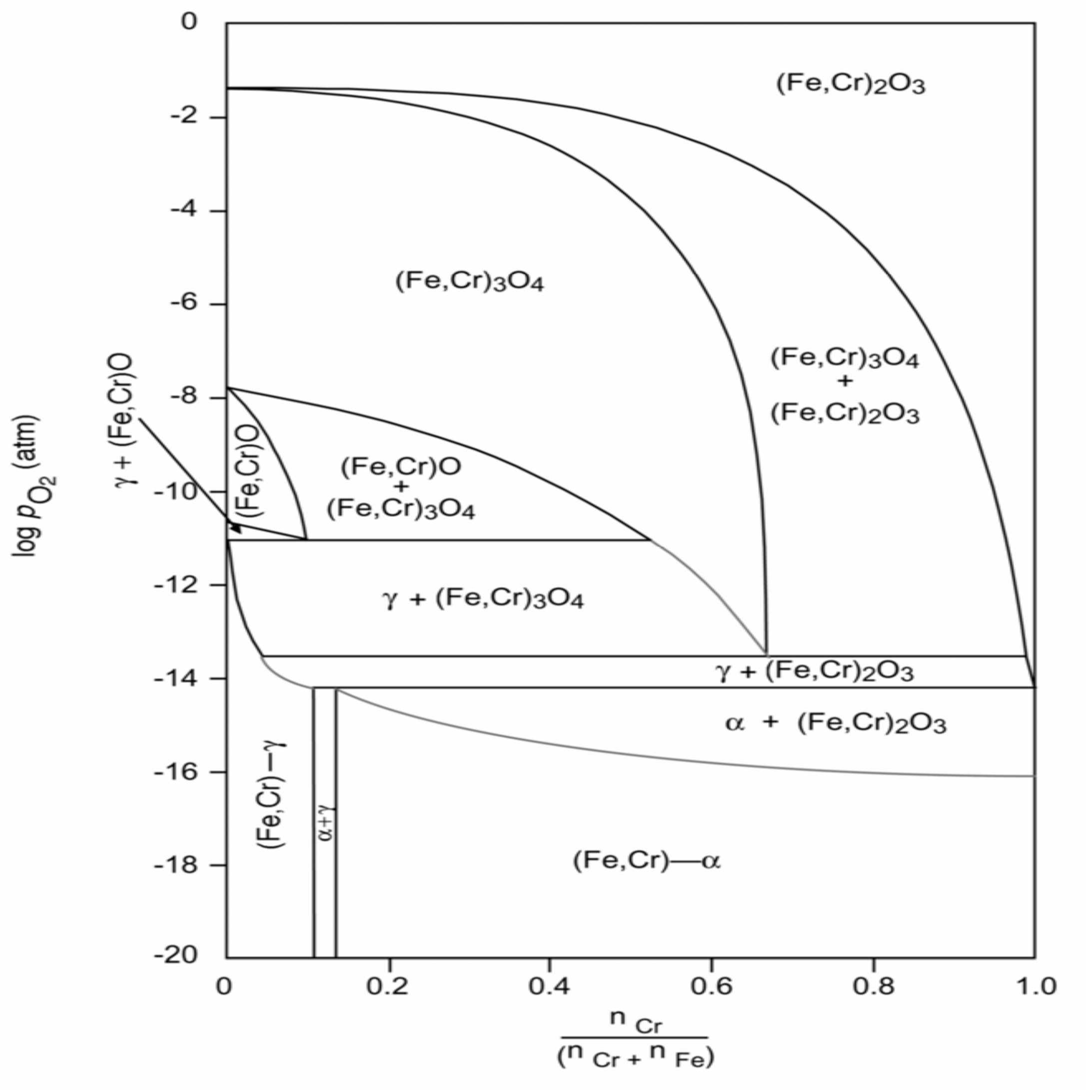
Fe-O Isobaric Diagram

Binary – Type 2 Diagram



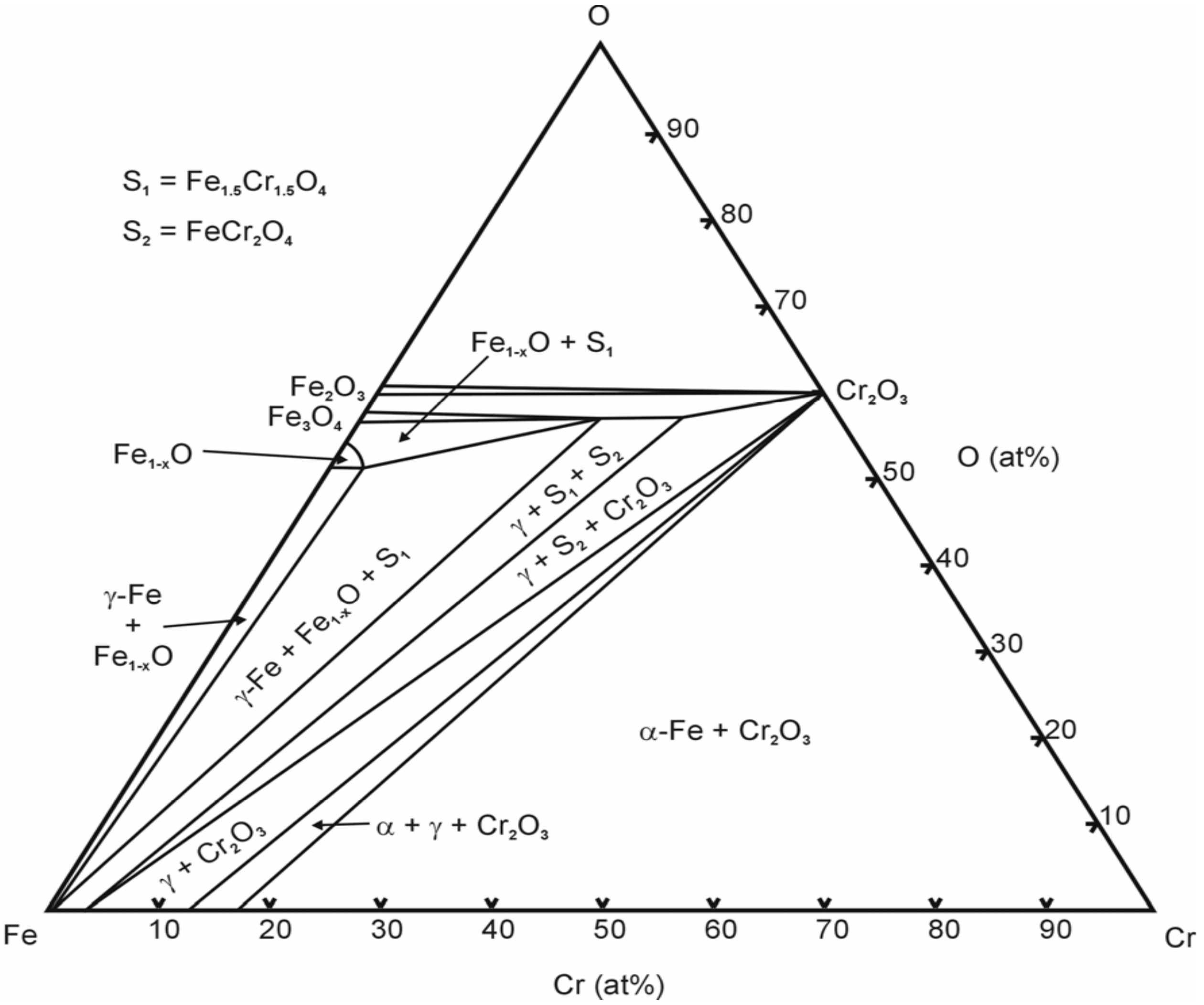
Fe-Cr-O Isothermal Diagram

Ternary – Type 2 Diagram

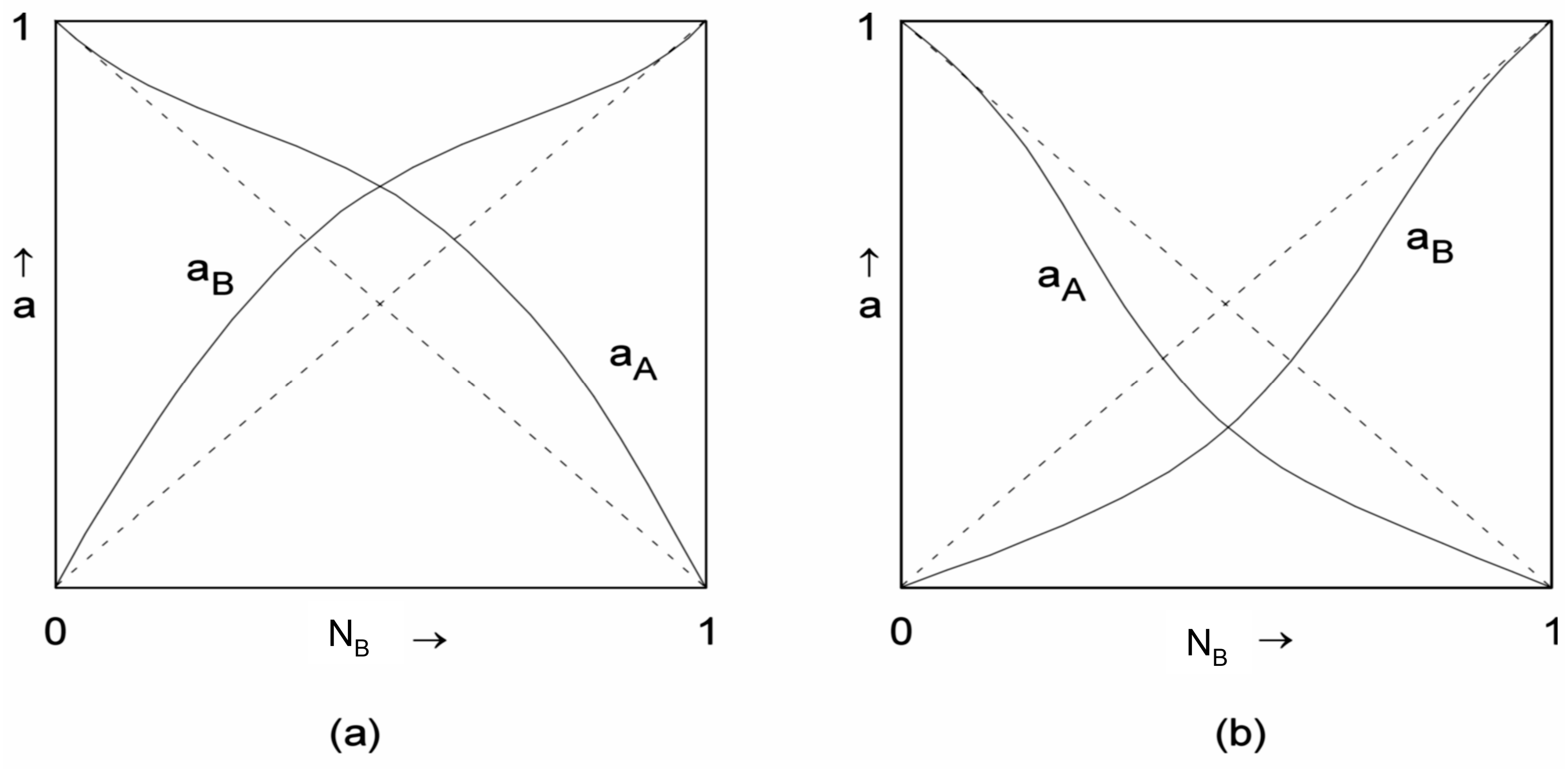


Fe-Cr-O Isothermal Section

Ternary – Type 3 Diagram



Solution Thermodynamics



(a)

(b)

Positive Deviation from Ideality

Negative Deviation from Ideality

Solution Thermodynamics

$a_i = N_i$	Ideal Solution
$a_i = \gamma_i N_i$	Real Solution, $\gamma_i = f(N_i)$
$a_i = \gamma_i(\infty) N_i$	Dilute Solution, $\gamma_i(\infty) = \text{constant}$

Sievert's Law

Consider Hydrogen Dissolving into Nickel

$$\tfrac{1}{2} H_2(g) = \underline{H}(inNi)$$

$$K = \frac{a_H}{p_{H_2}^{1/2}} = \frac{\gamma_H(\infty) N_H}{p_{H_2}^{1/2}}$$

$$N_H = \frac{K}{\gamma_H(\infty)} p_{H_2}^{1/2} = k_S \, p_{H_2}^{1/2}$$

Oxide Evaporation

Chromia Evaporation

$$Cr_2O_3(s) + \tfrac{3}{2}O_2(g) = 2CrO_3(g)$$

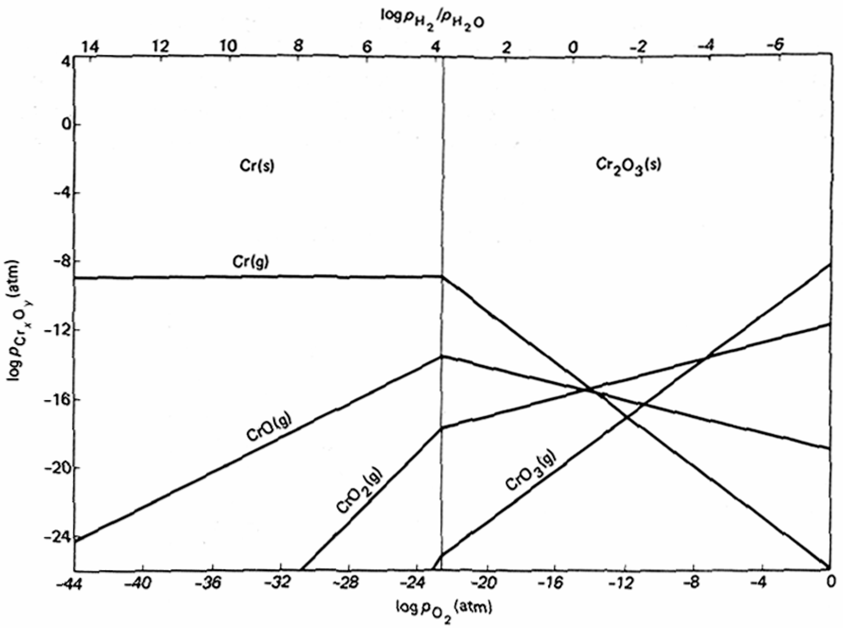
$$p_{CrO_3} = K^{\frac{1}{2}} a_{cr_2O_3}^{\frac{1}{2}} p_{O_2}^{\frac{3}{4}}$$

CHROMIA

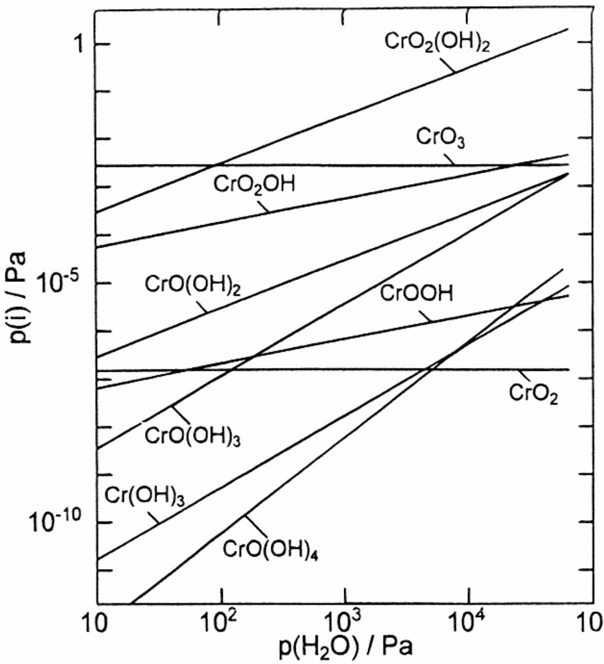
- At high T and high PO_2 volatile oxides develop

$$Cr_2O_3 + 3/2\ O_2 \rightarrow 2\ CrO_3(g)$$

$$Cr_2O_3 + 2\ H_2O + 3/2\ O_2 \rightarrow 2\ CrO_2(OH)_2$$



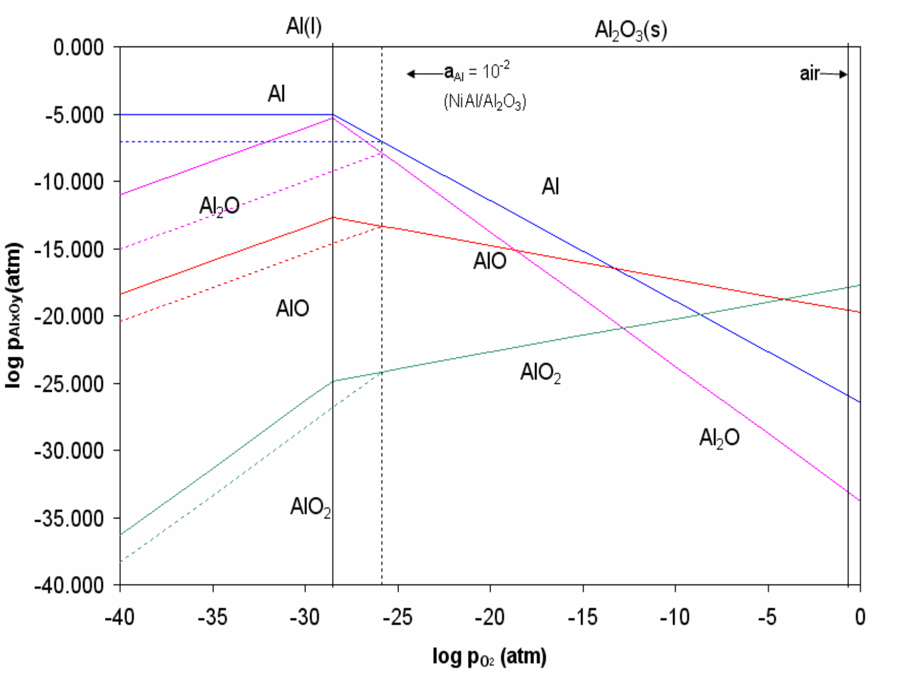
Cr-O volatile species at 1250K



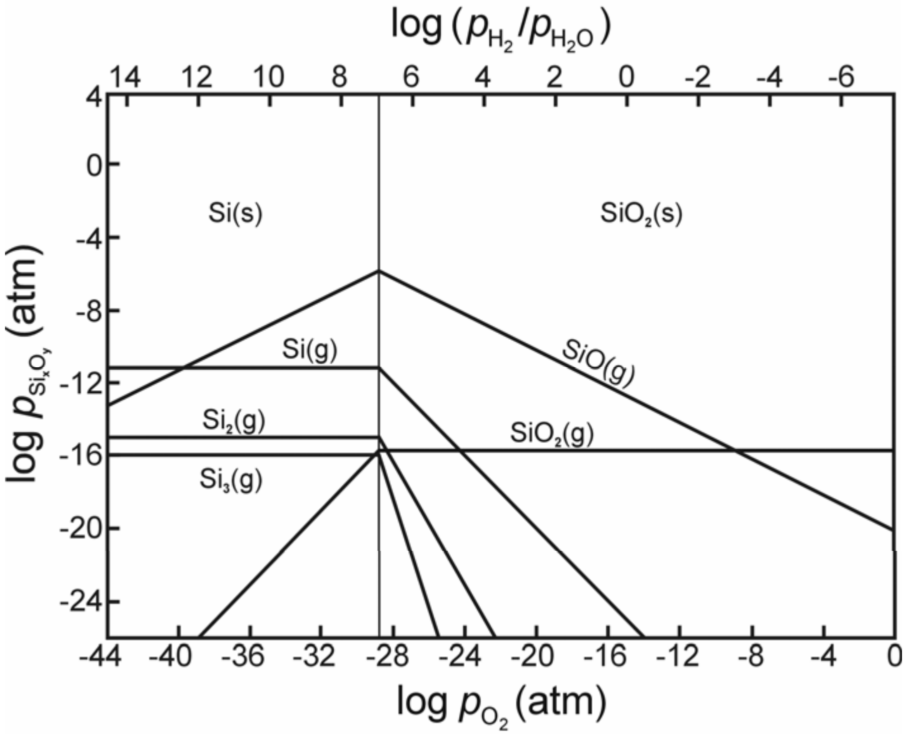
Partial pressures over Cr_2O_3 at 950C in humid air (PO_2=0.21 atm) with different H_2O partial pressures

Vapor Species Diagrams for the Al-O and Si-O Systems

Al – O 1473K



Si – O 1250K



Diffusion Fundamentals

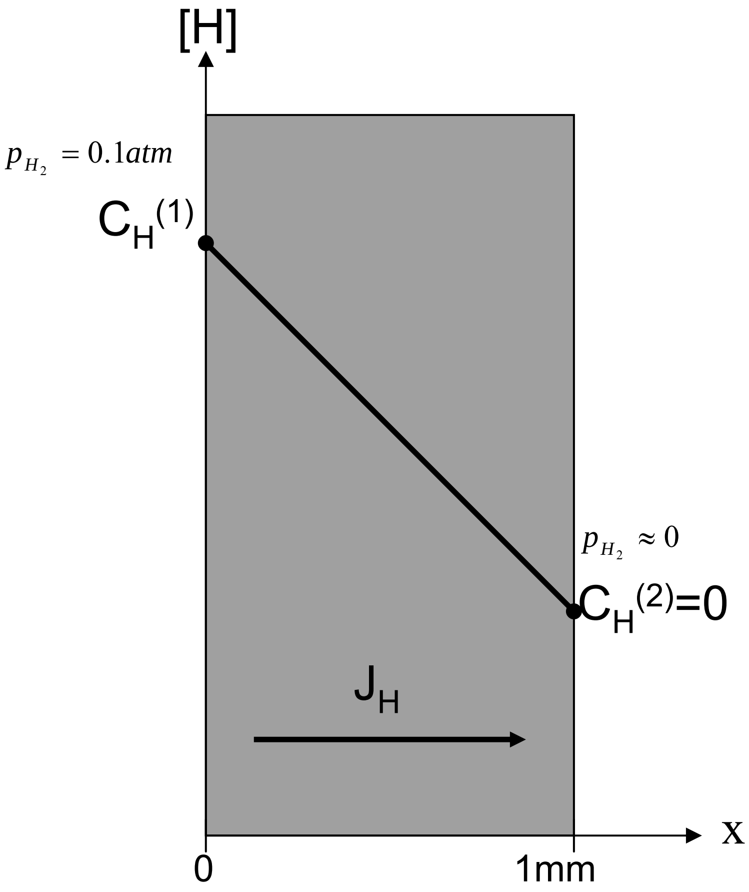
$$J_B = -\tilde{D}\frac{\partial C_B}{\partial x}$$

Fick's First law

$$\frac{\partial C_B}{\partial t} = \tilde{D}\frac{\partial^2 C_B}{\partial x^2}$$

Fick's Second Law

Steady State Diffusion of H_2 Through Ni
T=800°C



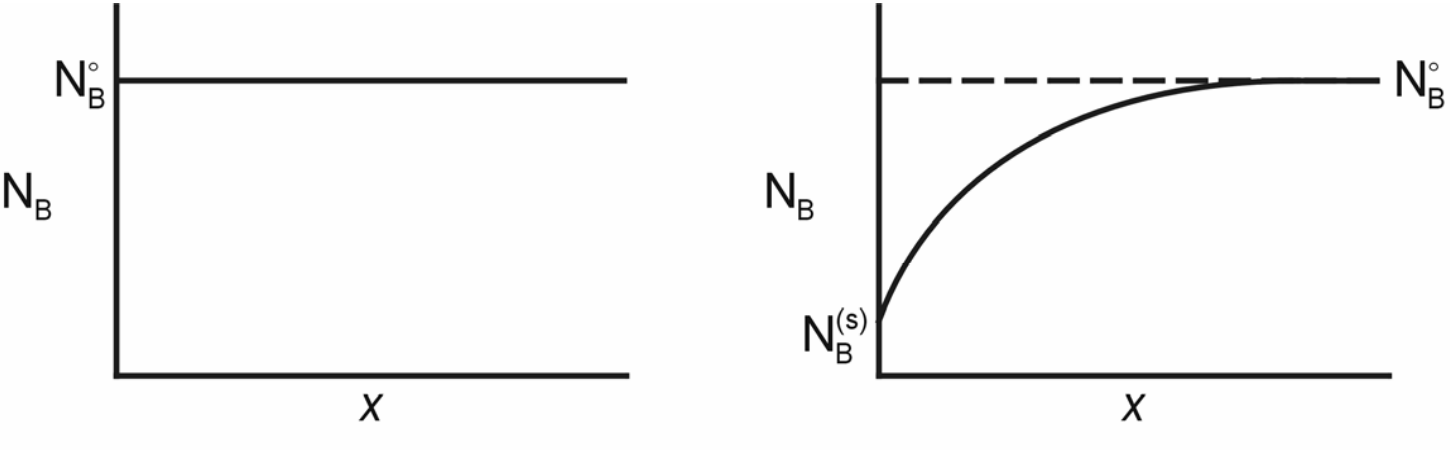
$$J_H = -D_H \frac{dc}{dx} = -D_H \frac{C_H^2 - C_H^1}{x}$$

$$J_H = D_H \frac{C_H^1}{x} = 6.88x10^{-5}(cm^2/s)\frac{2.09x10^{-5}(g/cm^3)}{0.1(cm)}$$

$$J_H = 1.44x10^{-8}(g/cm^2 \cdot s)$$

Fick's Second Law

Concentration Profile for a Solute B Being Lost by Evaporation



$$\frac{\partial N_B}{\partial t} = \tilde{D}\frac{\partial^2 N_B}{\partial x^2}$$

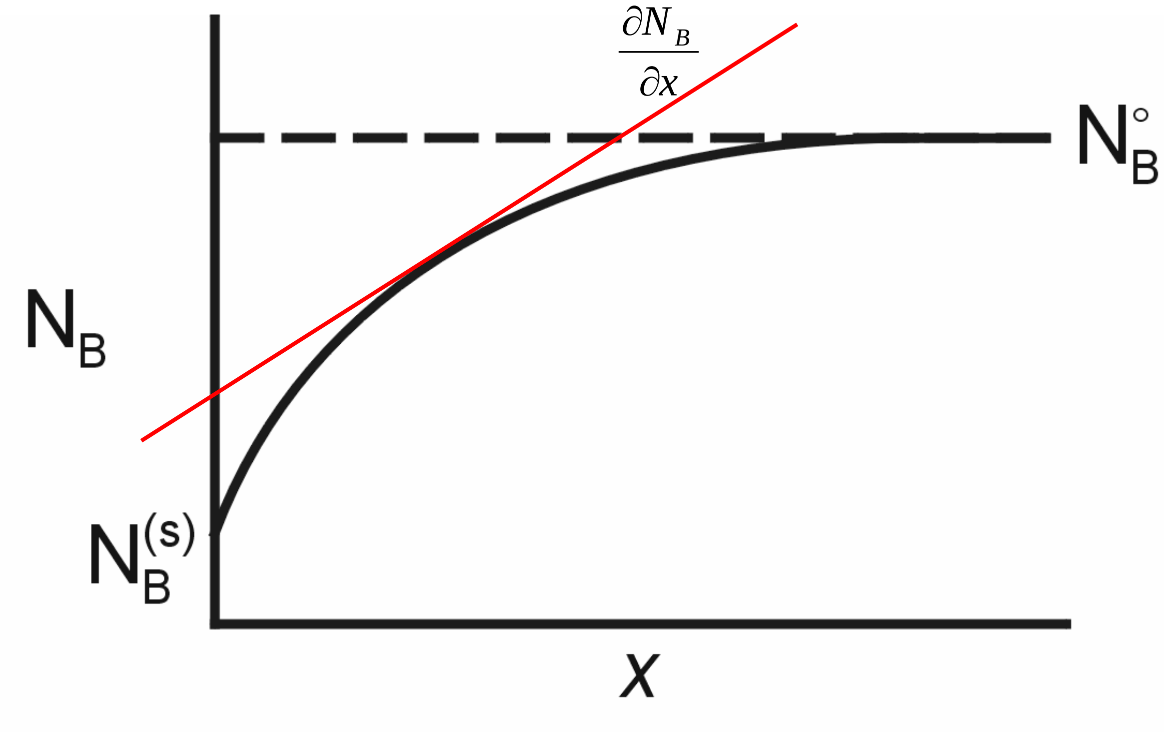
Boundary Conditions: At time t: $N_B = N_B^{(S)}$ at $x = 0$

$N_B = N_B^{o}$ at $x = \infty$

Solution $$N_B = N_B^S + \left(N_B^o - N_B^S\right) erf\left(\frac{x}{2\sqrt{Dt}}\right) \qquad x \geq 5\sqrt{Dt}$$

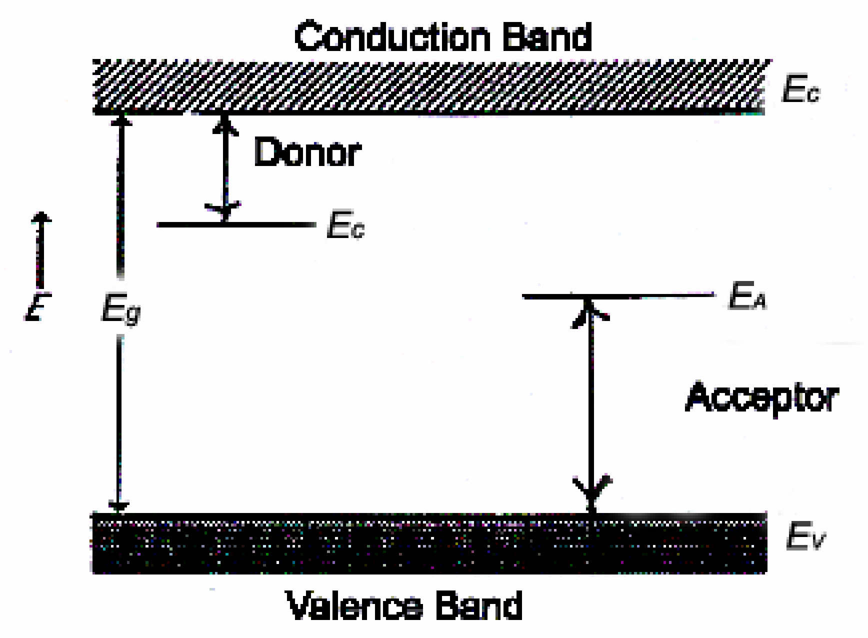
General Solution $$N_B = A_1 + B_1 erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Calculation of Local Flux



$$J_B = -\tilde{D}\frac{\partial C_B}{\partial x} = -\tilde{D}V_m\frac{\partial N_B}{\partial x}$$

Point Defects in Semiconductors



- Intrinsic and Extrinsic Elemental Semiconductors

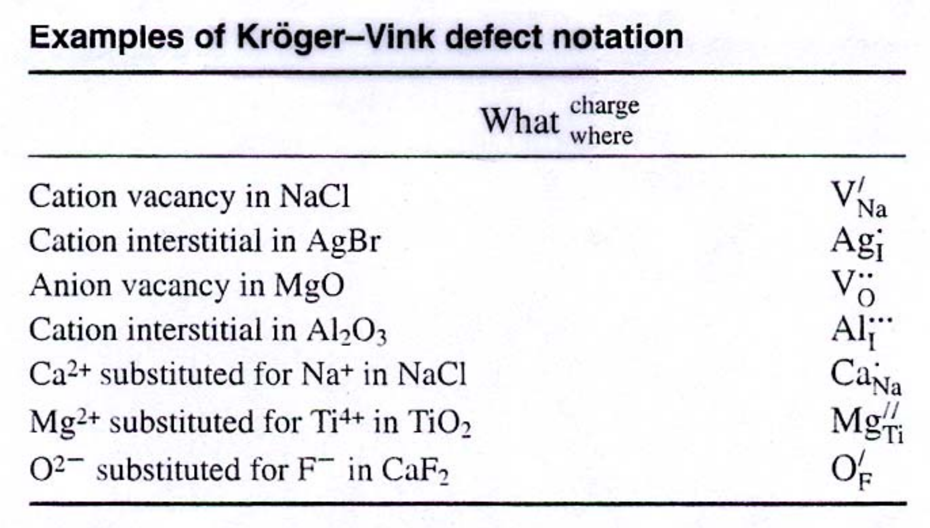
Intrinsic: $$n = p = K_i^\circ e^{-\frac{E_g}{2kT}}$$

Extrinsic: $$np = K_i^\circ e^{-\frac{E_g}{kT}}$$

-ionized native defects and dopants

Defects in Compounds (e. g. Oxides)
Defect Notations

- **The main symbol:** The defect species, which may be an ion, indicated by the atomic symbol for the species, or a vacant lattice site, denoted by V.
- **The subscript:** Indicates the lattice or interstitial site, I, occupied by the defect.
- **The superscript:** Indicates the difference in charge at the defect site relative to the charge at that site in the perfect crystal. A dot is used for an extra positive charge, and a slash denotes an extra negative charge.



Examples of Kröger–Vink defect notation

	$\text{What}^{\text{charge}}_{\text{where}}$
Cation vacancy in NaCl	V'_{Na}
Cation interstitial in AgBr	$Ag^{\bullet}_{I}$
Anion vacancy in MgO	$V^{\bullet\bullet}_{O}$
Cation interstitial in Al_2O_3	$Al^{\bullet\bullet\bullet}_{I}$
Ca^{2+} substituted for Na^+ in NaCl	$Ca^{\bullet}_{Na}$
Mg^{2+} substituted for Ti^{4+} in TiO_2	Mg''_{Ti}
O^{2-} substituted for F^- in CaF_2	O'_{F}

$$V'_{Na}$$

Important Defects:

Vacancies (cations and anions)
Interstitials
Foreign atoms
Electrons and holes
Charged defects
Various associated complexes

Conservation Rules

- **Conservation of mass:** Atoms are neither created nor destroyed within a system, but must be conserved
- **Conservation of charge:** The bulk of an ideal crystal is electrically neutral. Charged defects must be created in combinations that are electrically neutral. Matter can be added to or removed from a crystal only in electrically neutral combinations.
- **Conservation of structure** (lattice site ratios): The creation of lattice defects must not violate the inherent ratio of cation sites to anion sites in the structure. Thus cation and anion sites can be created or destroyed only in ratios that correspond to the stoichiometry of the compound (i.e., in electrically neutral combinations).
- **Conservation of electronic states:** The total number of electronic states in a system derives directly from the electronic states of the component atoms, and must be conserved.

Law of Mass Action is Applicable

aA + bB = cC + dD

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = e^{-\frac{\Delta G^\circ}{bT}}$$

Replace activities with concentrations

Stoichiometry and Defect Chemistry

Intrinsic Ionic Disorder is such that the stoichiometry of the compound is maintained.

Example: Schottky Disorder for the compound MX

$$Null = V_M' + V_X^\bullet$$

$$K_S = [V_M'][V_X^\bullet]$$

Extrinsic Ionic Disorder usually involves the addition of a dopant, but there are also cases where such disorder can be established by reactions of the compound with the gas and stoichiometry is not maintained.

Dopant $$Al_2O_3 \xrightarrow{NiO} 2Al_{Ni}^\bullet + 3O_O^x + V_{Ni}''$$

Gas Reaction $$\tfrac{1}{2}O_2 \xrightarrow{NiO} O_O^x + V_{Ni}'' + 2h^\bullet$$

Construction of a Kroger-Vink Diagram

Pure MX

No Dopant - Schottky Defects

$$[V_M'][V_X^\bullet] = K_s$$

$$np = K_i$$

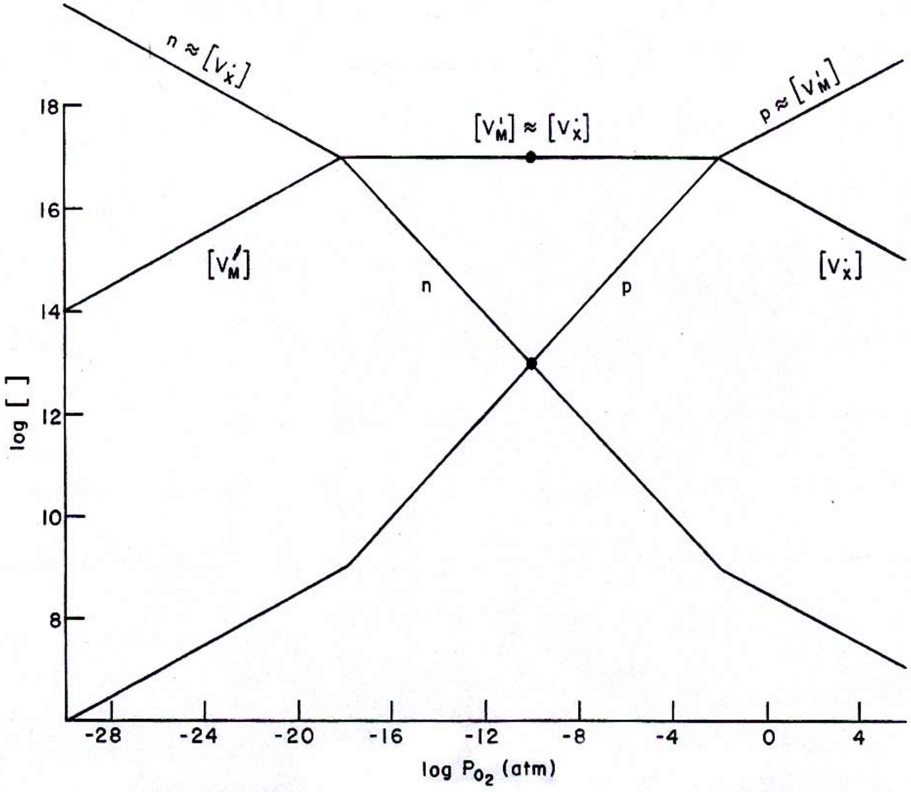
Equilibration with Atmosphere

$$\tfrac{1}{2}X_2(g) = X_X^x + V_M' + h^\bullet$$

$$K_R = \frac{[V_M']p}{P_{X_2}^{1/2}}$$

Electrical Neutrality

$$n + [V_M'] = p + [V_X^\bullet]$$



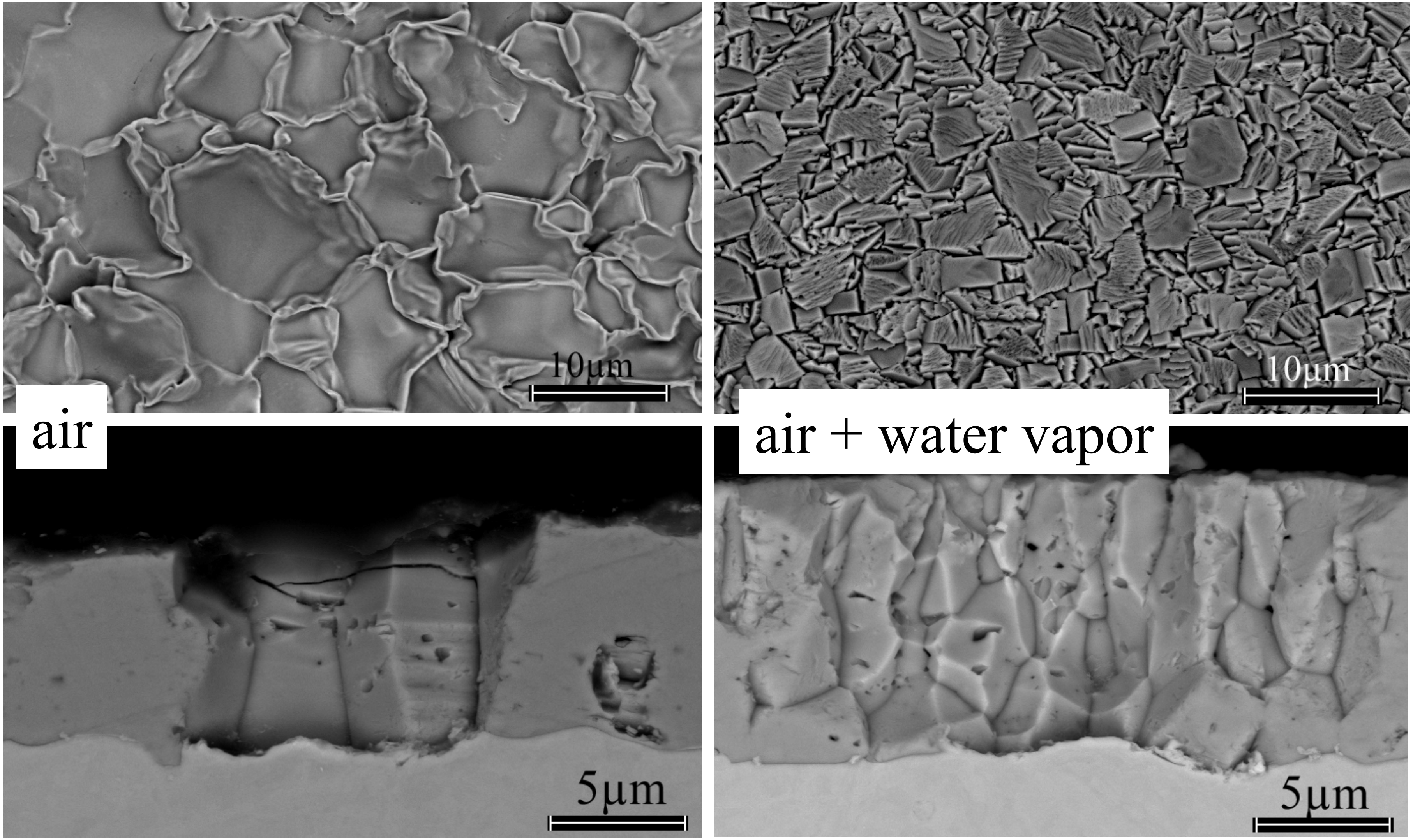
The Kröger-Vink diagram for MX. $K_S > K_i$

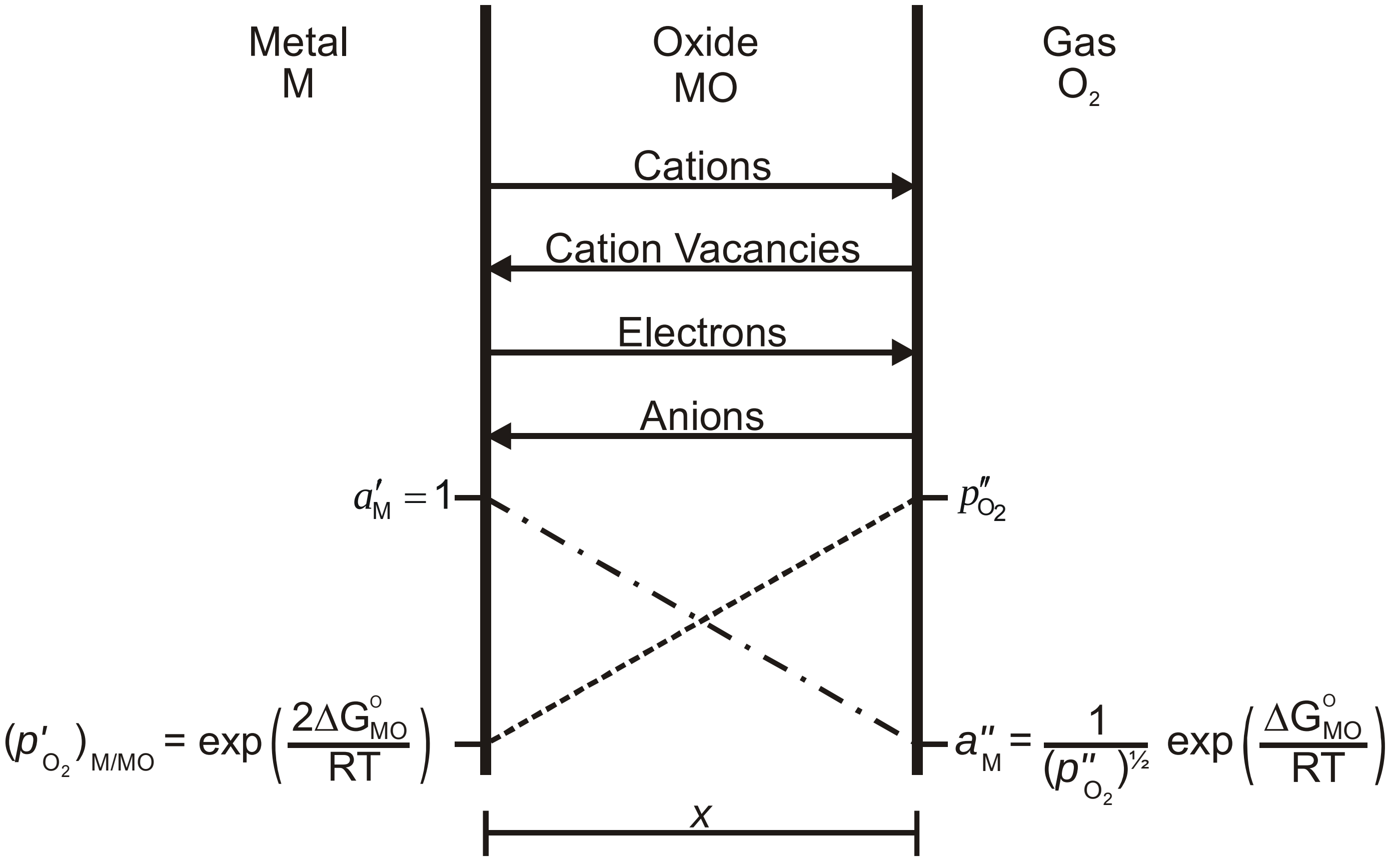
Growth of Oxides on Pure Metals

Focus on Diffusion-Controlled Growth

1. Simple Parabolic Oxidation Model
2. Effect of Oxygen Partial Pressure
3. Bulk vs. Grain Boundary Diffusion

Pure Ni exposed for 1 hour @ 1100°C





$M = M^{2+} + 2e^-$

or

$M + O^{2-} = MO + 2e^-$

$M^{2+} + 2e^- + \frac{1}{2}O_2 = MO$

or

$\frac{1}{2}O_2 + 2e^- = O^{2-}$

Overall reaction: $2M + O_2 = 2MO; \Delta G^\circ_{MO}$

Simplified Treatment of Diffusion-Controlled Oxidation

$$j_{M^{2+}} = -j_{V_M} = D_{V_M} \frac{C_{V_M}'' - C_{V_M}'}{x}$$

$$j_{M^{2+}} = \frac{1}{V_{ox}} \frac{dx}{dt} = D_{V_M} \frac{C_{V_M}'' - C_{V_M}'}{x}$$

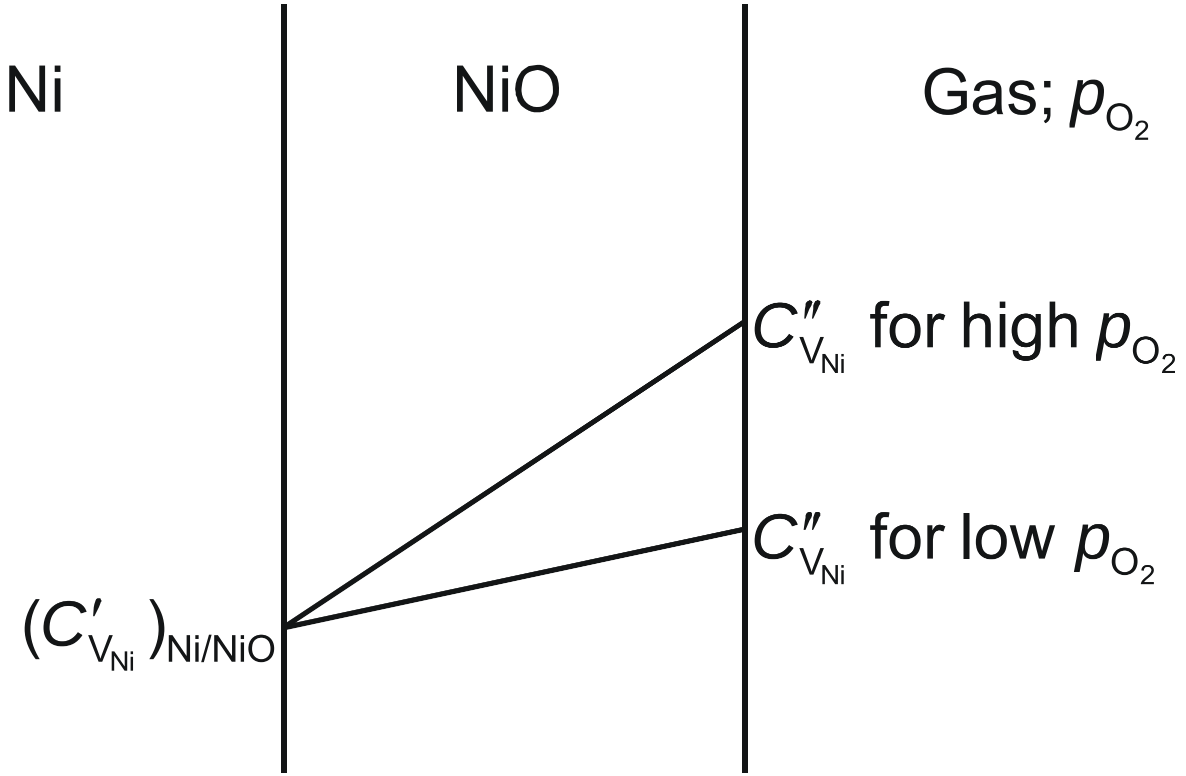
$$\frac{dx}{dt} = \frac{k'}{x}$$

$$k' = D_{V_M} V_{ox} (C_{V_M}'' - C_{V_M}')$$

$$x^2 = 2k't$$

Effect of oxygen partial pressure

(p-type oxide)



Ni

NiO

Gas; p_{O_2}

$C''_{V_{Ni}}$ for high p_{O_2}

$C''_{V_{Ni}}$ for low p_{O_2}

$(C'_{V_{Ni}})_{Ni/NiO}$

Effect of oxygen partial pressure

$$\tfrac{1}{2}O_2 = O_O^X + 2h^{\cdot} + V_{Ni}''$$

$$C_h^2 C_{V_{Ni}''} = K p_{O_2}^{1/2}$$

Electroneutrality Condition

$$C_h = 2C_{V_{Ni}''}$$

$$C_{V_{Ni}''} = const.\,p_{O_2}^{1/6}$$

General for p-type Scales

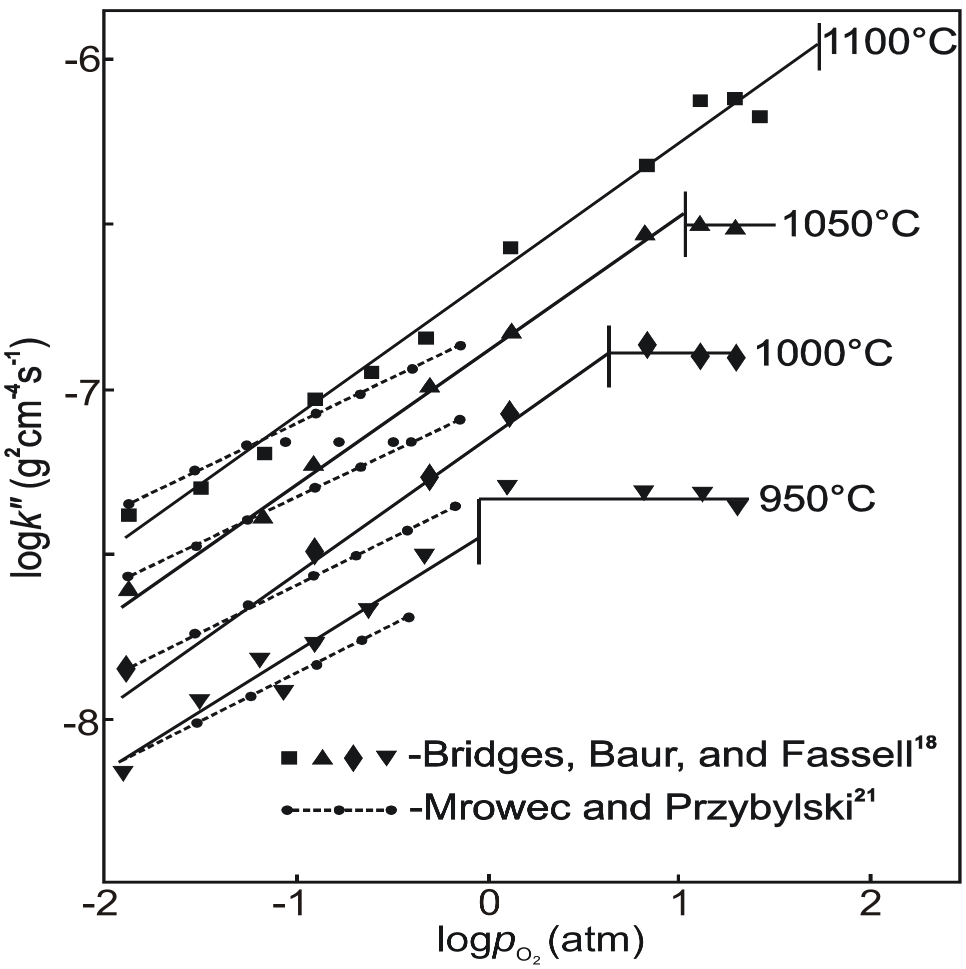
$$C_{V_M} = const.\,p_{O_2}^{1/n}$$

$$k' \propto \left[\left(p_{O_2}''\right)^{1/n} - \left(p_{O_2}'\right)^{1/n}\right]$$

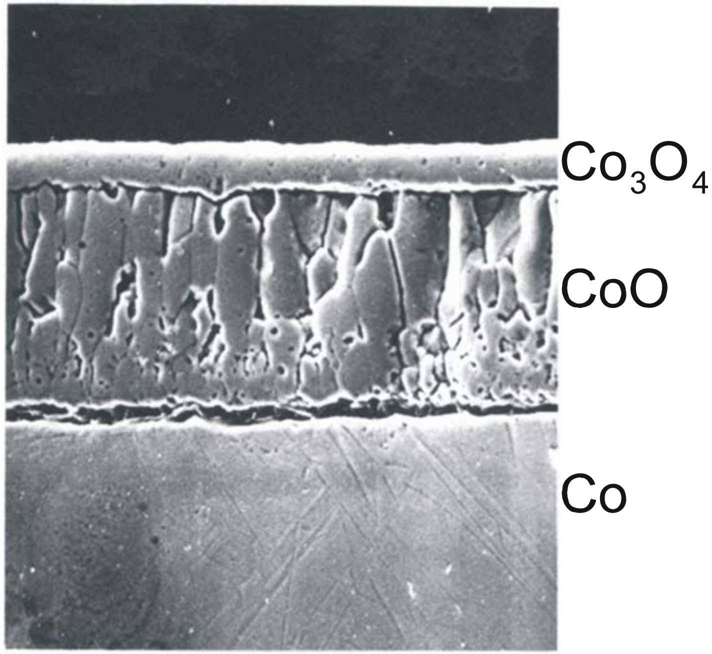
$$k' \propto \left(p_{O_2}''\right)^{1/n}$$

Effect of oxygen partial pressure

Oxidation of Co

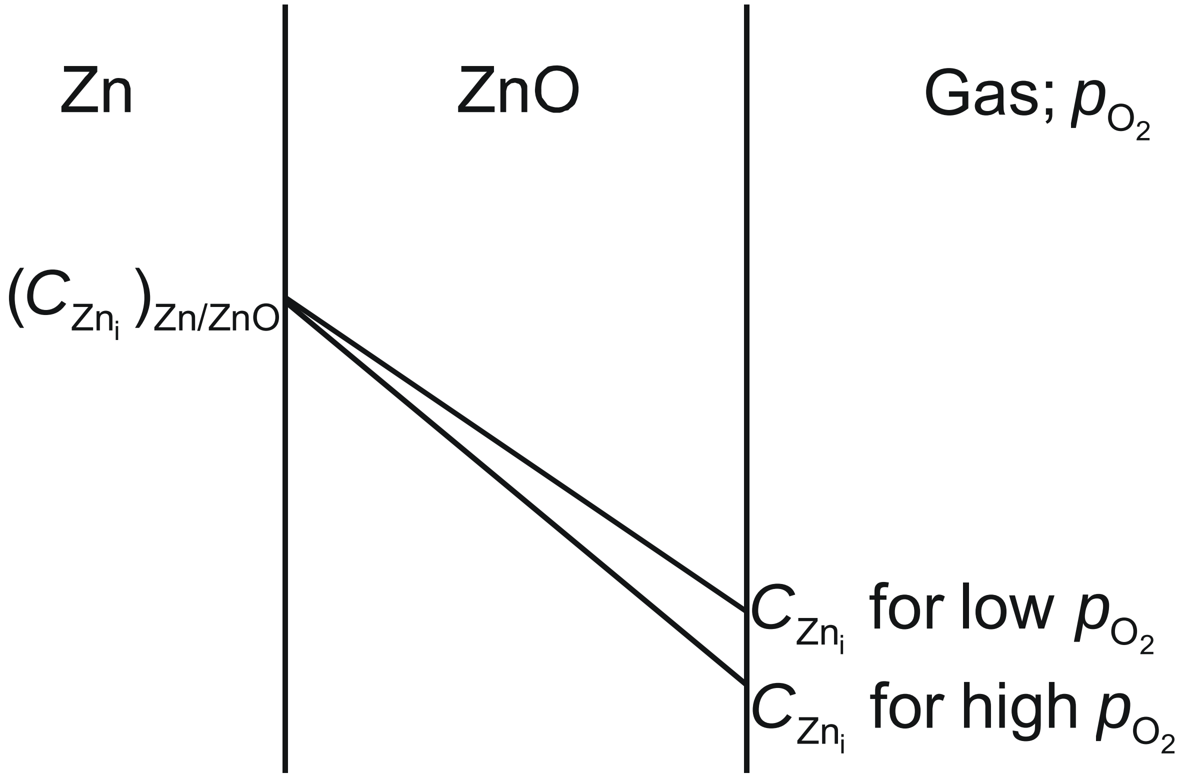


Cross-section of Co oxidized in Air at 750°C



Effect of oxygen partial pressure

(n-type oxide)



Effect of oxygen partial pressure

$$j_{M^{2+}} = \frac{1}{V_{ox}}\frac{dx}{dt} = D_{M_i}\frac{C'_{M_i} - C''_{M_i}}{x}$$

$$k' = D_{M_i} V_{ox}(C'_{M_i} - C''_{M_i})$$

$$ZnO = Zn_i^{\cdot\cdot} + 2e' + \tfrac{1}{2}O_2$$

$$K_1' = C_{Zn_i^{\cdot\cdot}} C_{e'}^2 p_{O_2}^{1/2}$$

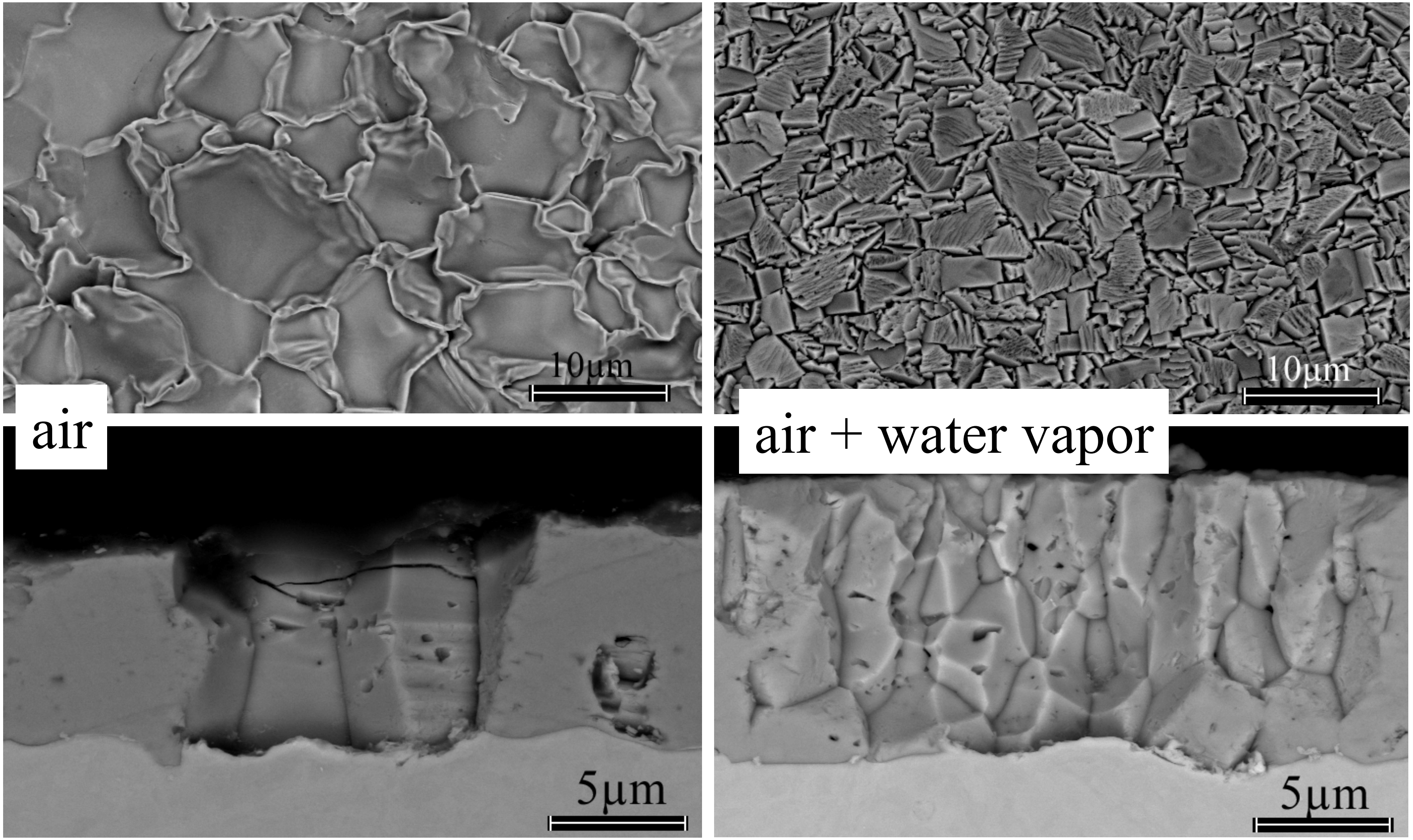
$$2C_{Zn_i^{\cdot\cdot}} = C_{e'}$$

$$K_1' = 4C_{Zn_i^{\cdot\cdot}}^3 p_{O_2}^{1/2}$$

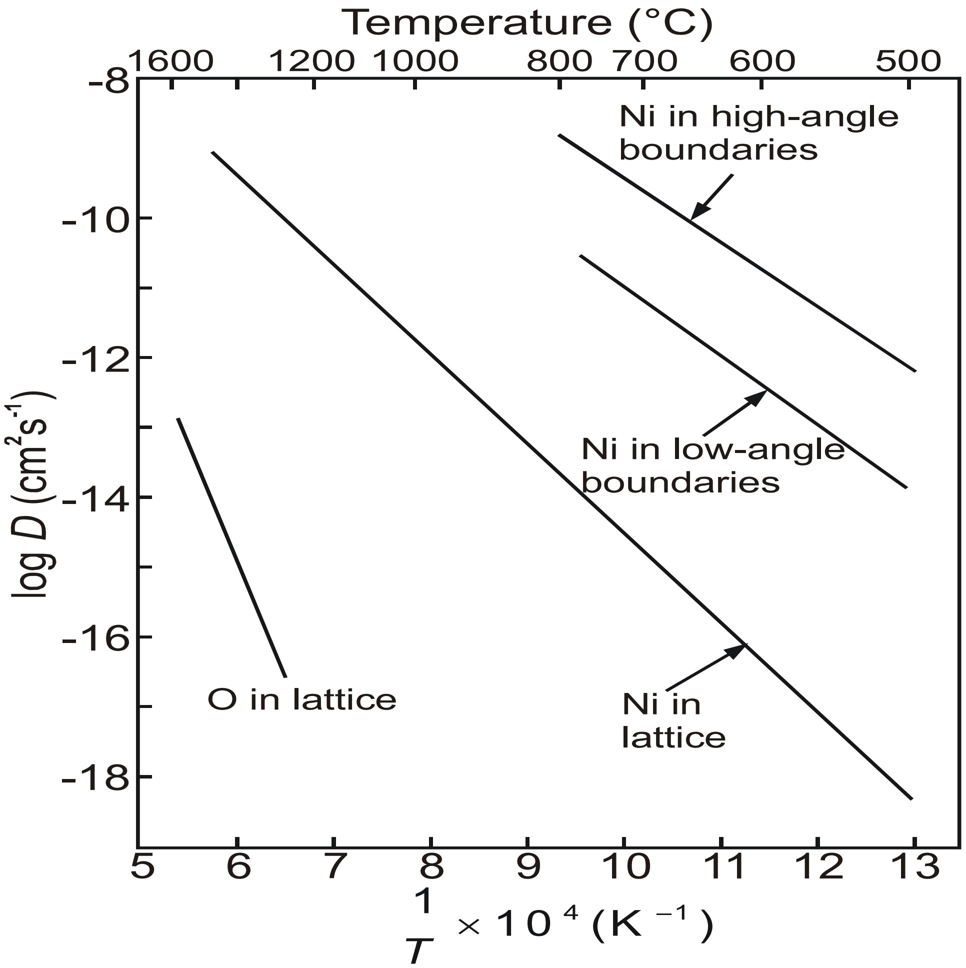
$$C_{Zn_i^{\cdot\cdot}} = \left(K_1'/4\right)^{1/3} p_{O_2}^{-1/6} = const.p_{O_2}^{-1/6}$$

$$k'_{ZnO} = const.'\left[\left(\frac{1}{p_{O_2}'}\right)^{1/6} - \left(\frac{1}{p_{O_2}''}\right)^{1/6}\right] \qquad k' \neq f\left(p_{O_2}\right)$$

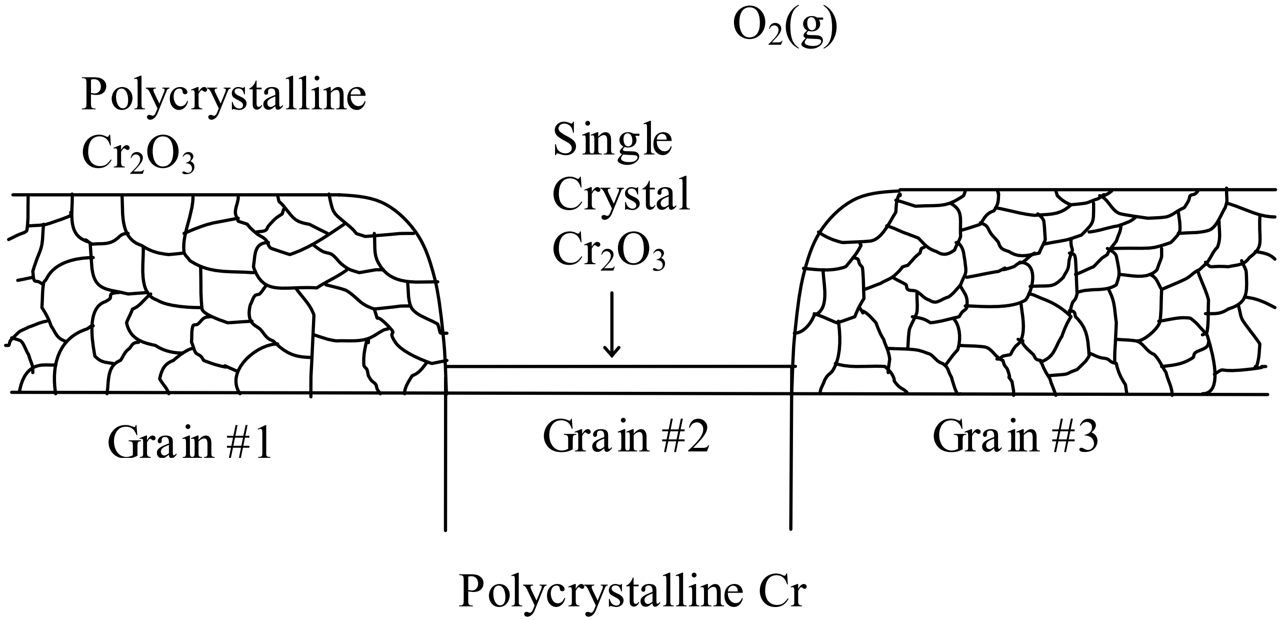
Pure Ni exposed for 1 hour @ 1100°C



Transport Paths - NiO

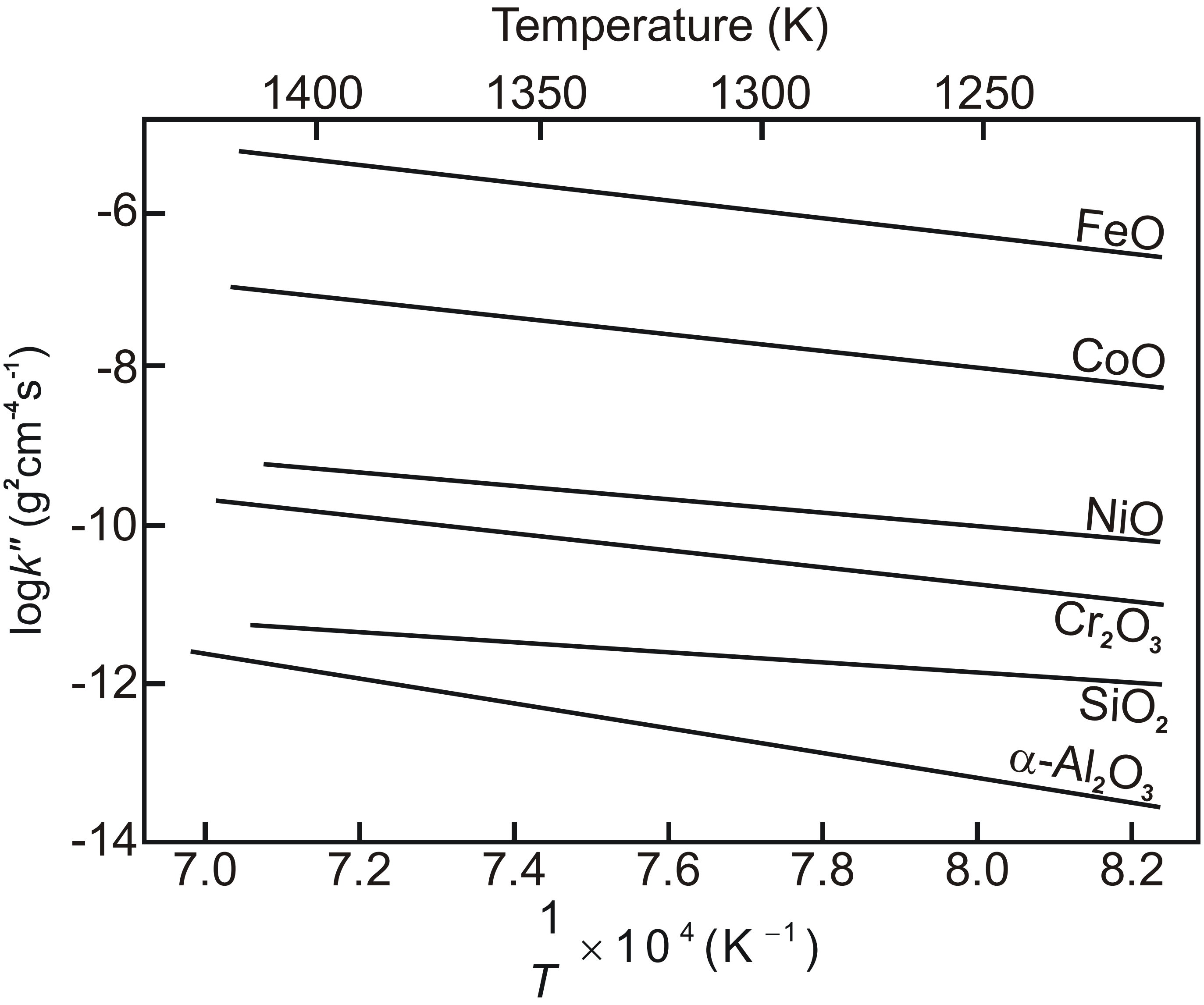


Oxidation of Chromium



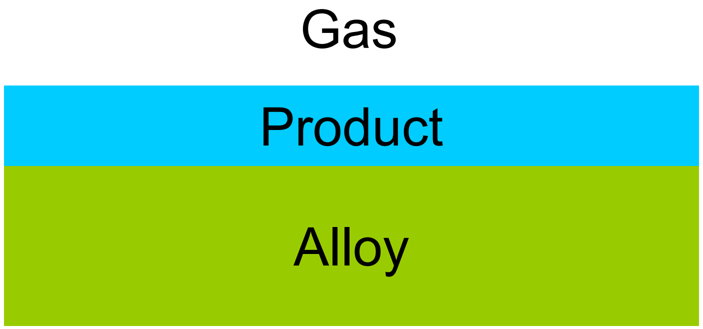
Caplan, D. and Sproule, G. I., *Oxid. Metals*, **9** (1975) 459

Relative growth rates of several oxides



Selective Oxidation

The approach to developing high temperature corrosion resistance in alloys is to have the reactants, namely the alloy and the gas, form a reaction product that separates the reactants and that allows slow transport of the reactants through it.



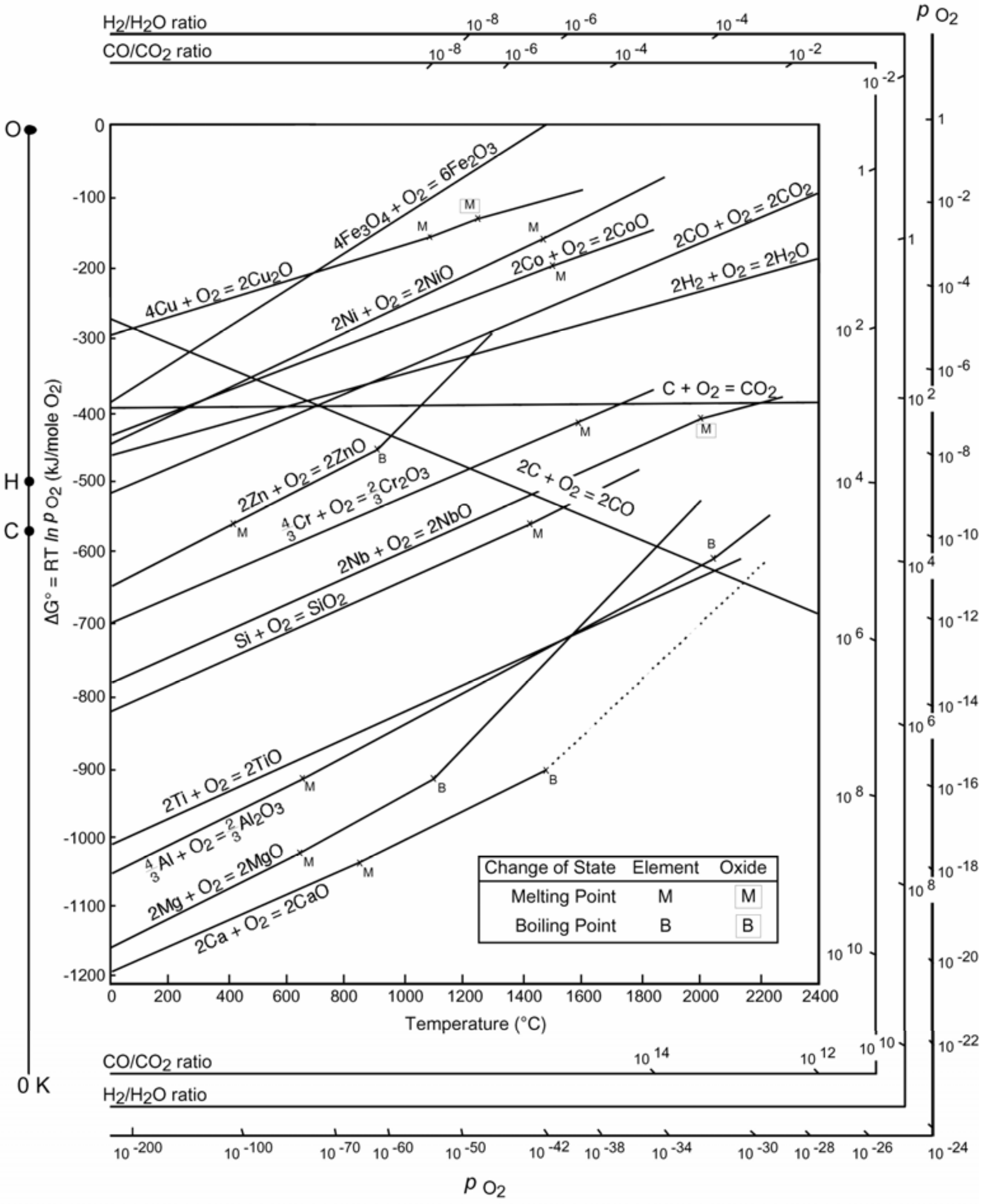
Gas

Product

Alloy

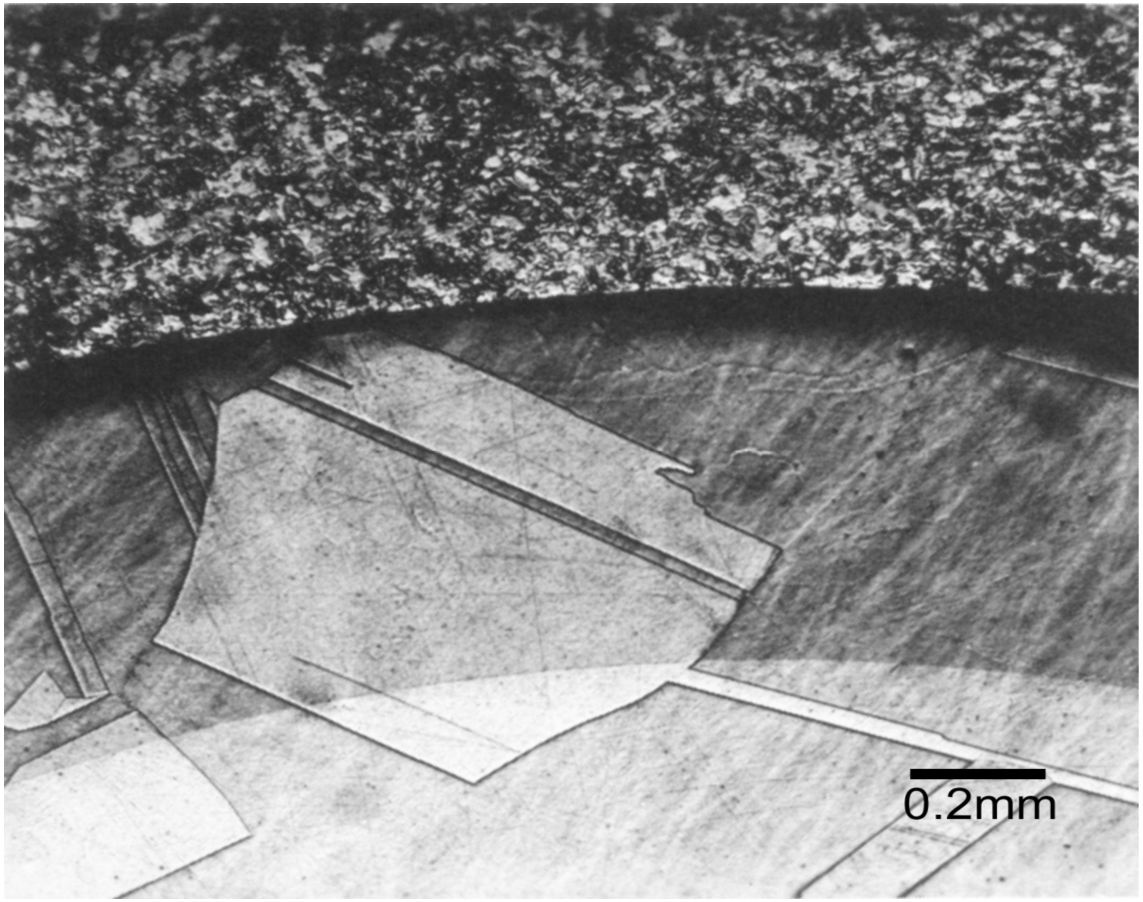
Most environments encountered in practice contain some oxygen, hence protective barriers are usually α-Al_2O_3, Cr_2O_3 and SiO_2.

Ellingham (Richardson) Diagram



Internal Oxidation

$T = 700 - 900^{o}C$

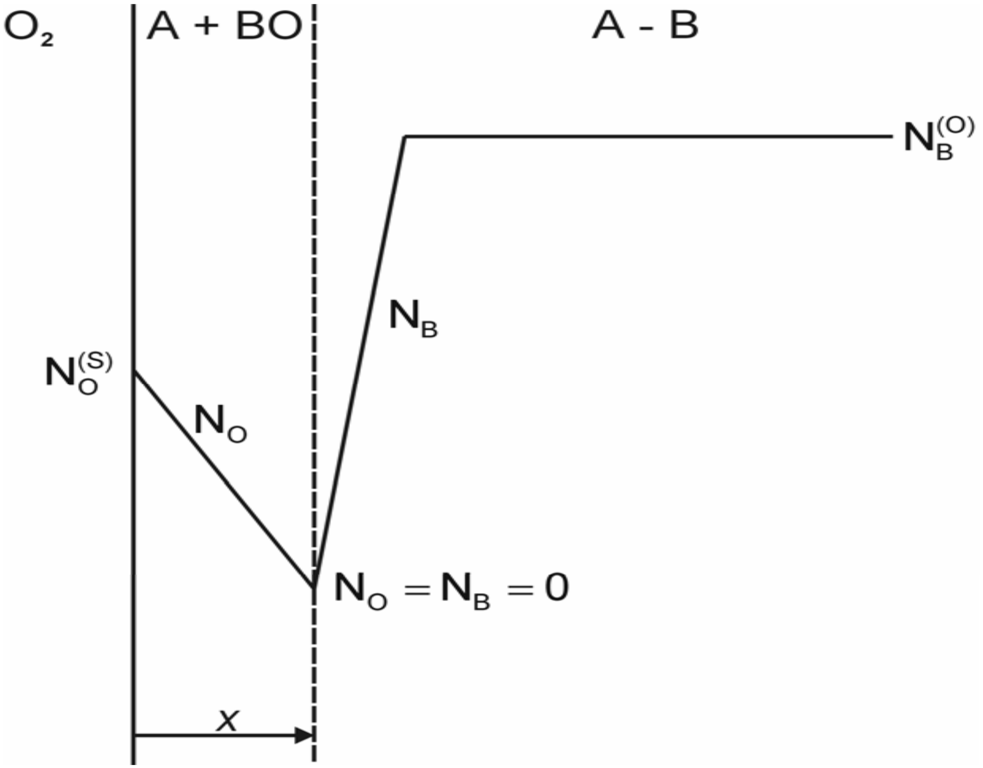


Mount

Internal oxidation zone

Cu-1 wt%Ti Alloy

Internal Oxidation Kinetics



$$J_O = \frac{dm}{dt} = D_O \frac{N_O^{(S)}}{XV_m} \quad \text{(moles cm}^{-2}\text{s}^{-1}\text{)}$$

$$m = \frac{N_B^{(o)} \nu X}{V_m} \quad \text{(moles cm}^{-2}\text{s}^{-1}\text{)}$$

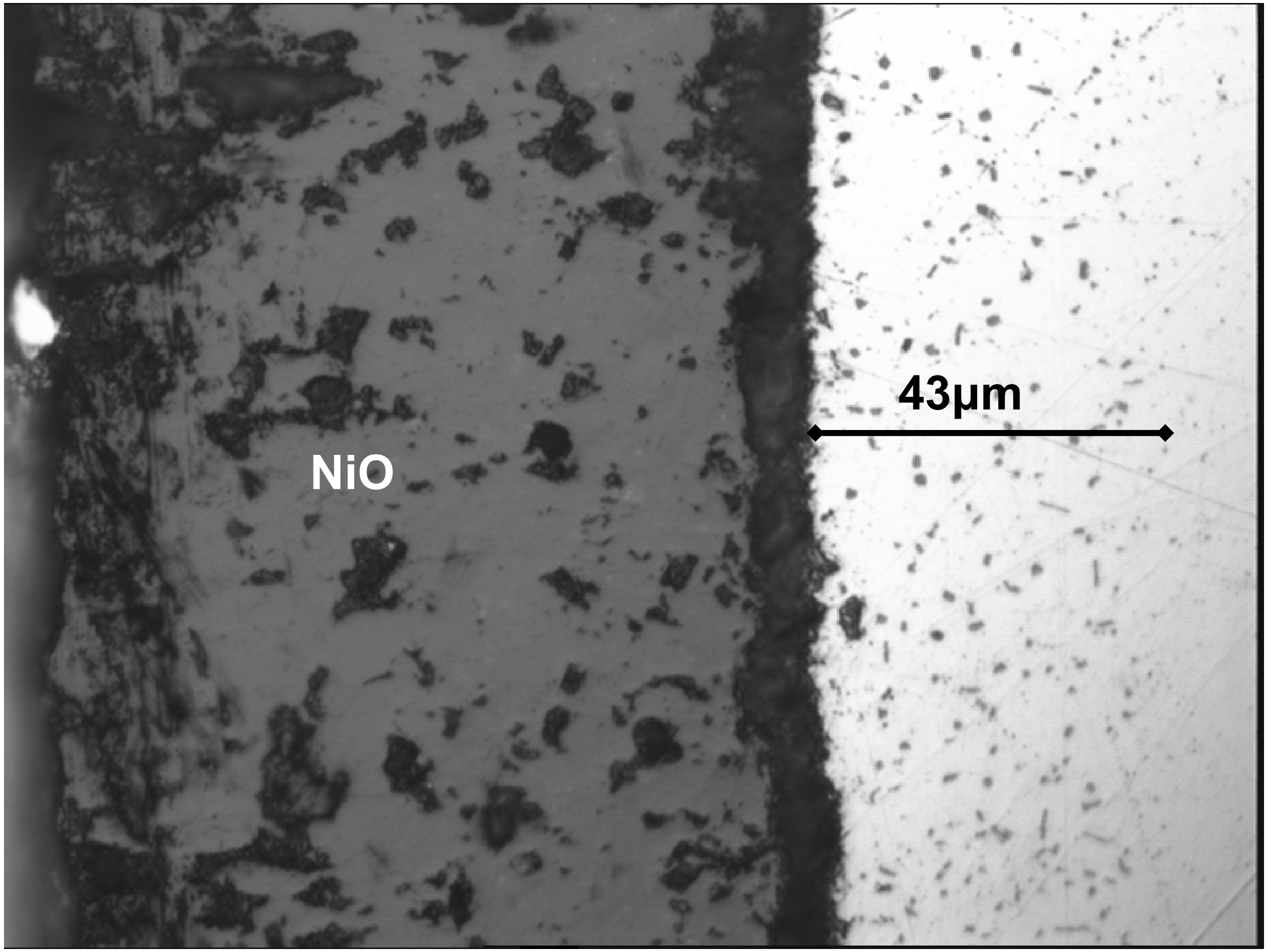
$$\frac{dm}{dt} = \frac{N_B^{(o)} \nu}{V_m} \frac{dX}{dt}$$

$$D_O \frac{N_O^{(S)}}{XV_m} = \frac{N_B^{(o)} \nu}{V_m} \frac{dX}{dt}$$

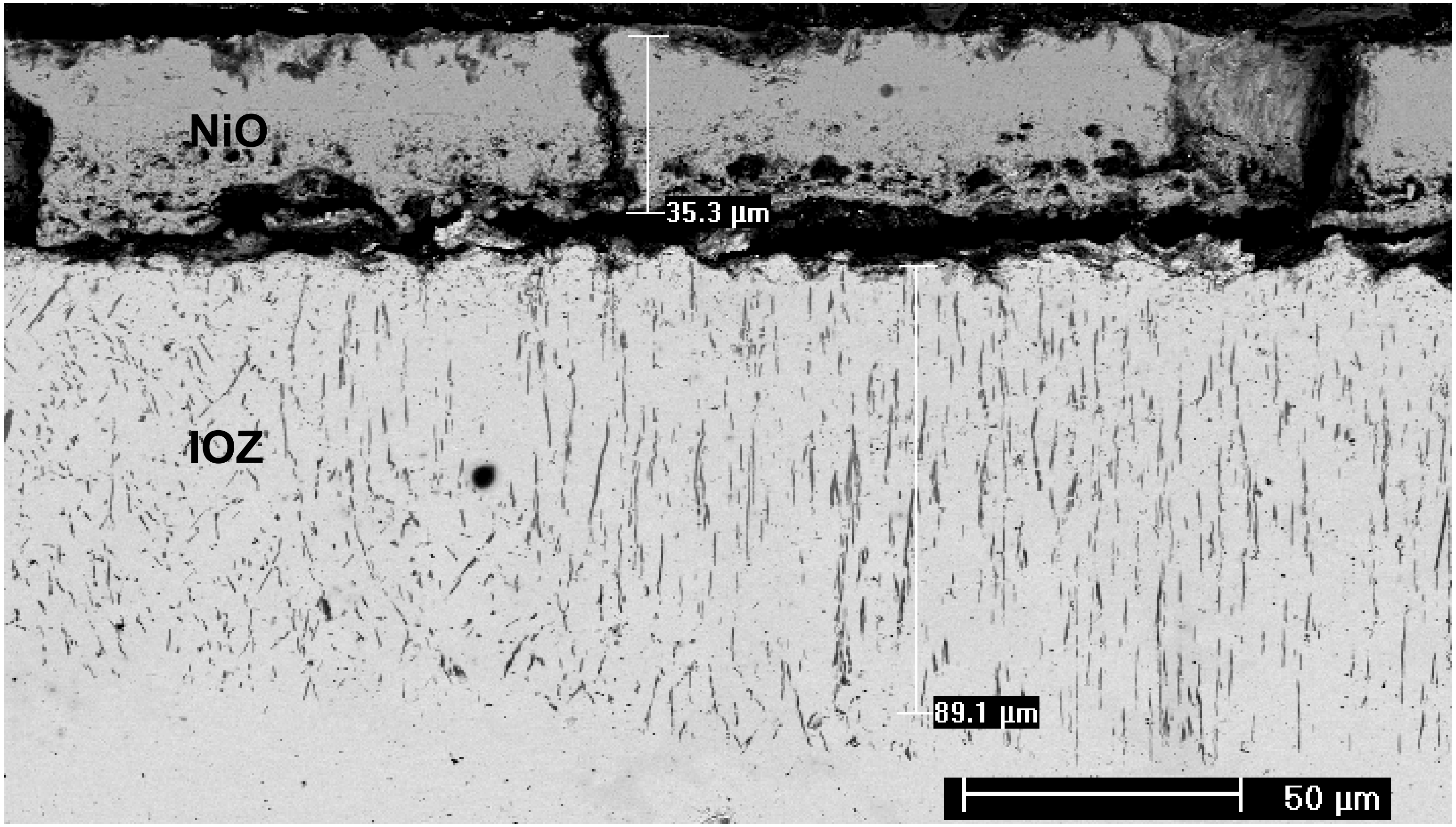
$$XdX = \frac{N_O^{(S)} D_O}{\nu N_B^{(o)}} dt$$

$$X = \left[\frac{2 N_O^{(S)} D_O}{\nu N_B^{(o)}} t \right]^{1/2}$$

Ni -1 wt%Cr - Dry Air
T = 1000°C, t = 24h



Ni - 1wt% Al - Dry Air
T = 1000°C, t = 24h



Apparent Oxygen Permeability in Ni

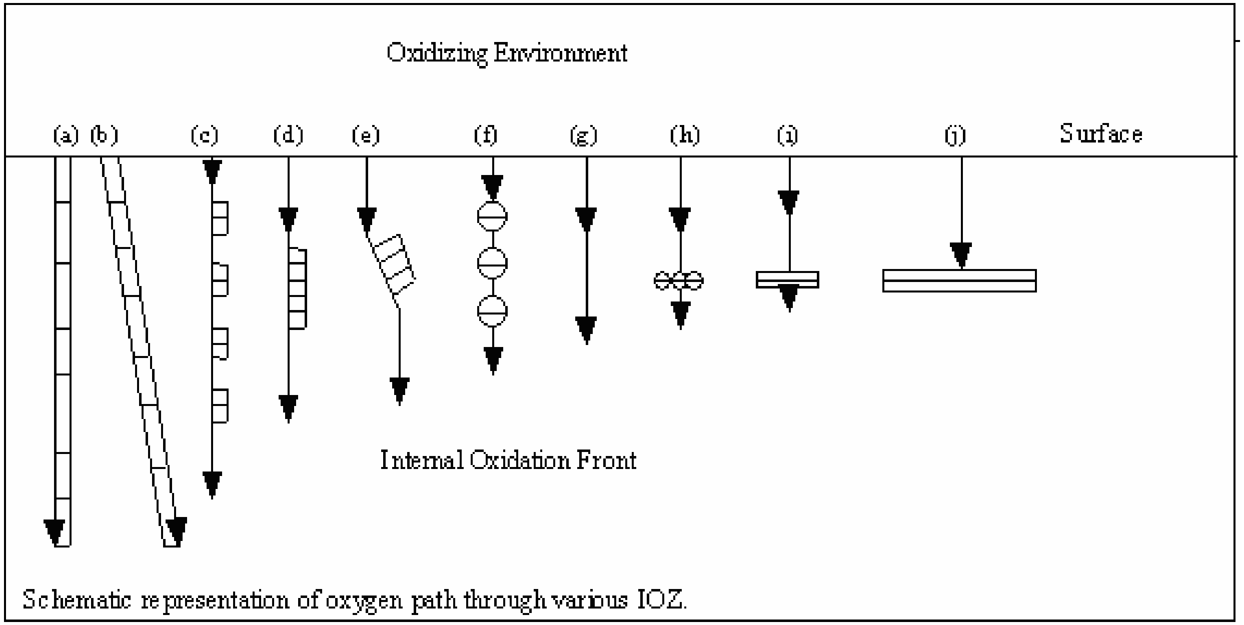
- **J-W Park and C. J. Altstetter, Met. Trans. A, <u>18A</u>, 43 (1987)**

  At 1000°C: $N_O^{(S)}D_O$ = 4.2 x 10^{-12} cm^2/s

$$\left(N_O^{(S)}D_O\right)_{App.} = \left[\frac{X^2 \nu N_B^{(o)}}{2t}\right] = \frac{0.75 N_B^{(o)} X^2}{8.64x10^4 s}$$

Alloy	N_B	Atmosphere	X (µm)	$(N_O D_O)_{App}$ (cm^2/s)
Ni-1Cr	0.0113	Dry Air	42.9	1.8 x 10^{-12}
Ni-1Al	0.0215	Dry Air	89.1	1.5 x 10^{-11}

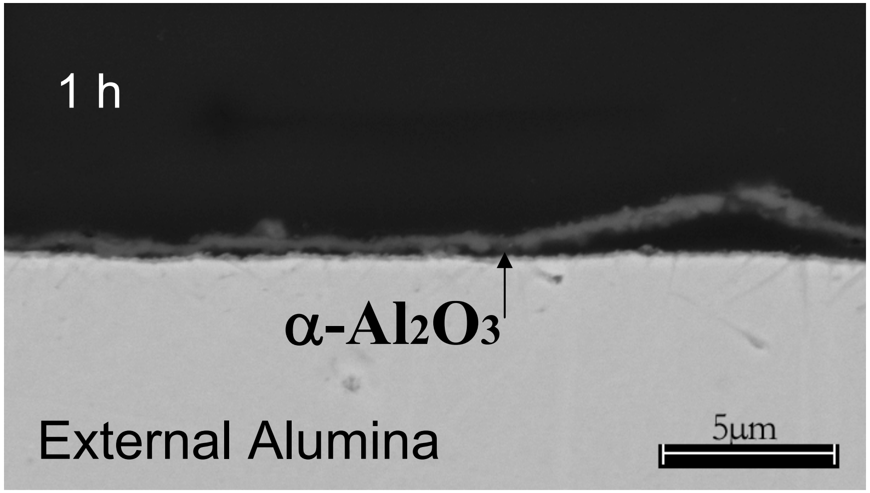
Effect of Internal Oxide Morphology on Apparent Oxygen Permeability

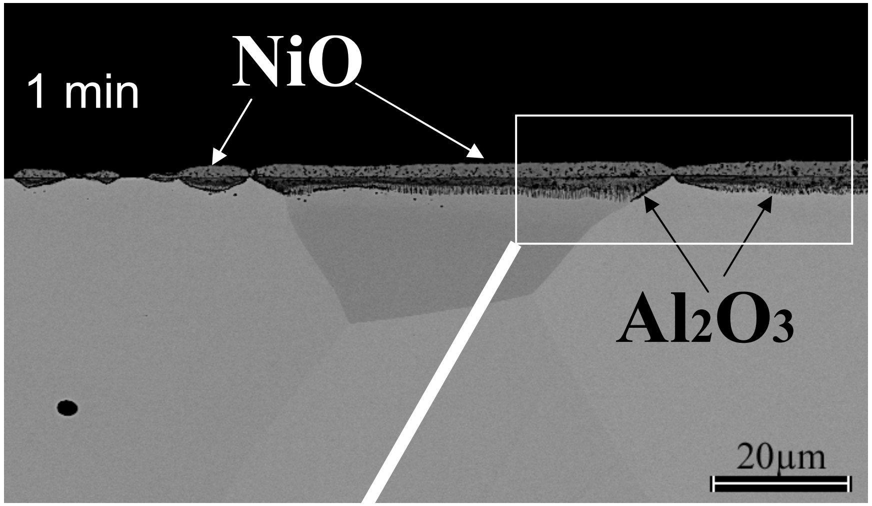


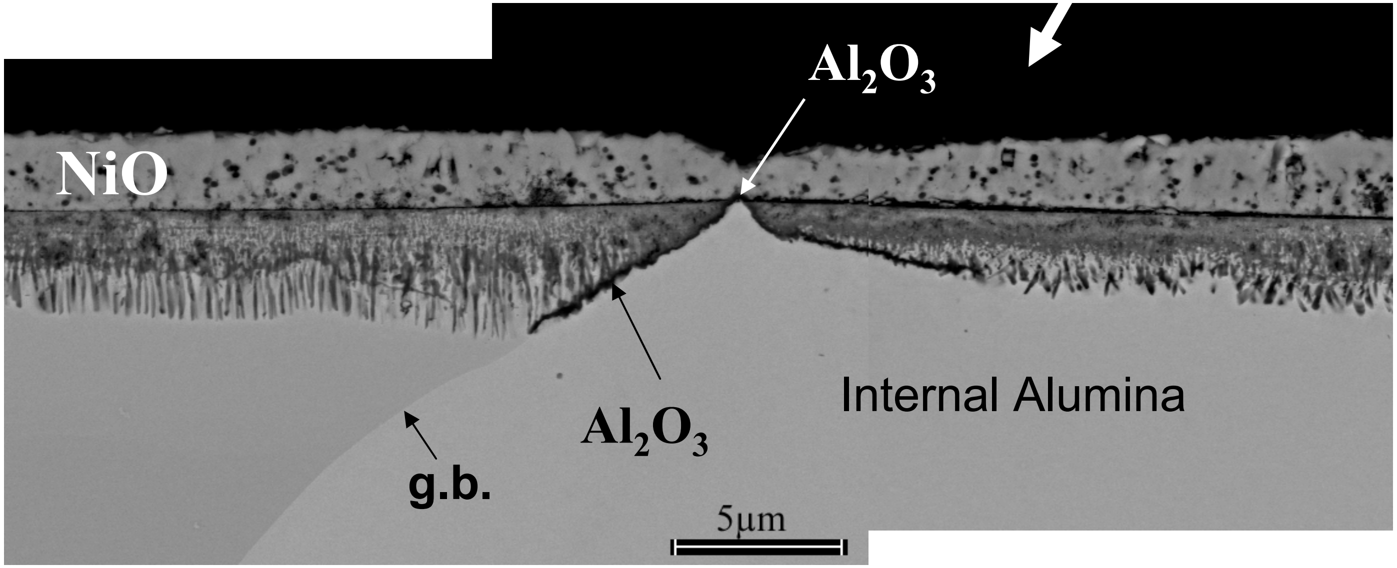
Schematic representation of oxygen path through various IOZ.

F. H. Stott, G. C. Wood: Materials Science and Technology, 4, 1072 (1988).

Cross-sections of Ni-8Cr-6Al oxidized @ 1100°C

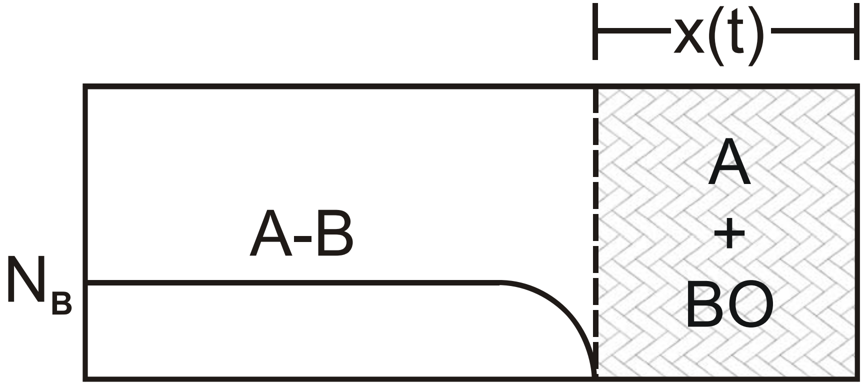




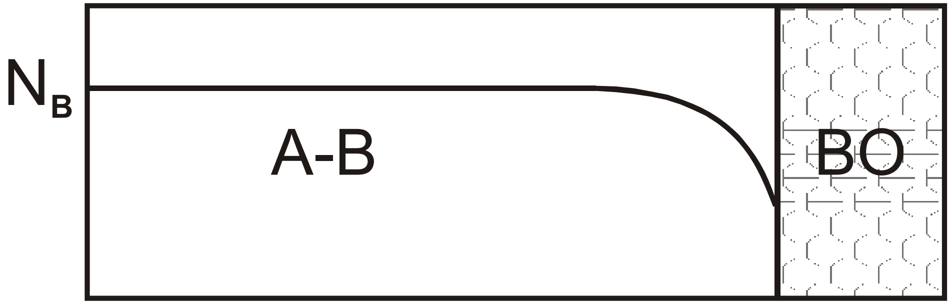


Transition to External Scale Formation

a.



b.



Transition to External Scale Formation

Equating the molar flux of solute B to that required to create a critical volume fraction of oxide $\frac{fAdX}{V_m} = \left[\frac{AD_B}{V_m}\frac{\partial N_B}{\partial x}\right]dt$

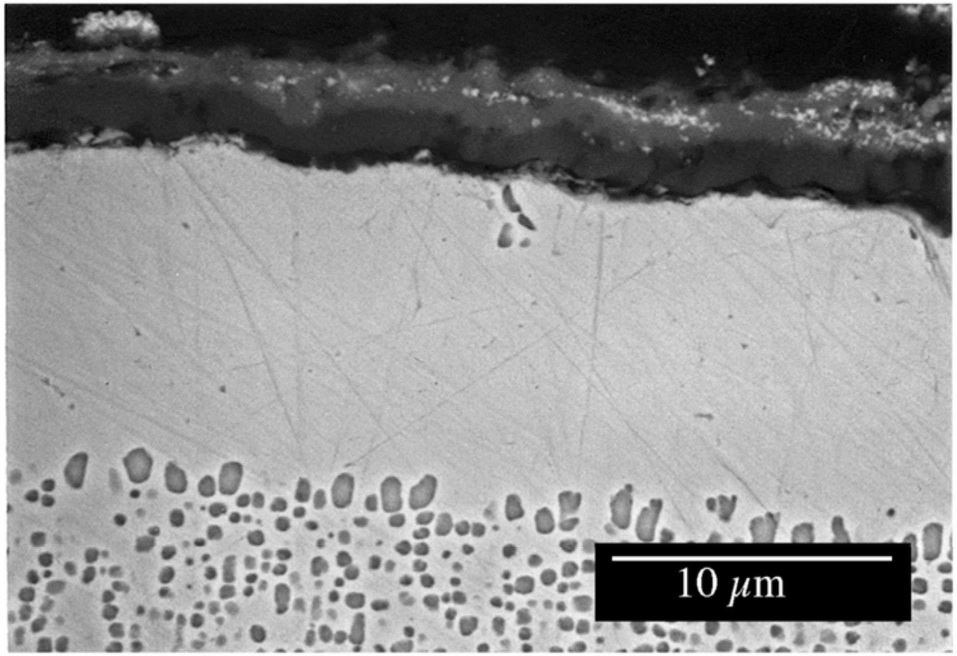
$$N_B^{(o)} > \left[\frac{\pi g^*}{2\nu} N_O^{(S)} \frac{D_O V_m}{D_B V_{ox}}\right]^{1/2}$$

Maintaining the Growth of an External Scale

Equating the molar flux of solute B to that being required for oxide growth $J_B = \frac{D_B}{V_m}\left(\frac{\partial N_B}{\partial x}\right)_{x=0} = \frac{1}{\nu} \bullet \frac{1}{2} \bullet \frac{k_p^{1/2}}{M_O} t^{-1/2}$

$$N_B^{(o)} = \frac{V_m}{32\nu}\left(\frac{\pi k_p}{D_B}\right)^{1/2}$$

PWA 1484 oxidized at 1100°C

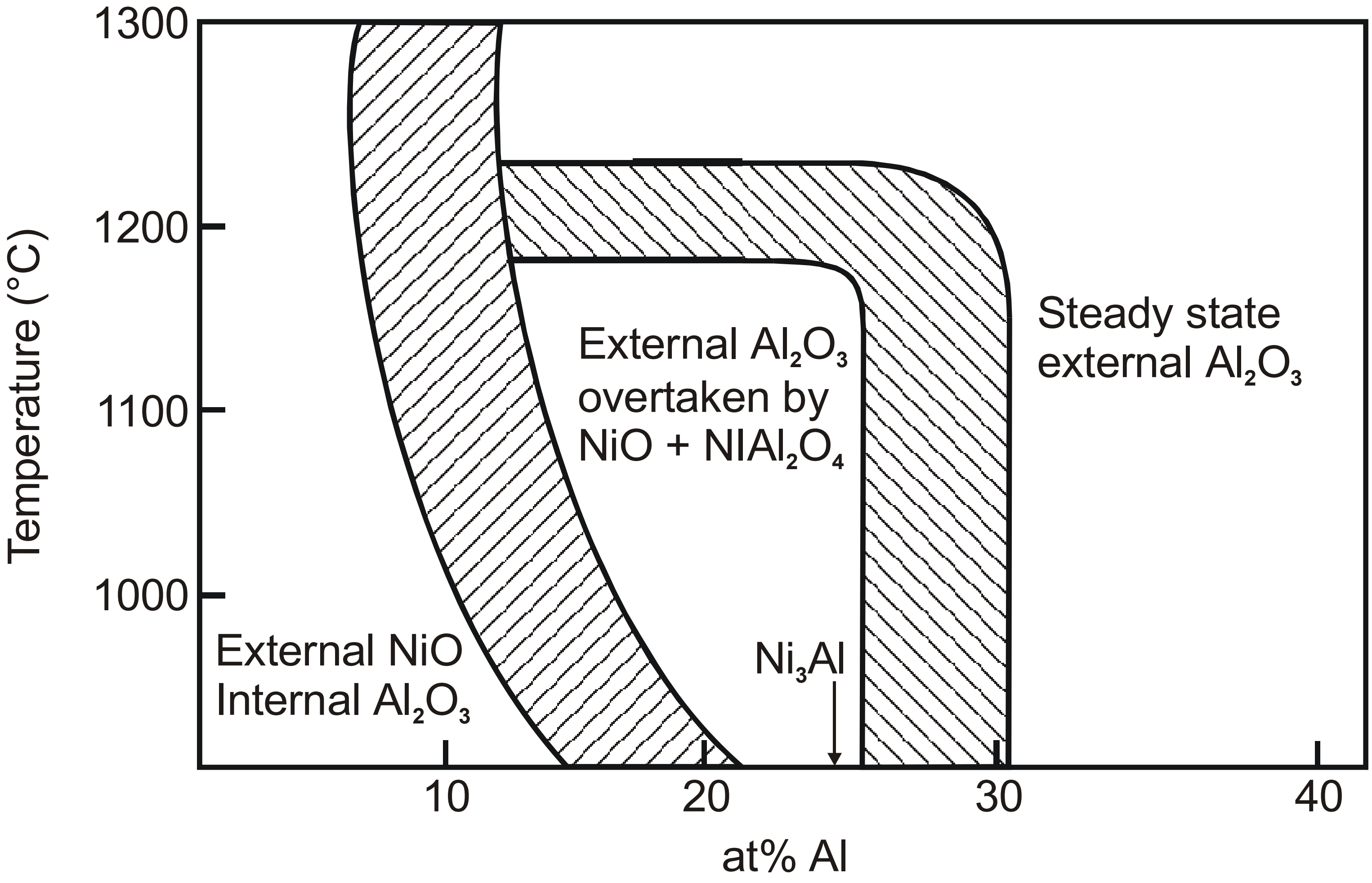


Transient Oxide

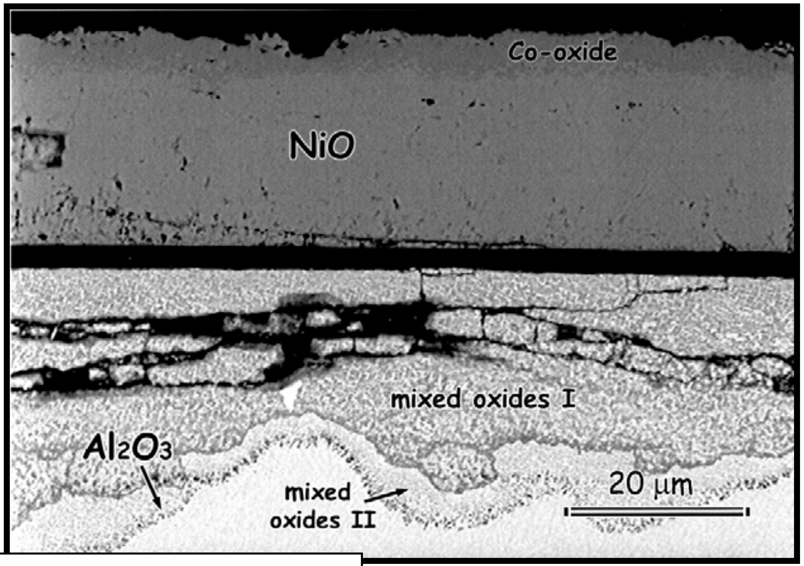
Alumina

Al Depletion

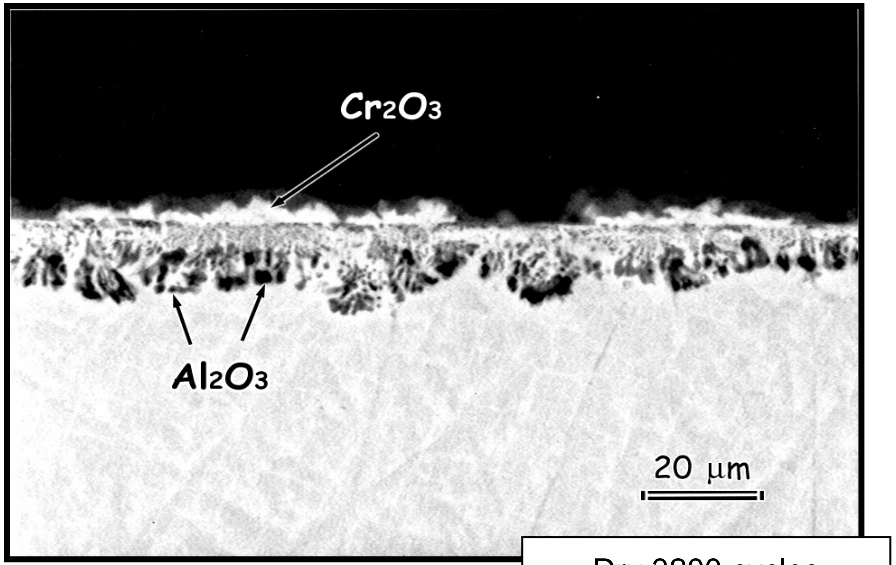
Effect of Temperature and Al Content on the Formation and Continued Growth of External Alumina on Ni-Al Alloys



PWA 1484 @ 700°C



Wet 3200 cycles

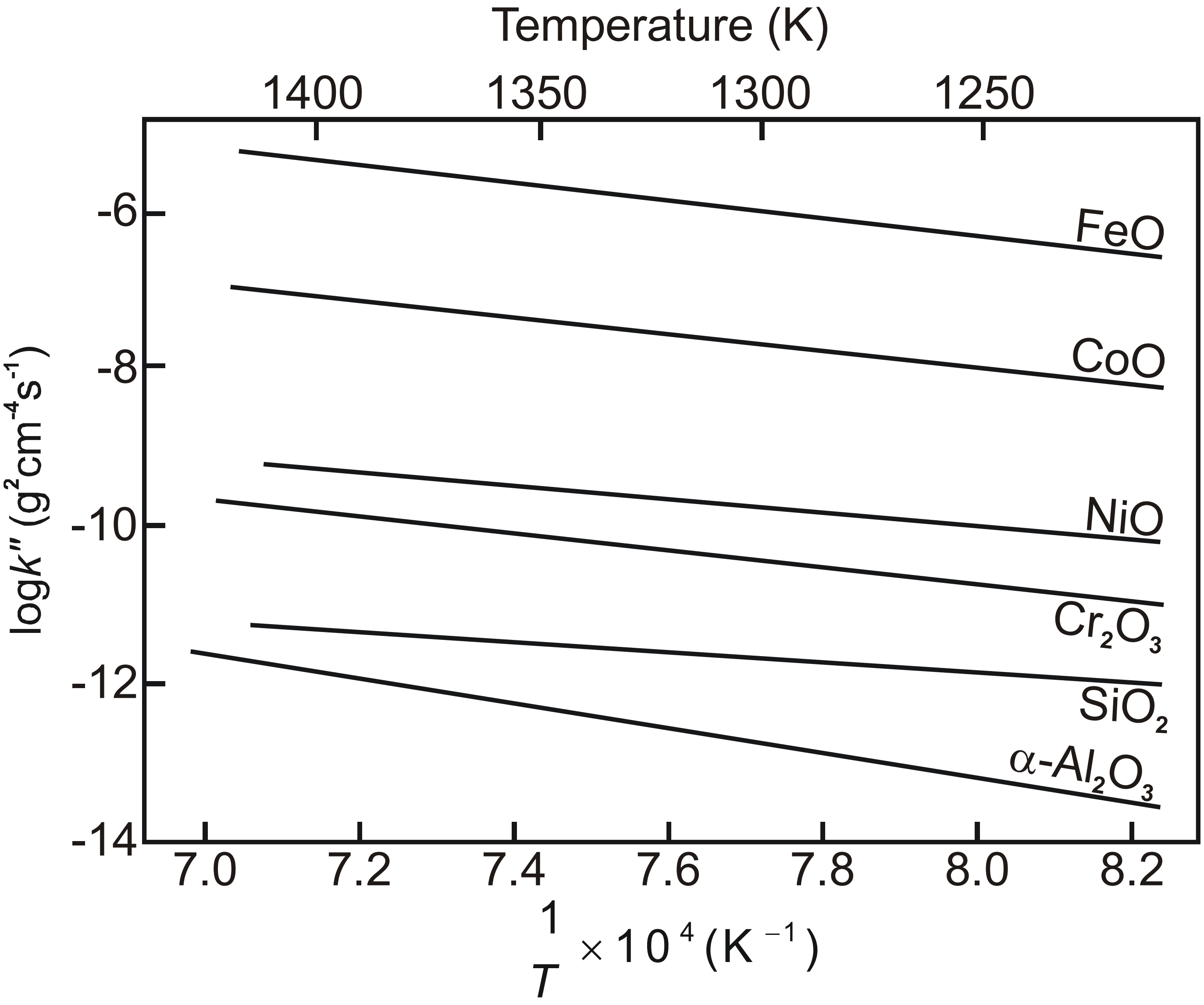


Dry 3200 cycles

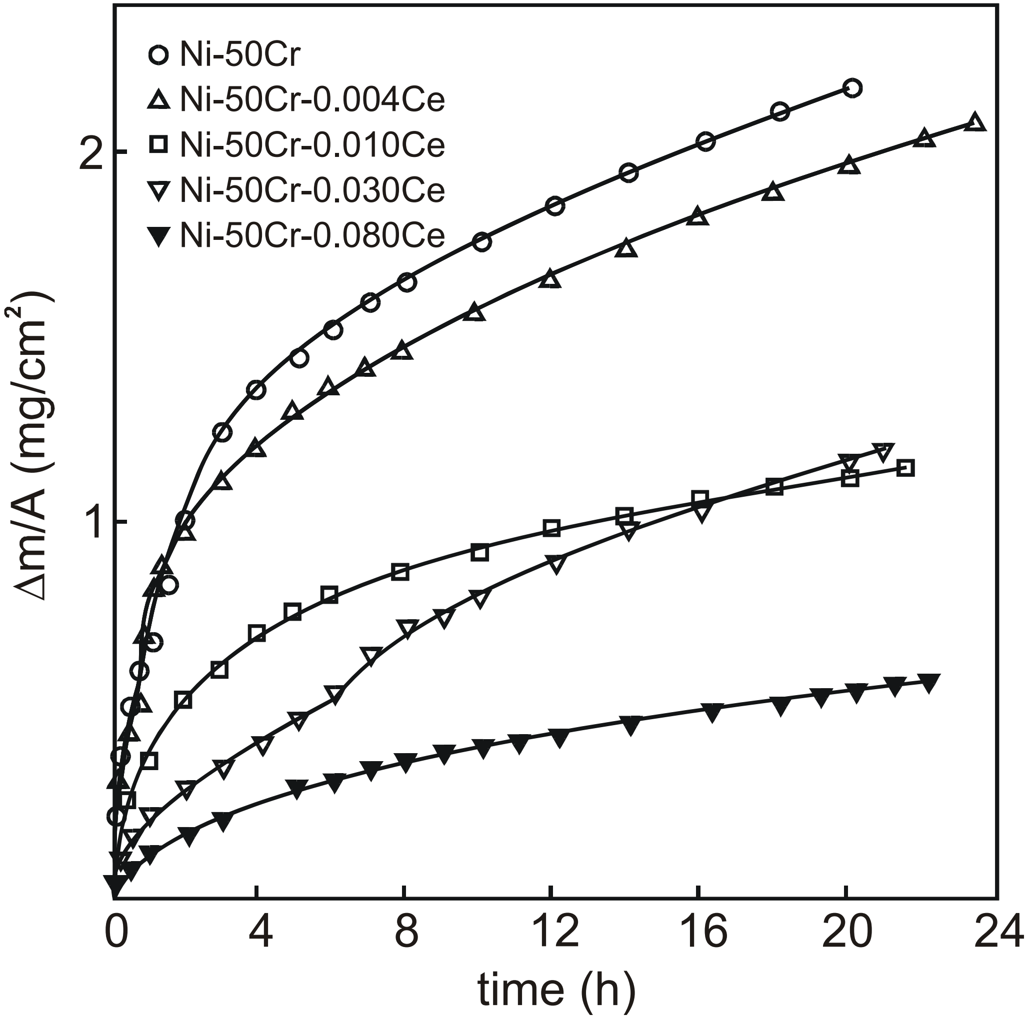
700°C

Aluminum and chromium not selectively oxidized

Relative Growth Rates of Several Oxides



Isothermal Oxidation – RE Effect

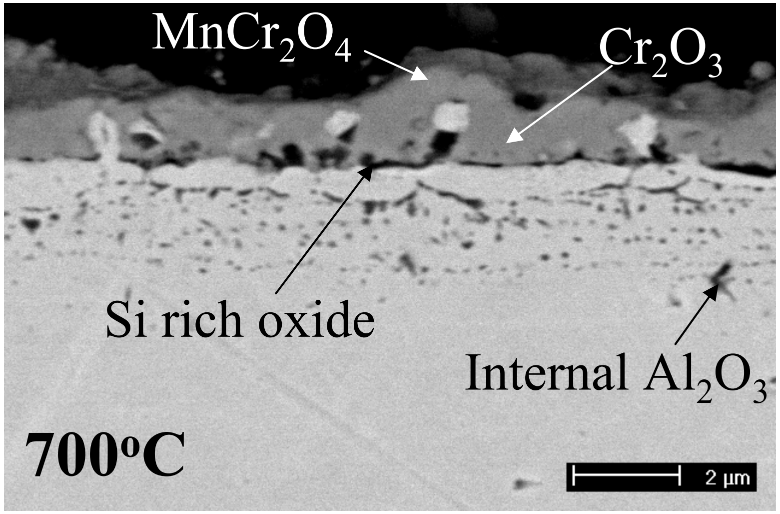


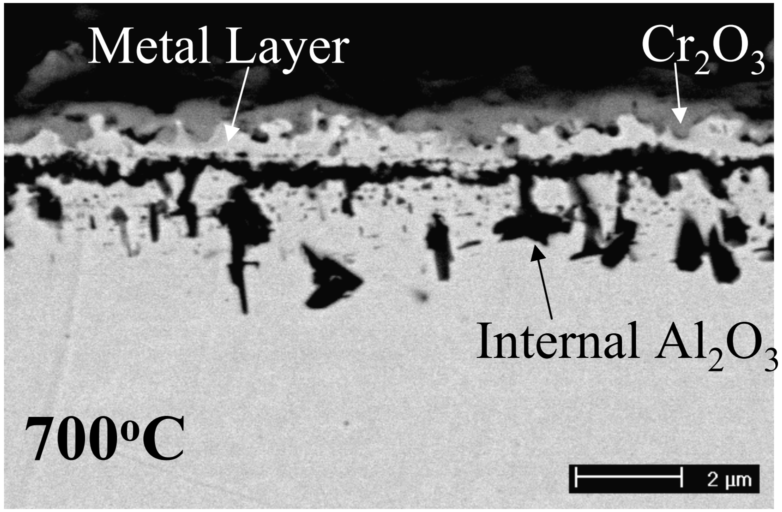
Ecer, and Meier, Oxid. Of Metals, 1979

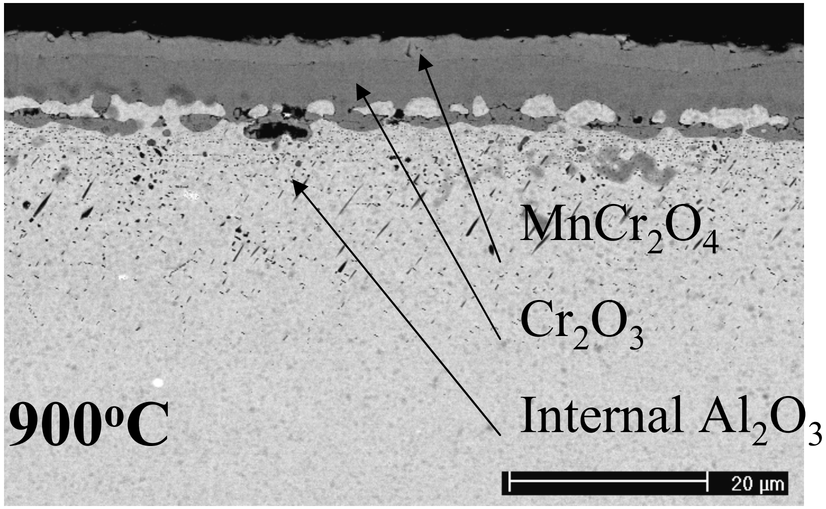
Singh, Ecer, and Meier, Oxid. Of Metals, 1982

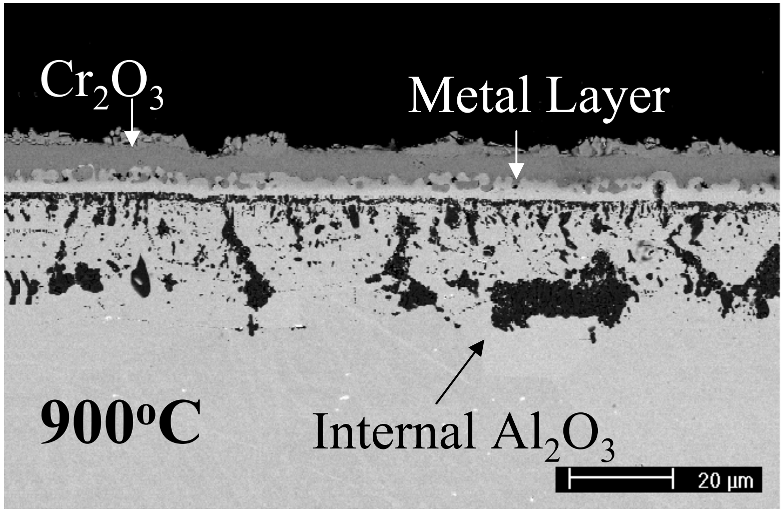
Internal Oxidation of Impurities

Crofer | **AL453**

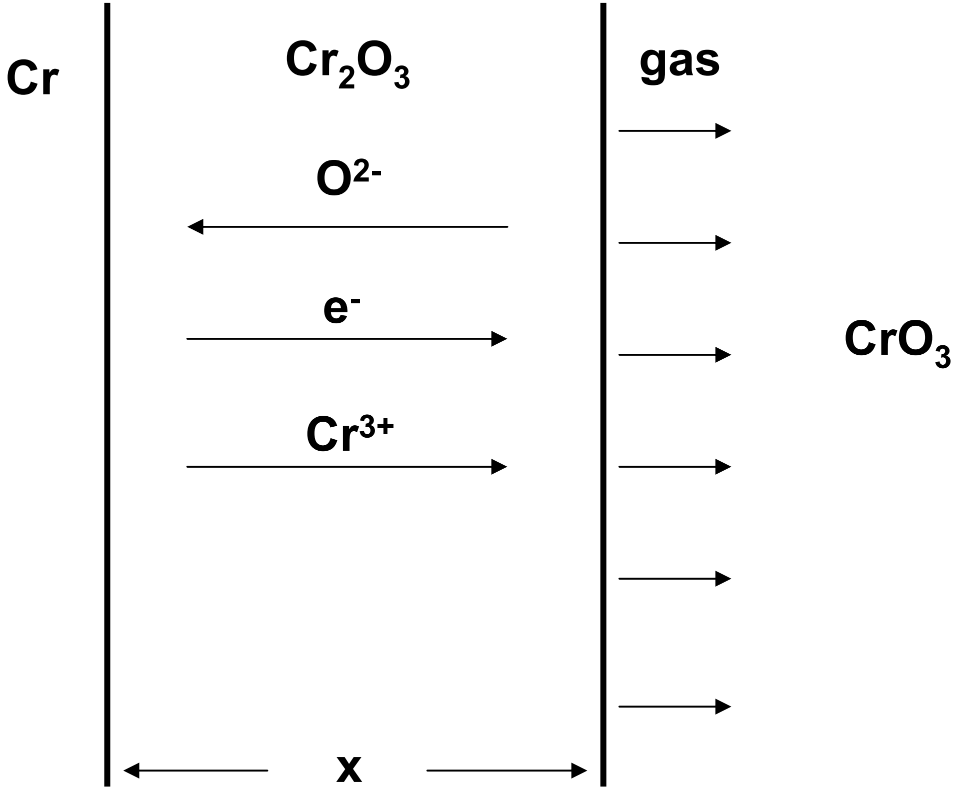








Oxide Vaporization



Cr

Cr_2O_3

gas

O^{2-}

e^-

Cr^{3+}

CrO_3

x

$$Cr_2O_3(s) + \frac{3}{2}O_2(g) = 2CrO_3(g)$$

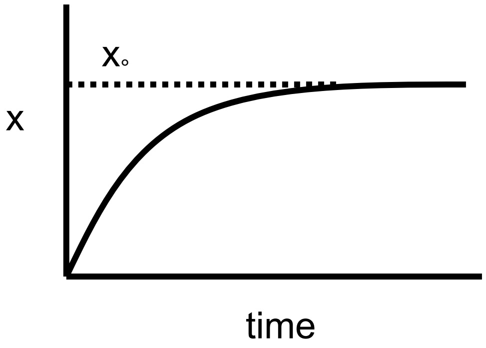
Oxide Vaporization

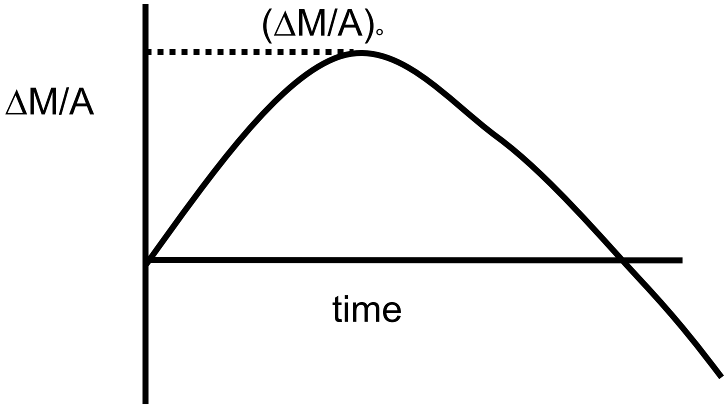
- Diffusion Process in Series with a Vaporization Process

$$\frac{dx}{dt}=\frac{k_p}{x}-k_v$$

- k_p is parabolic growth constant, k_v is vaporization constant. When oxide stops growing $\frac{dx}{dt}=0$

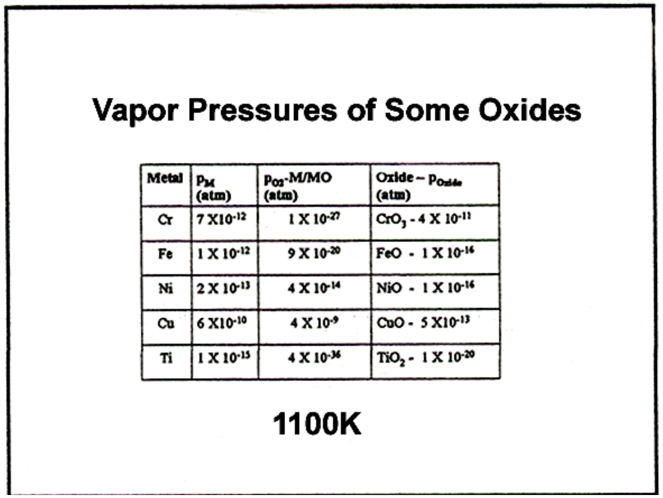
$$x_0=\frac{k_p}{k_v}$$





- causes increased metal consumption
- this effect increases with oxygen pressure, gas flow rate and temperature

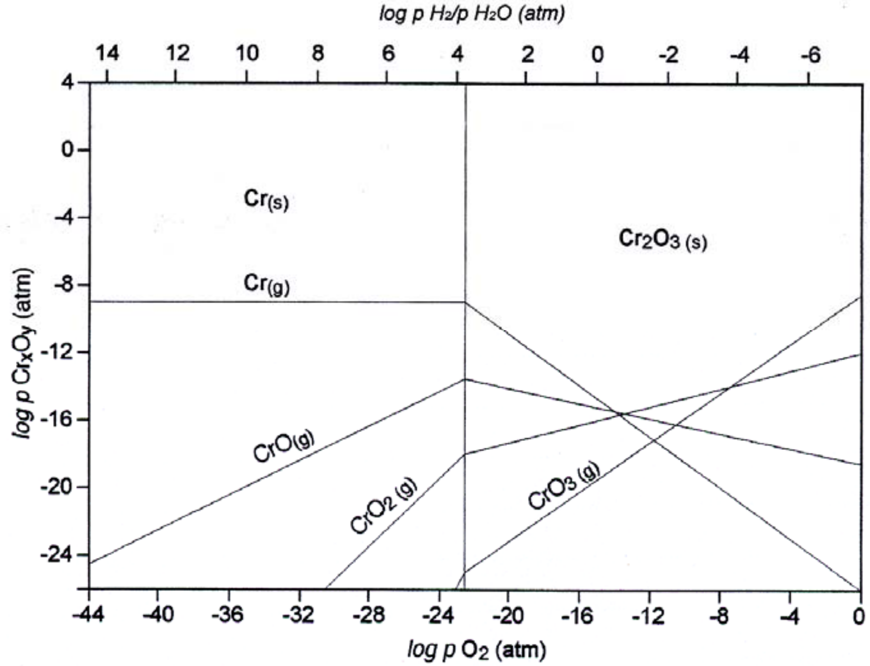
Oxide Vaporization



Vapor Pressures of Some Oxides

Metal	p_M (atm)	p_{O_2}-M/MO (atm)	Oxide – p_{Oxide} (atm)
Cr	7 X10^{-12}	1 X 10^{-27}	CrO_3 - 4 X 10^{-11}
Fe	1 X 10^{-12}	9 X 10^{-20}	FeO - 1 X 10^{-16}
Ni	2 X 10^{-13}	4 X 10^{-14}	NiO - 1 X 10^{-16}
Cu	6 X10^{-10}	4 X 10^{-9}	CuO - 5 X10^{-13}
Ti	1 X 10^{-15}	4 X 10^{-36}	TiO_2 - 1 X 10^{-20}

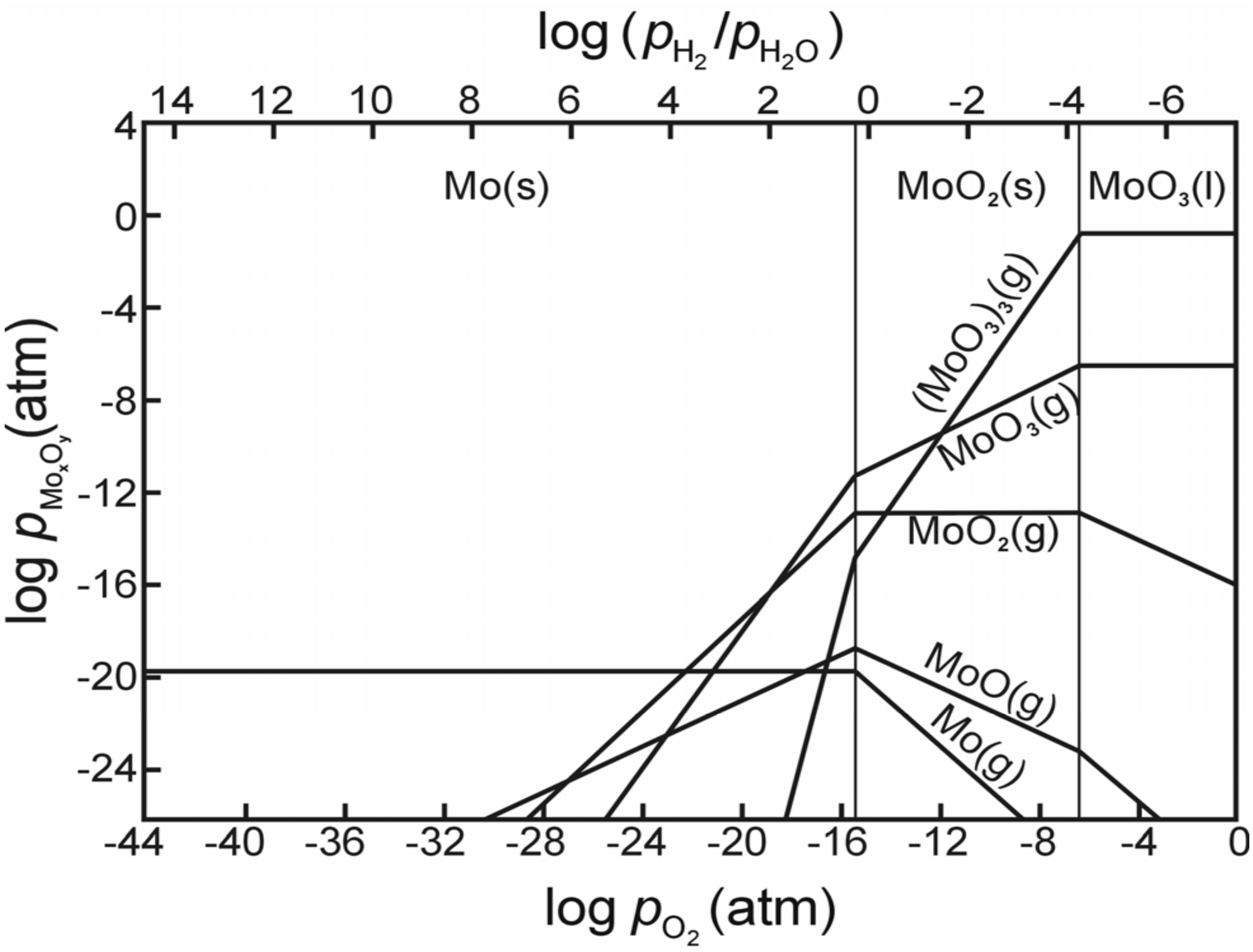
1100K



Vapor species diagram for the Cr-O system at 1250°K

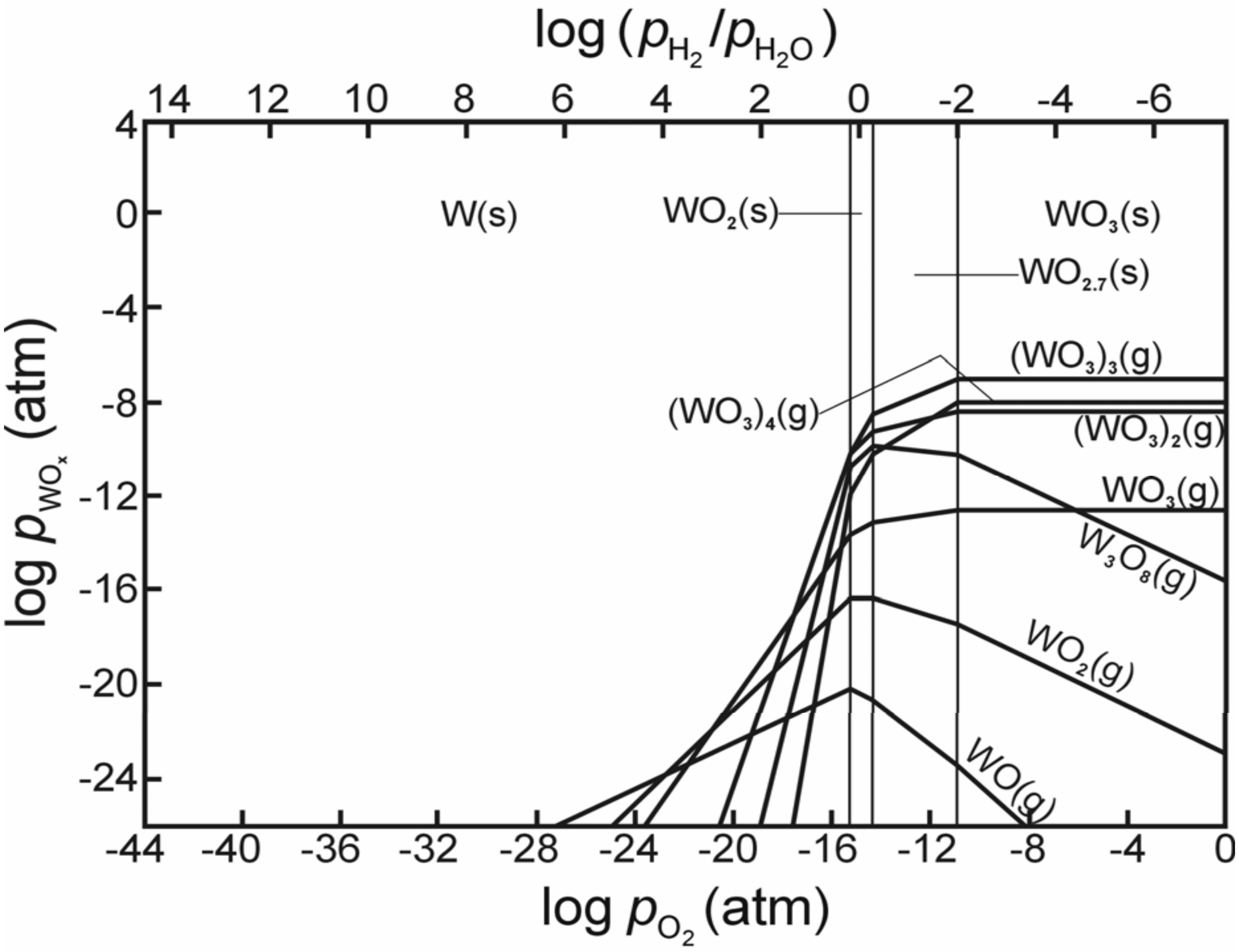
Vapor Species Diagram for the Mo-O System

T = 1250K

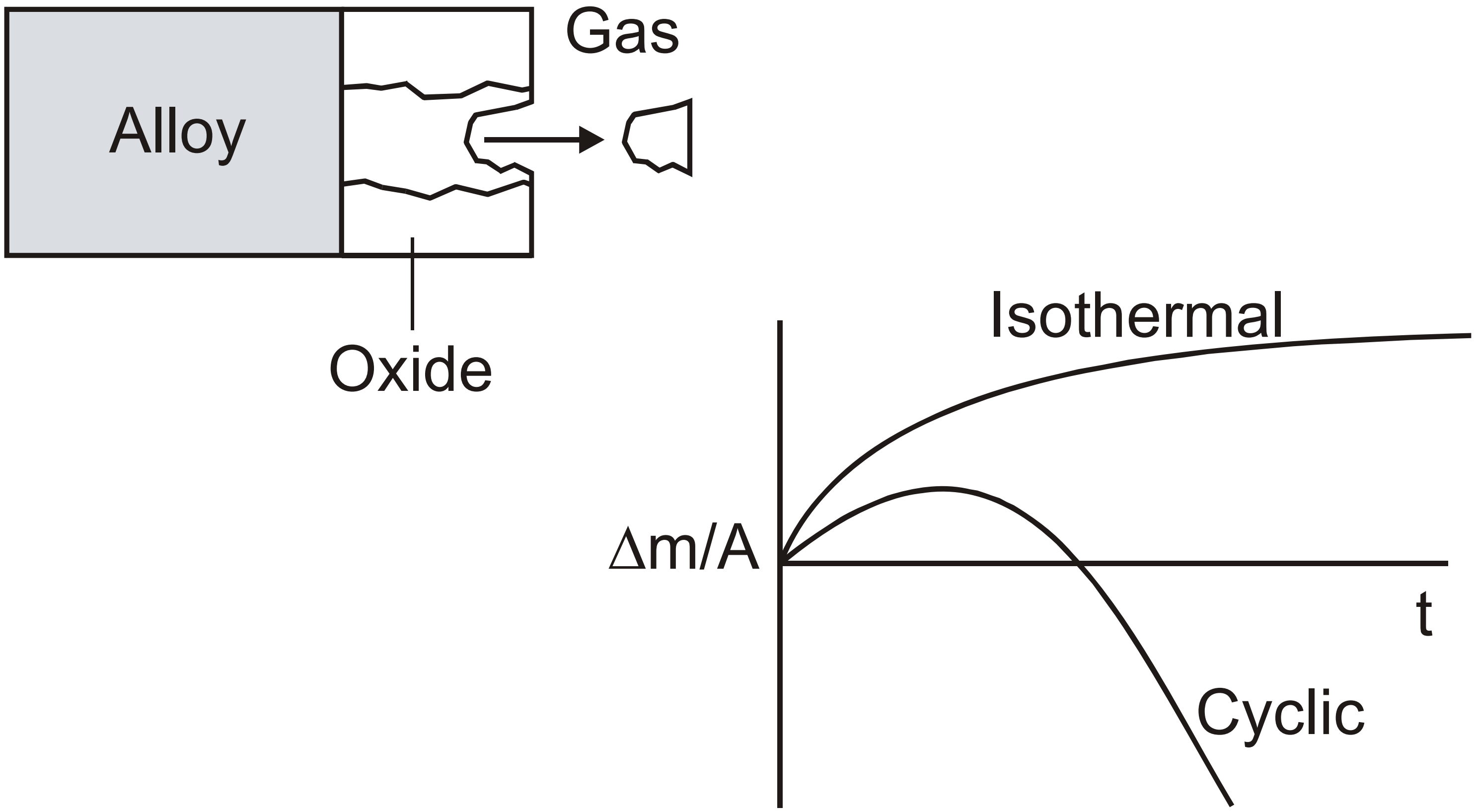


Vapor Species Diagram for the W-O System

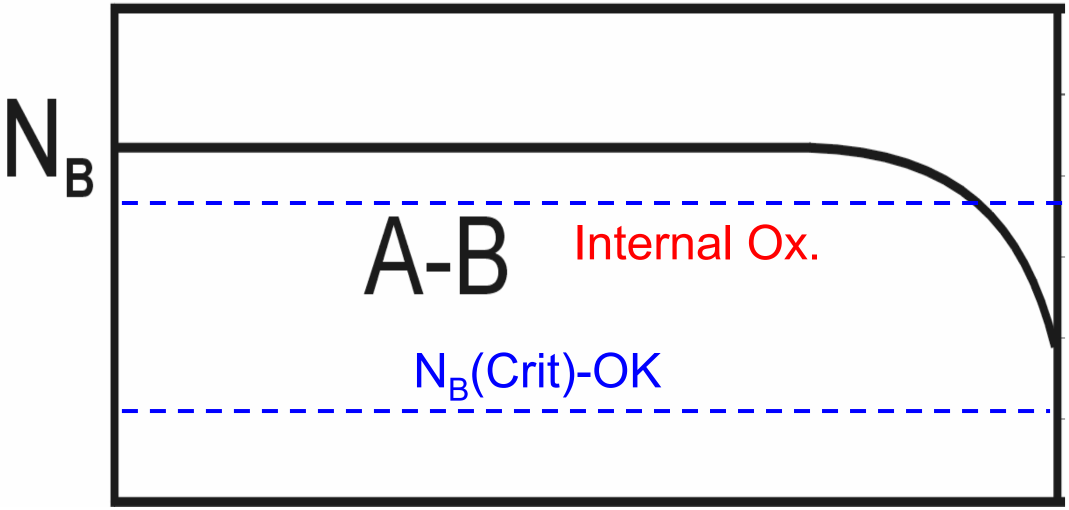
T = 1250K



Cyclic Oxidation



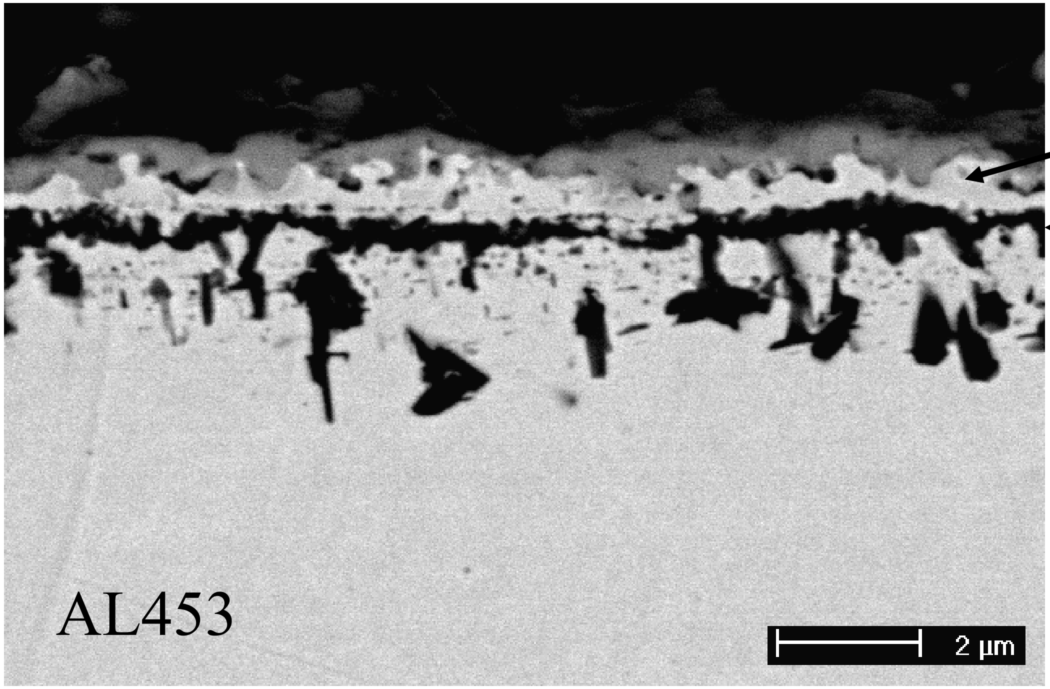
Effects of Alloy Depletion and Scale Spallation



Origins of Oxide Stress

- Growth Stresses – stresses arising from the nature of the oxide growth process
- Thermal Stresses – stresses arising form the thermal expansion mismatch between metal and oxide.
- Applied Loads

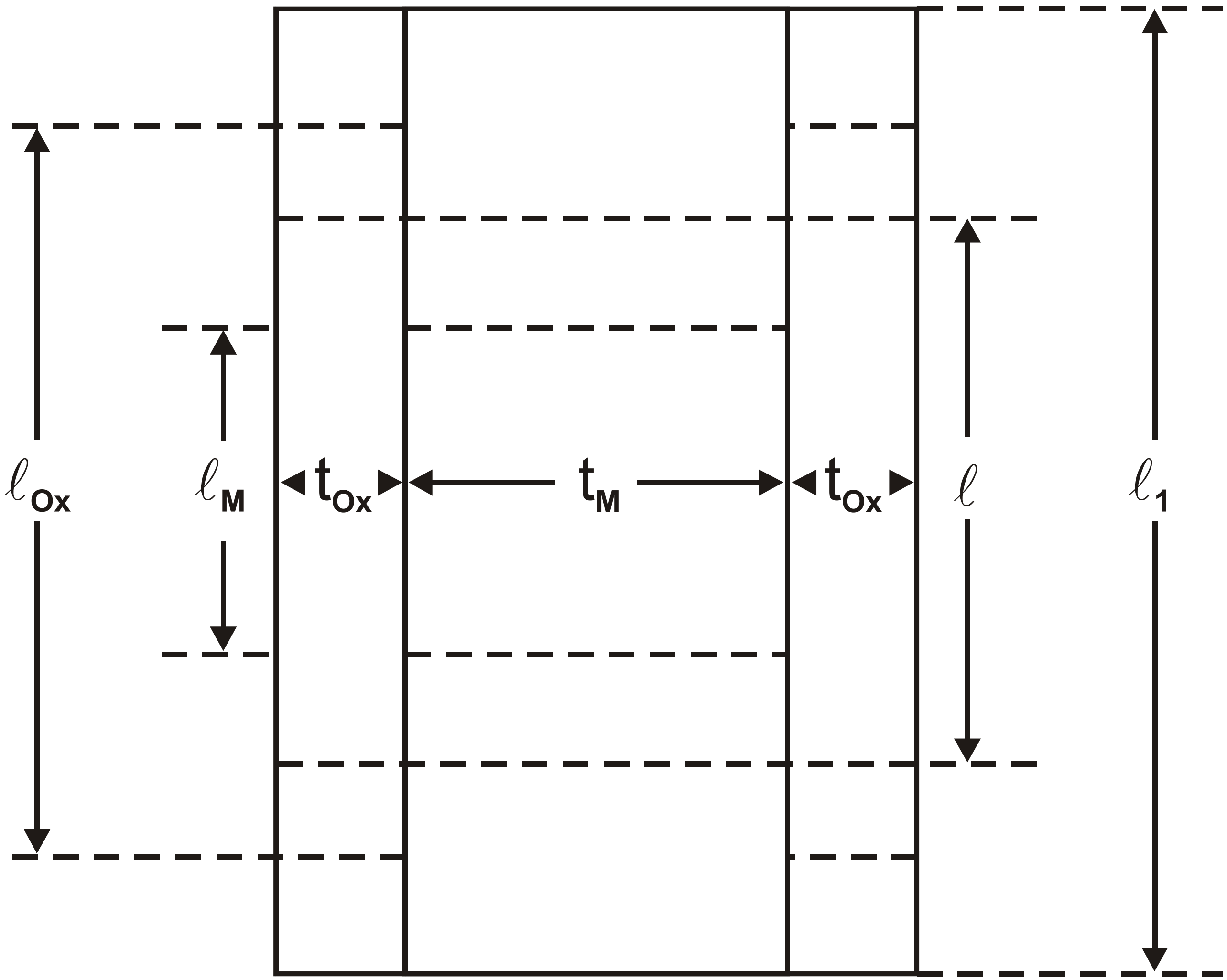
Stress Generation by Internal Oxidation



Extruded Metal

Internal Al_2O_3

Thermal Stress



Origin of Thermal Stress

$$\varepsilon_{thermal}^{metal} = \alpha_M \Delta T \qquad \varepsilon_{thermal}^{Ox} = \alpha_{Ox} \Delta T \qquad \Delta T = T_L - T_H$$

$$\varepsilon_{mech}^{metal} = \frac{\sigma_M (1-\nu_M)}{E_M} \qquad \varepsilon_{mech}^{Ox} = \frac{\sigma_{Ox} (1-\nu_{Ox})}{E_{Ox}}$$

$$\varepsilon_{thermal}^{metal} + \varepsilon_{mechanical}^{metal} = \varepsilon_{thermal}^{Ox} + \varepsilon_{mechanical}^{Ox}$$

$$\sigma_M t_M + 2\sigma_{Ox} t_{Ox} = 0 \qquad \text{Force Balance}$$

$$\alpha_M \Delta T - \frac{2\sigma_{Ox} t_{Ox} (1-\nu_M)}{t_M E_M} = \alpha_{Ox} \Delta T + \frac{\sigma_{Ox} (1-\nu_{Ox})}{E_{Ox}}$$

$$\sigma_{Ox} = \frac{-(\alpha_{Ox} - \alpha_M)\Delta T}{\frac{2t_{Ox}(1-\nu_M)}{t_M E_M} + \frac{(1-\nu_{Ox})}{E_{Ox}}}$$

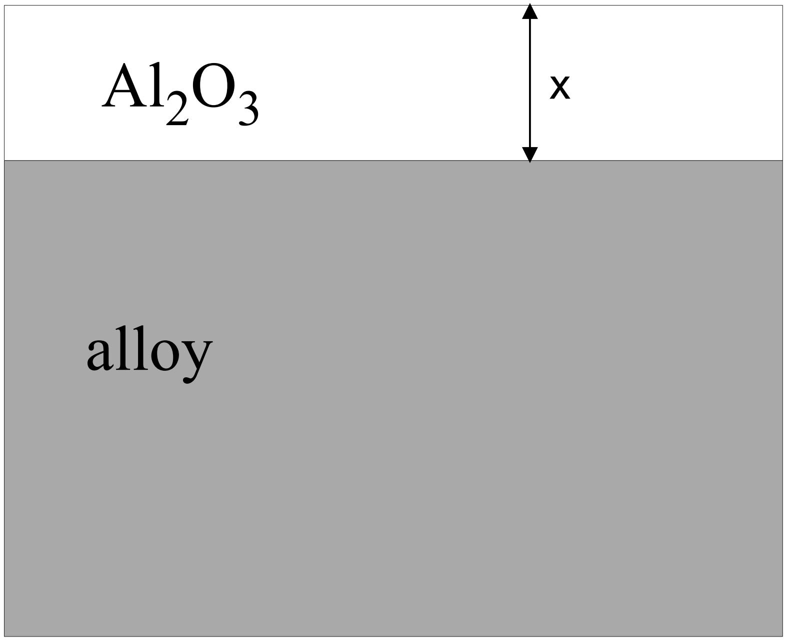
Timoshenko, S. P., *J. Opt. Soc. Amer.*,**11** (1925) 233

$$\sigma_{Ox} = \frac{-E_{Ox}(\alpha_{Ox} - \alpha_M)\Delta T}{(1-\nu)\left(1 + 2\frac{t_{Ox} E_{Ox}}{t_M E_M}\right)} \qquad \text{If } \nu_M \approx \nu_{Ox}$$

Thermal Stress if $t_{Ox} << t_M$

$$\sigma_{Ox} = \frac{-E_{Ox}(\alpha_{Ox} - \alpha_M)\Delta T}{(1-\nu)}$$

Oxide Failure

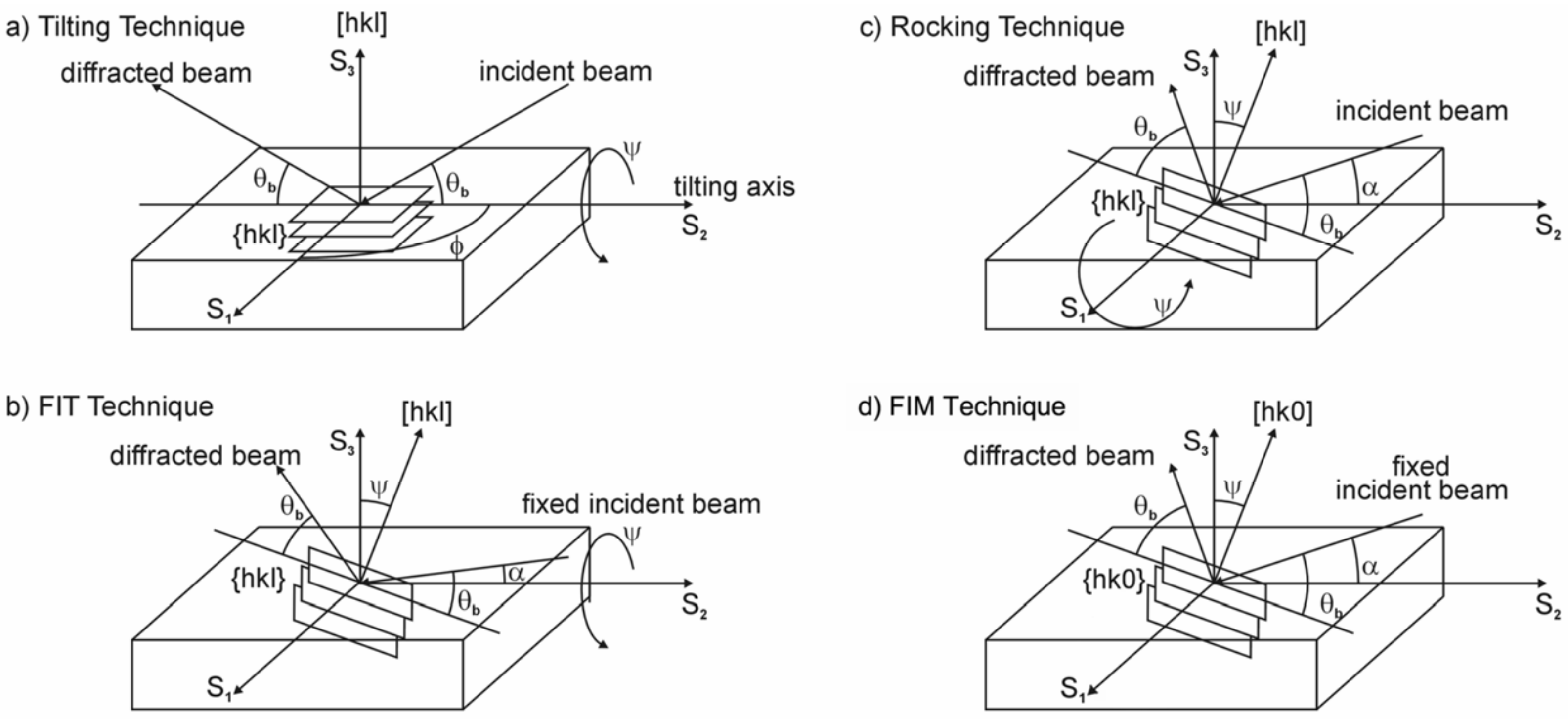


Stored elastic energy of alumina ≈ $f(s_{ox}, x_{ox})$

Fracture resistance of the alumina/alloy interface ≈ f(morphology, composition)

Stresses in Oxides

XRD Techniques



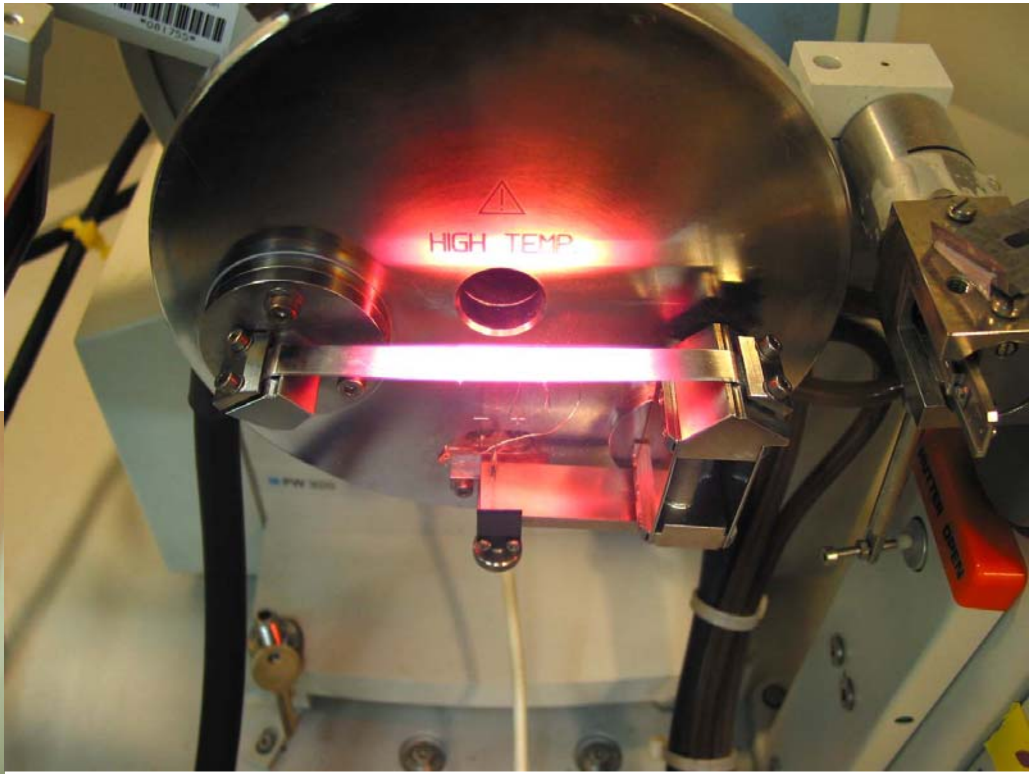
Stress from $d_{(hkl)}$ v. $\sin^2\psi$

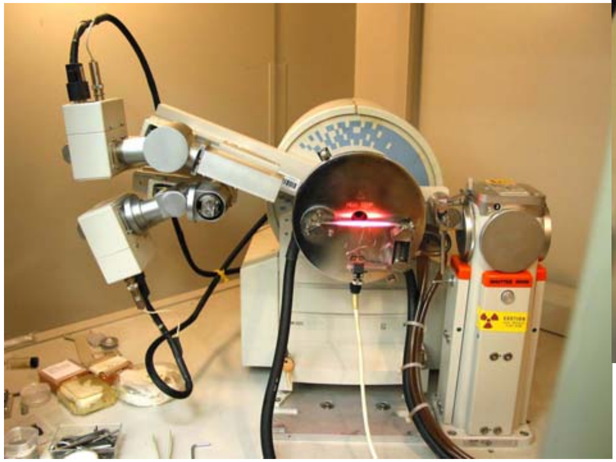
$$\varepsilon_{\Psi} = \frac{d_{\Psi} - d_0}{d_0} = {}^1\!/_2\, s_2(hkl)\sigma_o \sin^2\psi + 2s_1(hkl)\sigma_o$$

$$d_{\psi} = {}^1\!/_2\, s_2 \cdot \sigma_o \cdot d_o \cdot \sin^2\psi + d_o\left(2s_1 \cdot \sigma_o + 1\right)$$

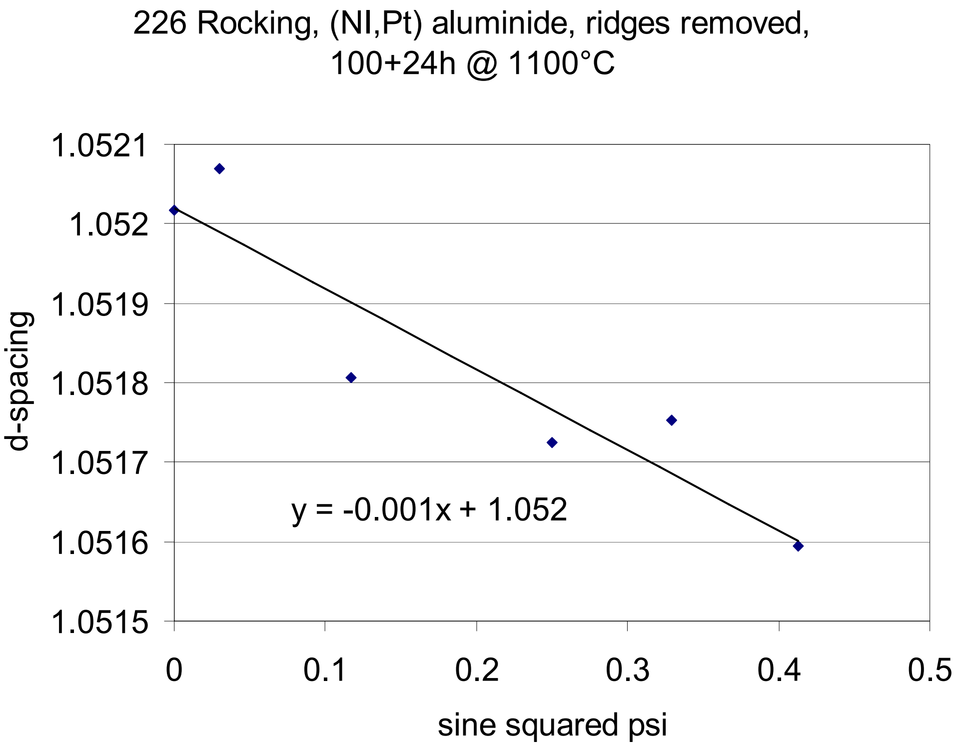
$$\text{slope} = {}^1\!/_2\, s_2 \cdot \sigma_o \cdot d_o$$

Growth Stress Measurements, FIM/Rocking





Growth Stress Measurement for Alumina Formed on a Pt-Modified Aluminide Bond Coat at 1100°C

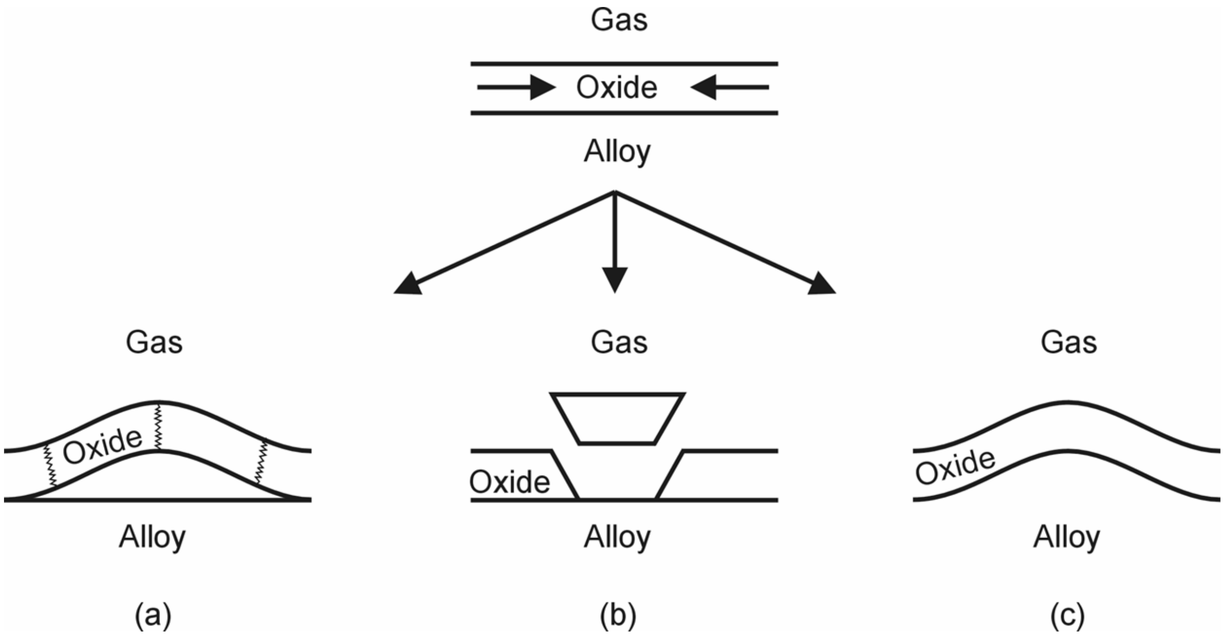


Growth Stress

= -0.3±0.1GPa

After 124 h exposure

Response to Stresses

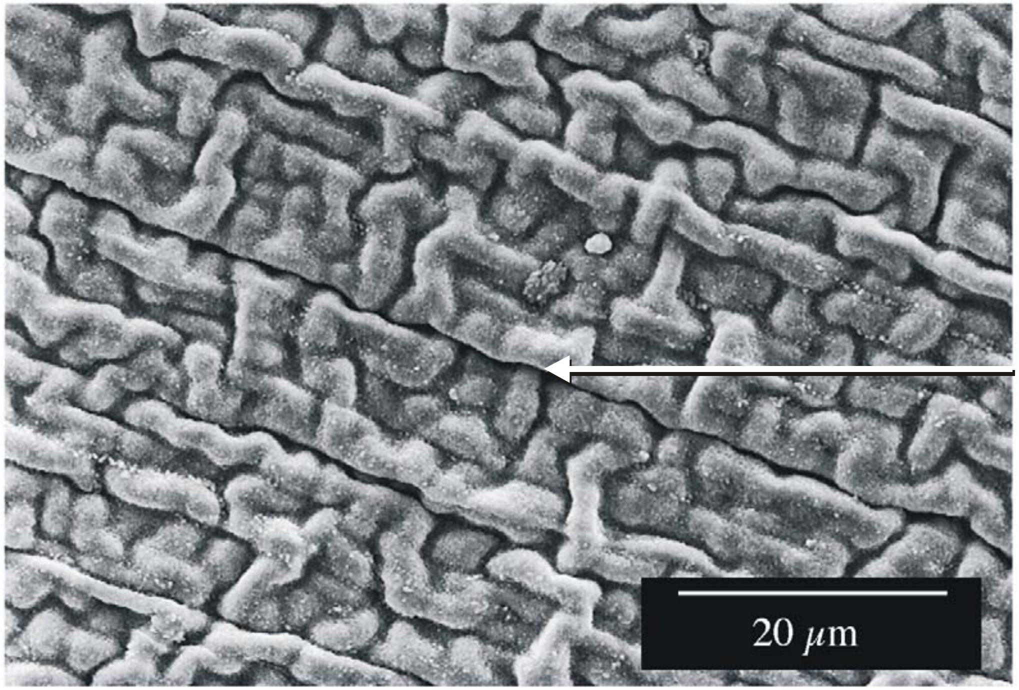


buckling of the oxide

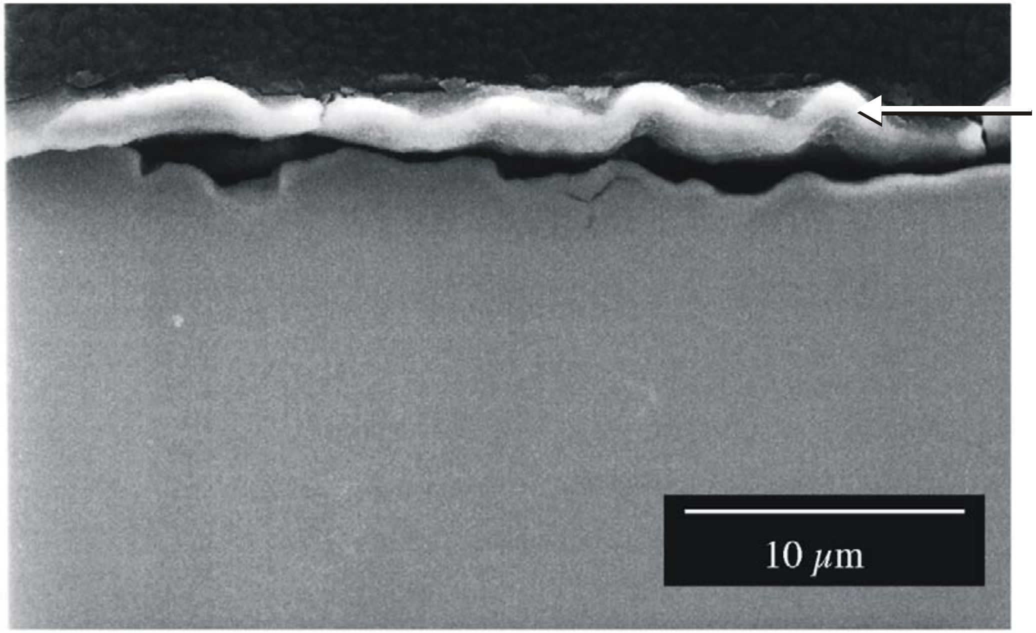
shear cracking of the oxide

plastic deformation of the oxide and alloy

Example of Buckling



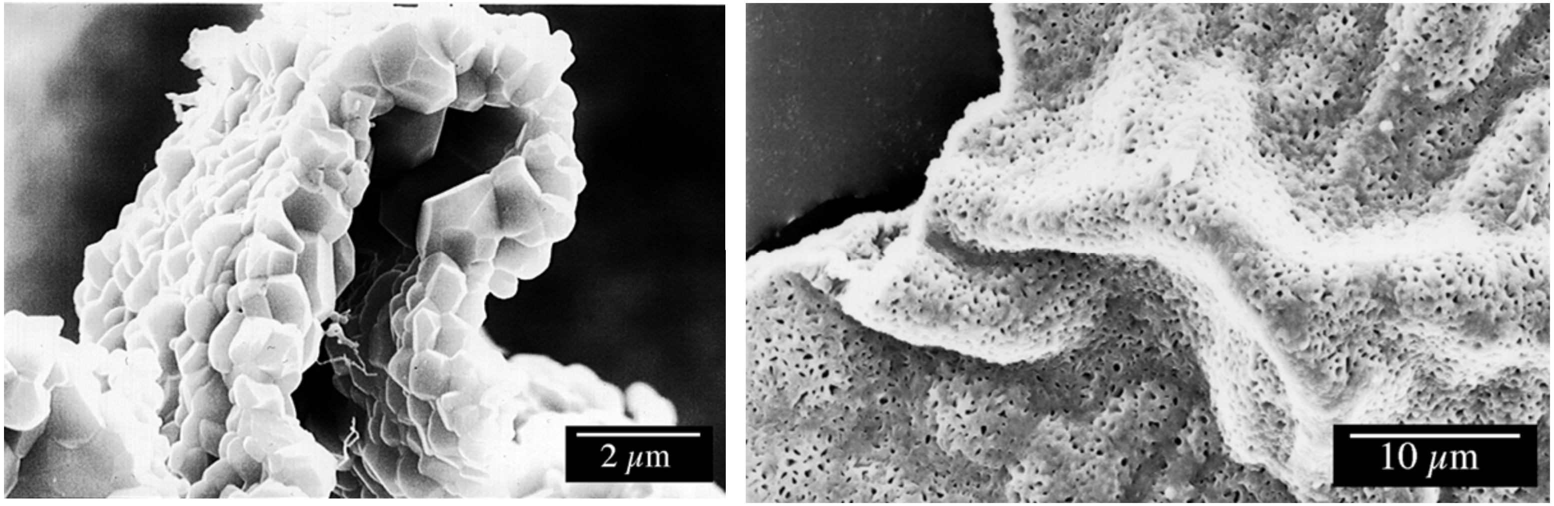
Polishing mark



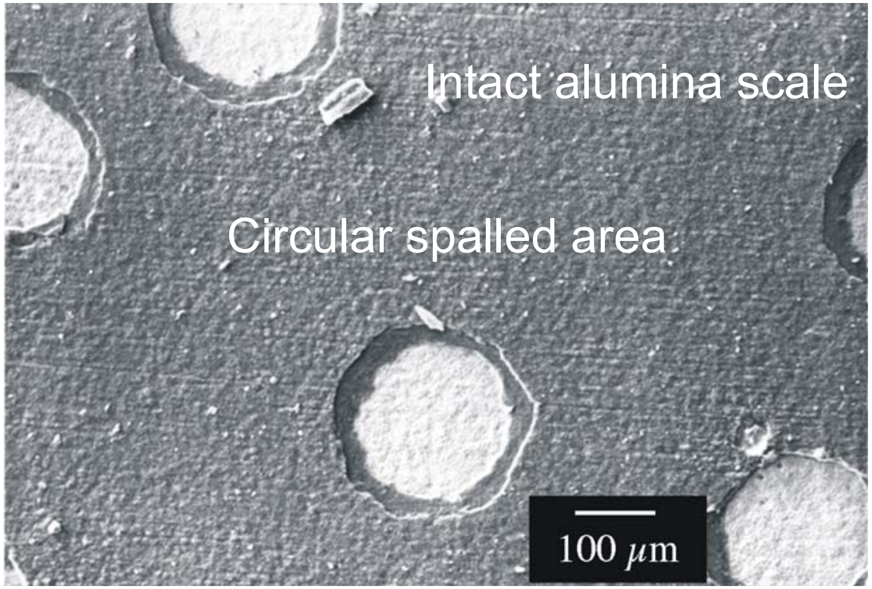
Alumina scale

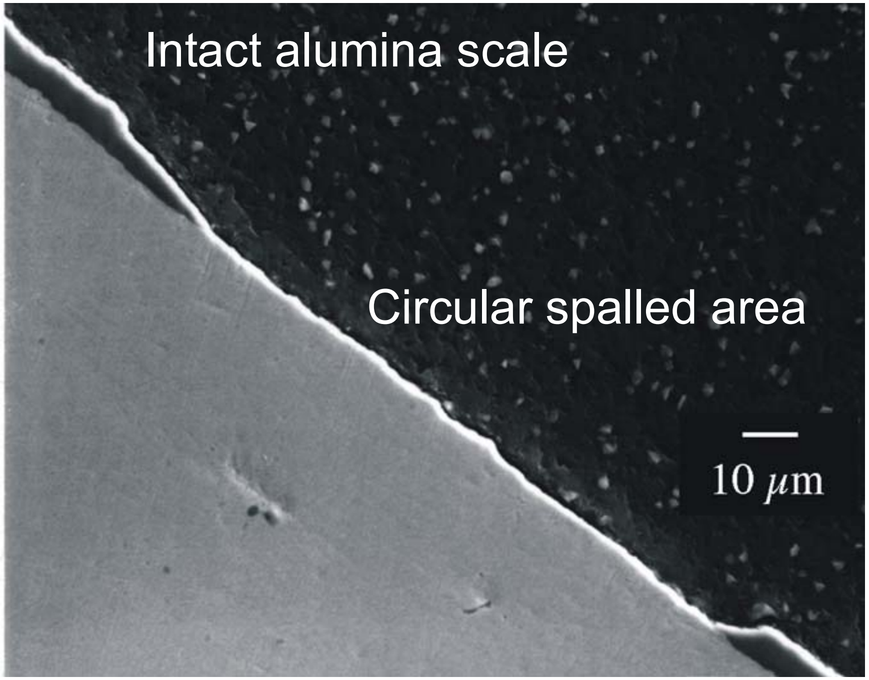
Spallation of Alumina Scale by Buckling

FeCrAl (TMP) oxidized at 1100°C for 120 hours.

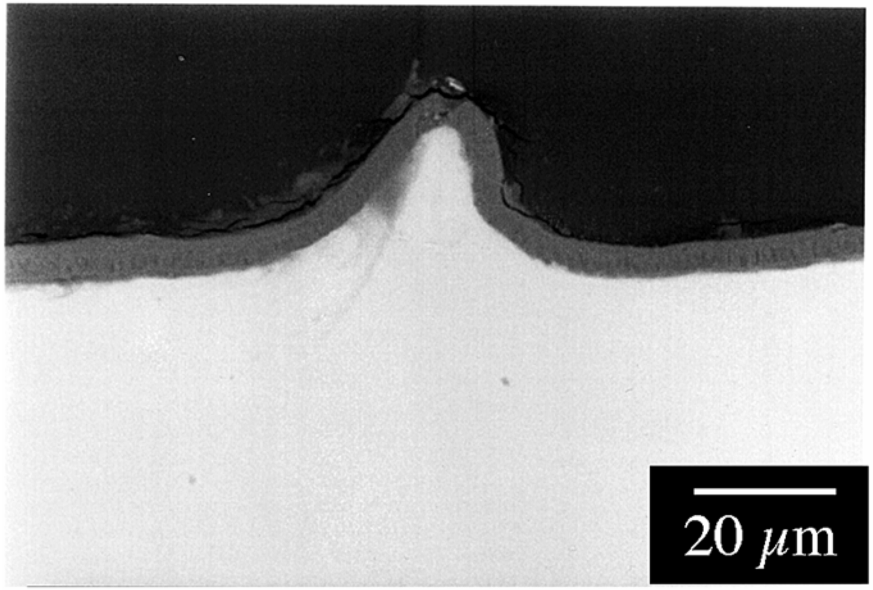


Circular Buckles

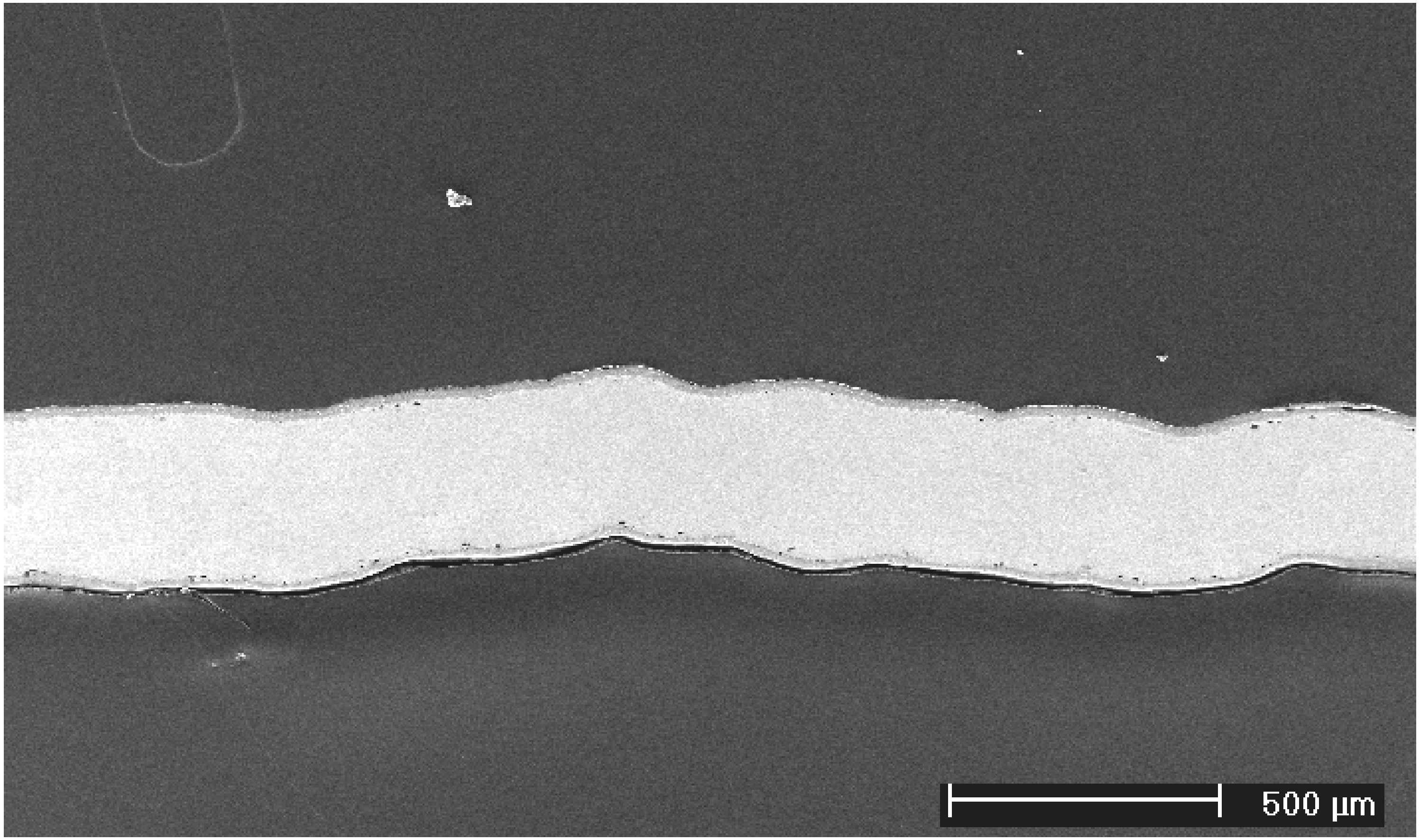




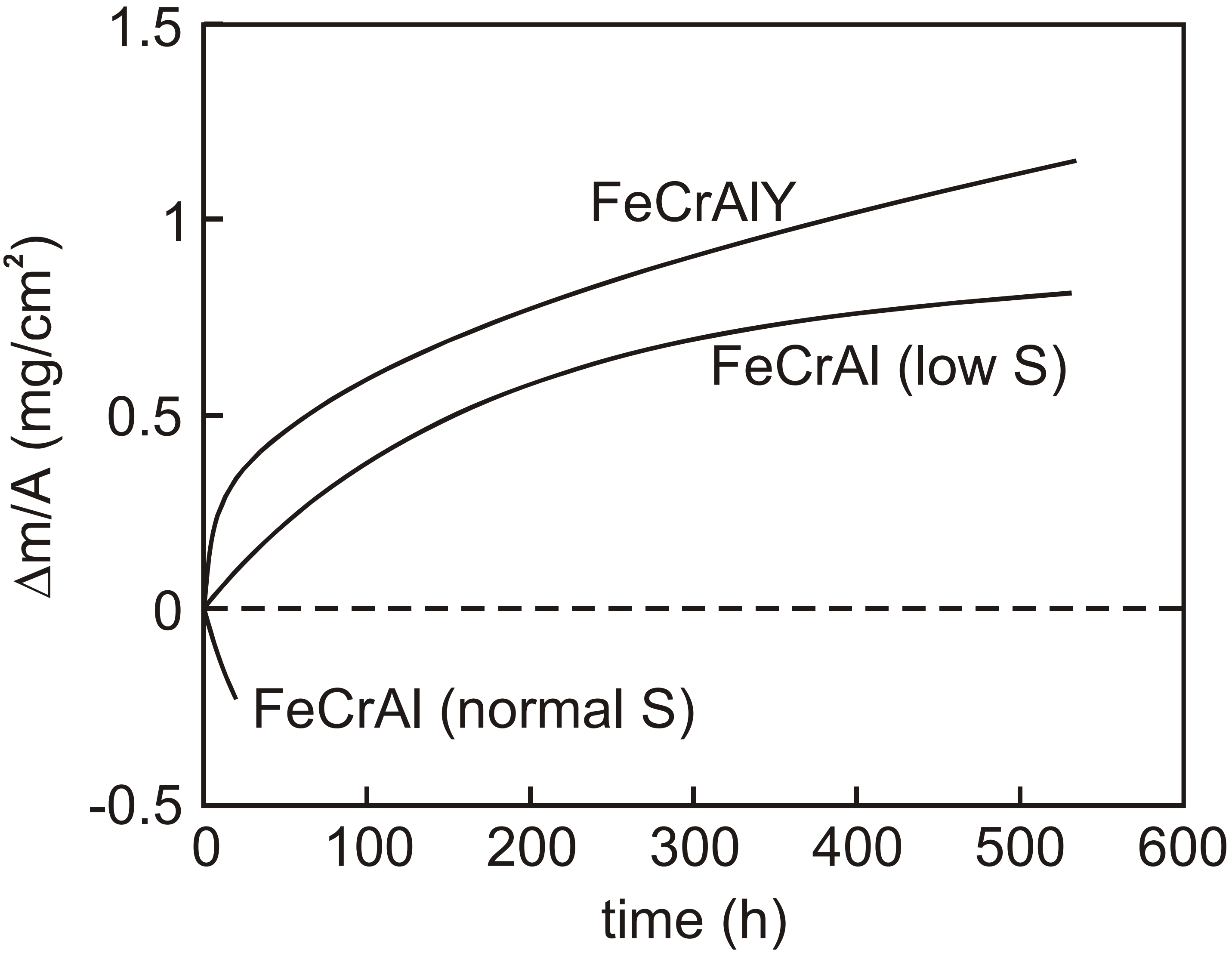
FeCrAlTi Cyclically Oxidized for 288h at 1100°C



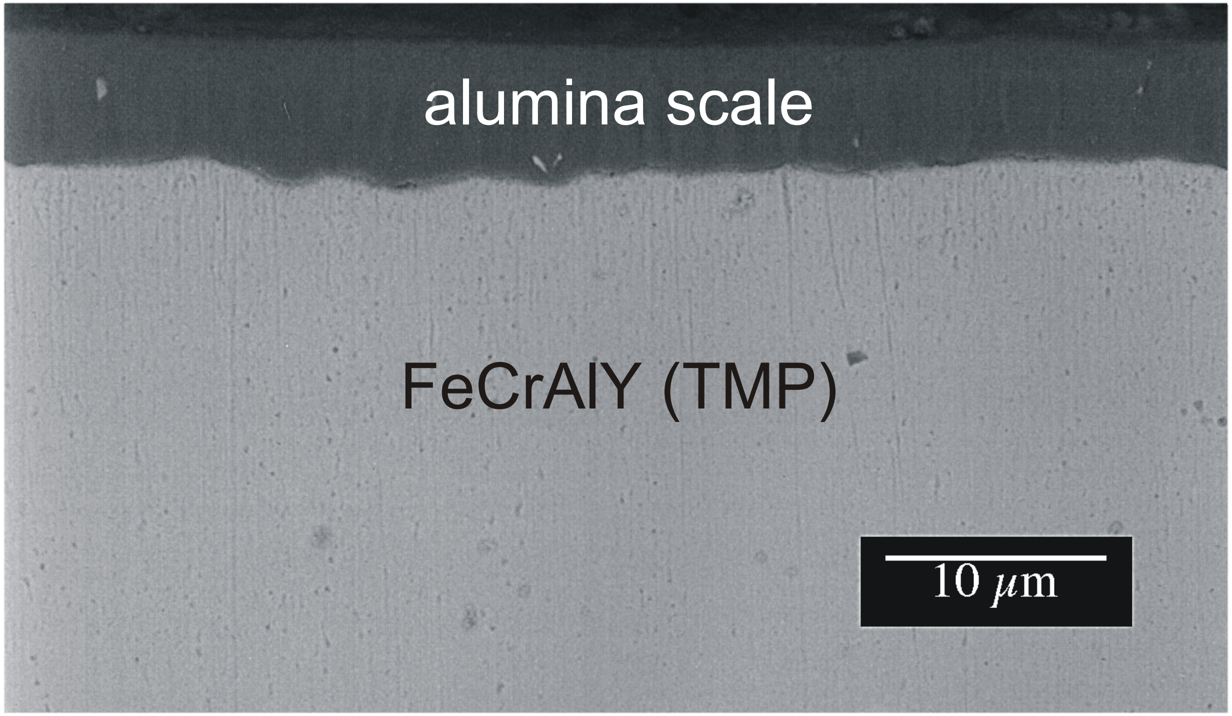
Deformation of Crofer During Cyclic Oxidation



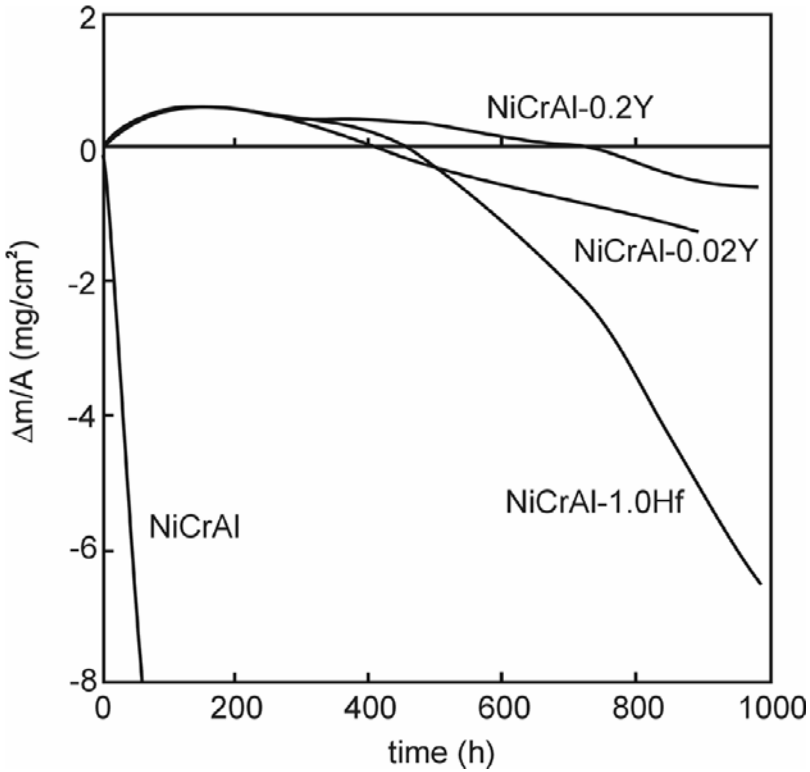
Effect of Sulfur and Reactive Element



Effect of Yttrium

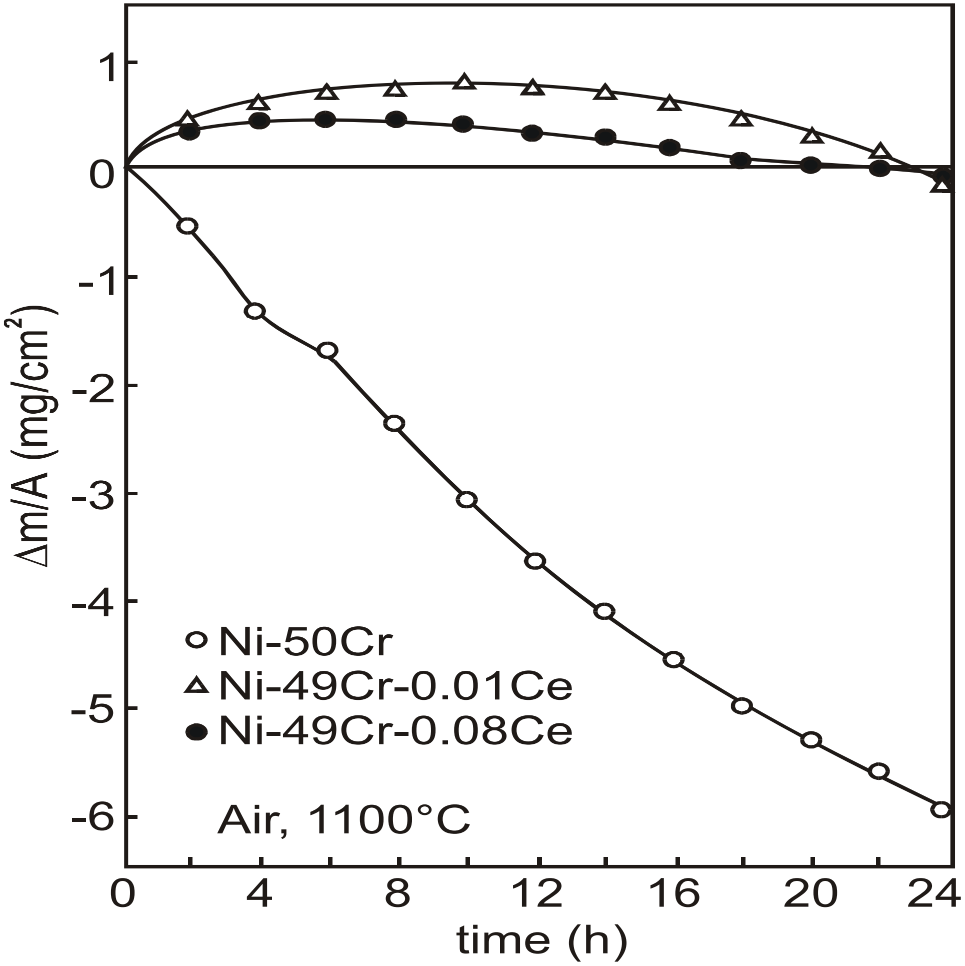


Long Term Cyclic Oxidation Testing



Cyclic oxidation kinetics for several Ni-Cr-Al alloys exposed at 1100°C.

Reactive Element Effect for a Chromia Former

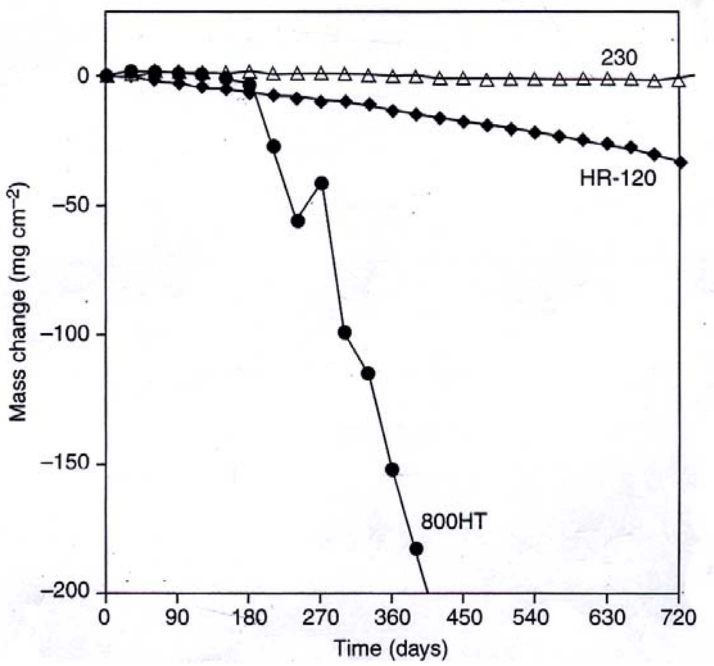


Cyclic
Oxidation

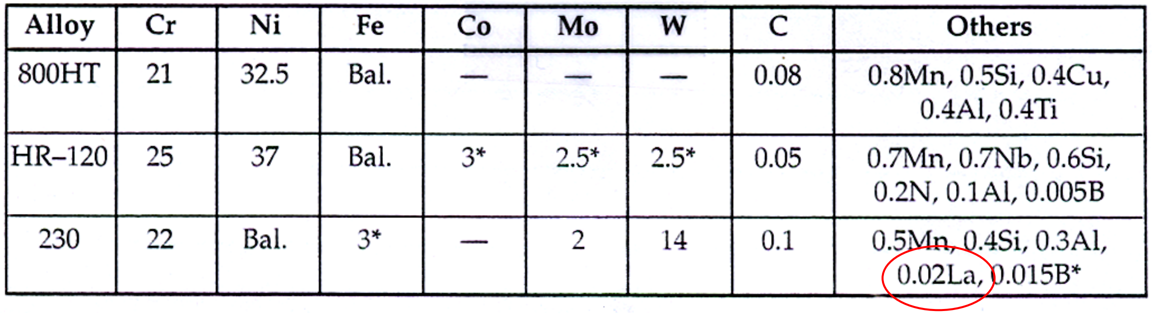
Cyclic Oxidation Degradation and Breakaway

- Alloys initially are Cr_2O_3-formers

982°C 30 day cycles



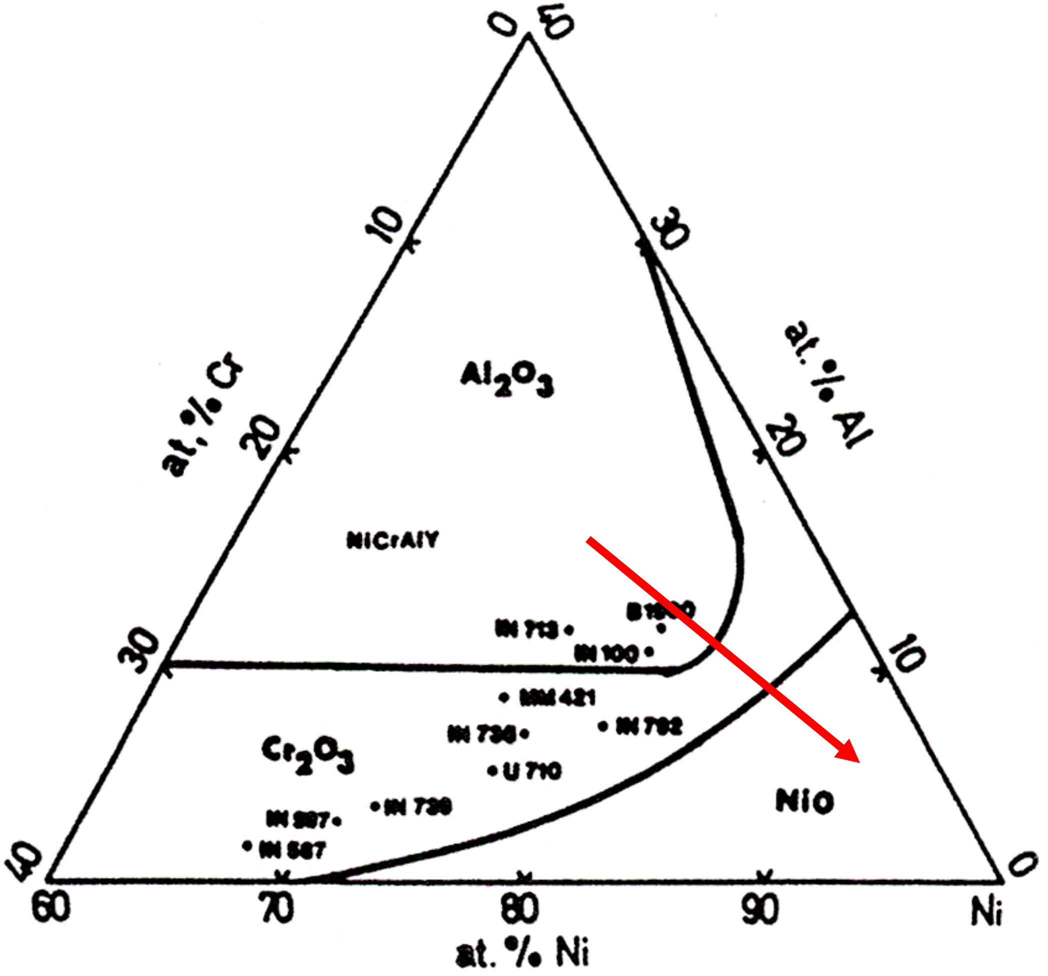
wt%



Alloy	Cr	Ni	Fe	Co	Mo	W	C	Others
800HT	21	32.5	Bal.	—	—	—	0.08	0.8Mn, 0.5Si, 0.4Cu, 0.4Al, 0.4Ti
HR–120	25	37	Bal.	3*	2.5*	2.5*	0.05	0.7Mn, 0.7Nb, 0.6Si, 0.2N, 0.1Al, 0.005B
230	22	Bal.	3*	—	2	14	0.1	0.5Mn, 0.4Si, 0.3Al, 0.02La, 0.015B*

More adherent oxide

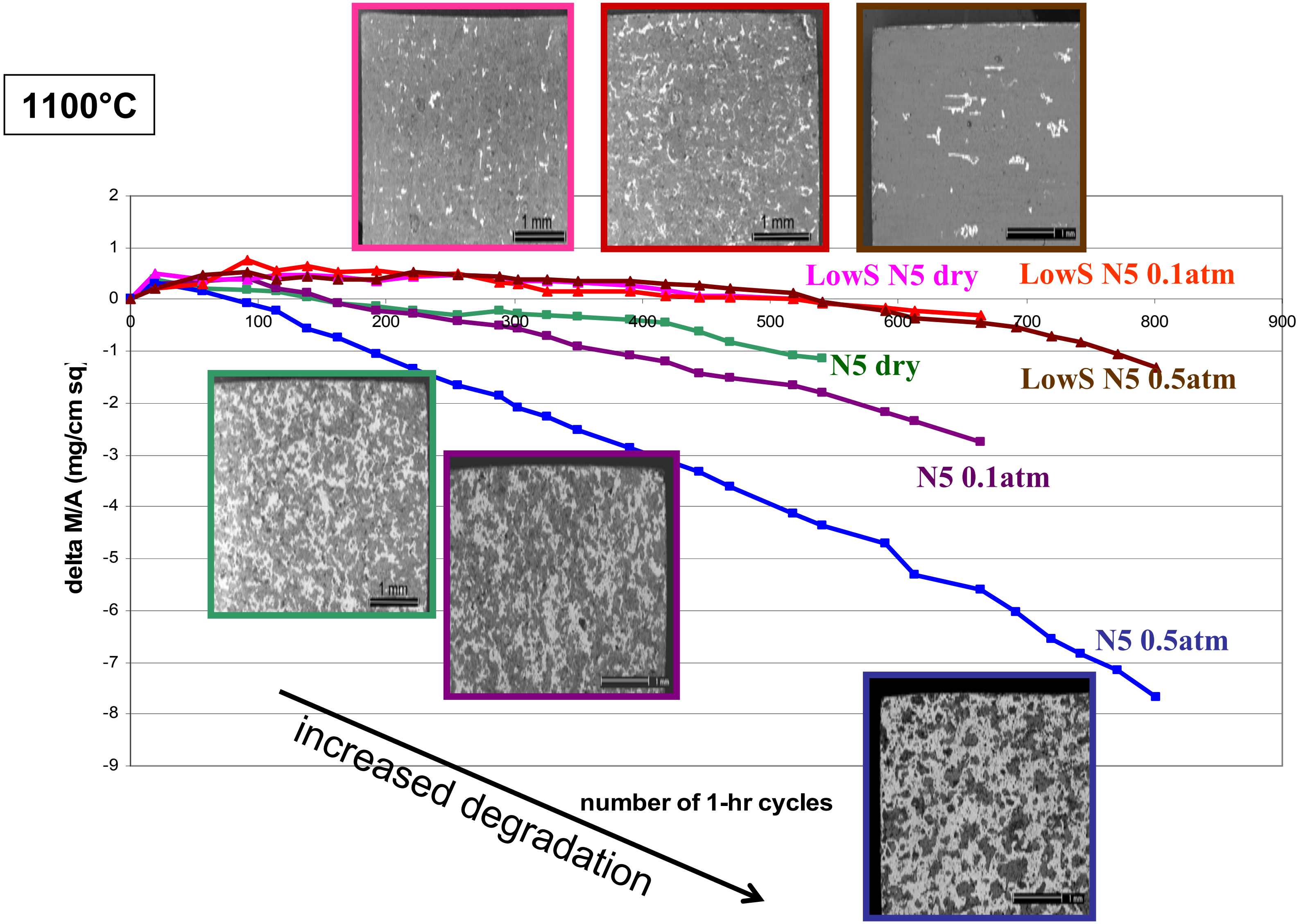
Ni-Cr-Al Cyclic Oxidation Degradation



Water Vapor Effects on High Temperature Oxidation

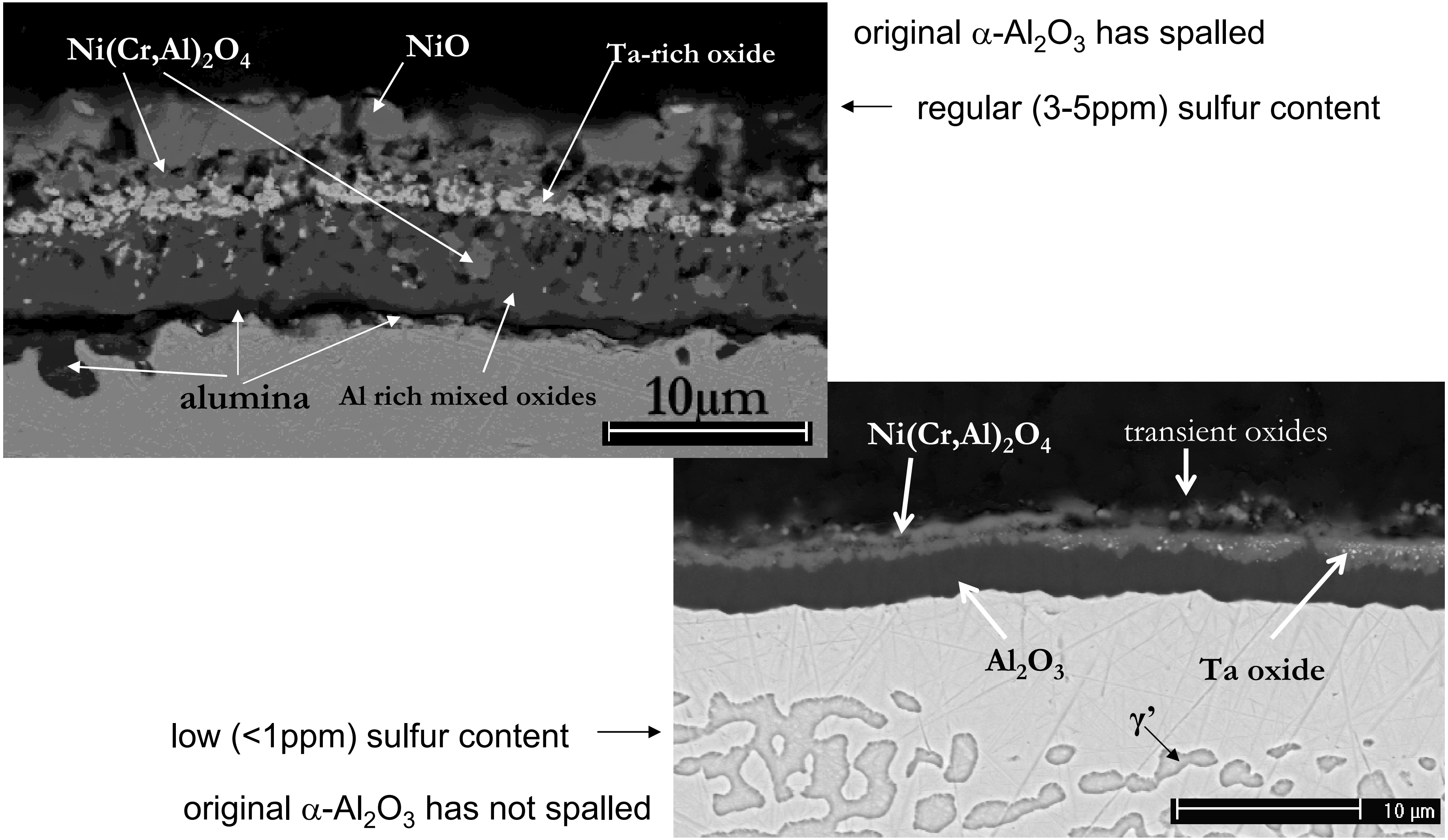
- **The effects produced by water vapor on the high temperature oxidation of alloys depends on the alloy system.**
- **In the case of oxidation resistant alloys such as Al_2O_3- and Cr_2O_3-formers, water vapor affects the oxidation resistance adversely.**

Effect of Water Vapor on Cracking and Spalling of α-Al_2O_3 Scales



- The presence of water vapor in the oxidizing gas mixture causes the α-Al_2O_3 scales to crack and spall more profusely than in dry gases

René N5 oxidized for 802 cycles @ 1100°C in air with 0.5atm water vapor



original α-Al_2O_3 has spalled

← regular (3-5ppm) sulfur content

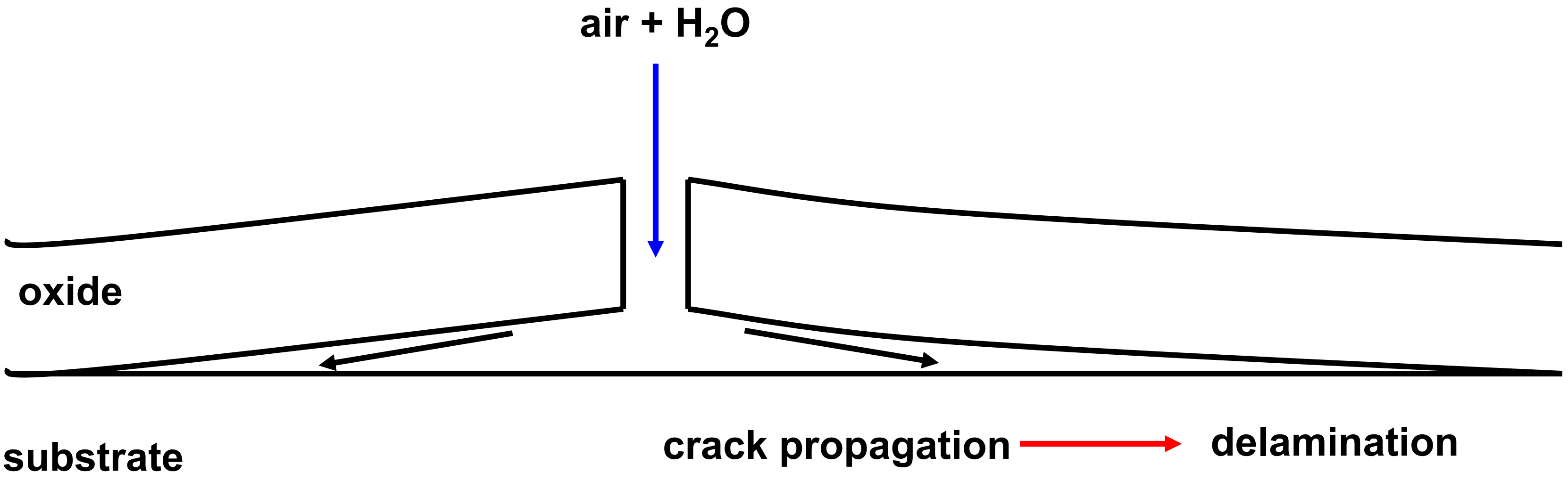
low (<1ppm) sulfur content →

original α-Al_2O_3 has not spalled

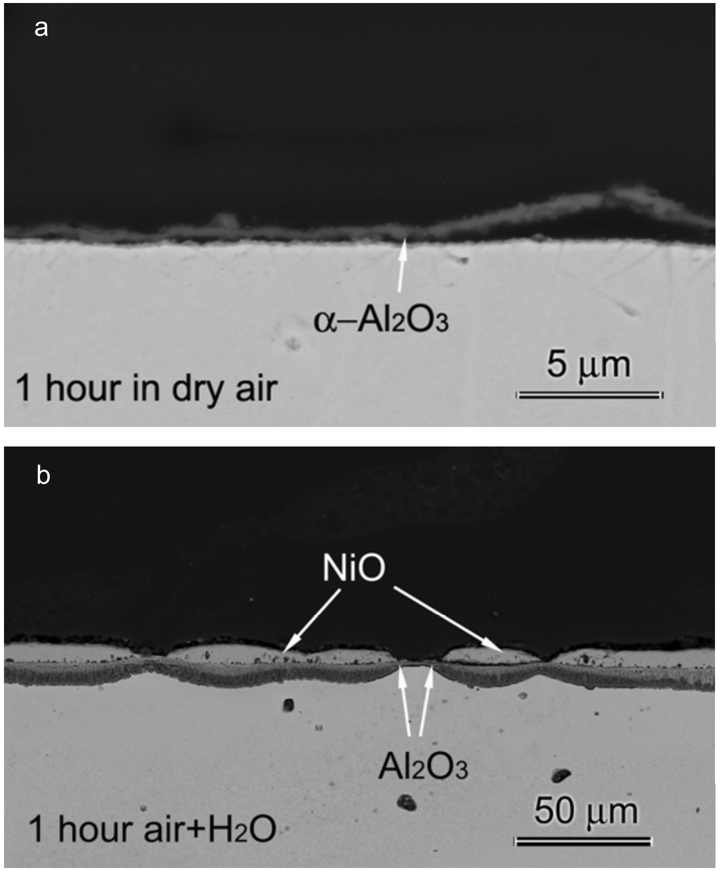
- Cracking and spalling becomes less pronounced for very adherent TGO scales; in other words, the cracking and spalling under water vapor conditions tests becomes less evident as the interfacial toughness between α-Al_2O_3 and substrate becomes greater.

Mechanism: Stress Corrosion Cracking

- Although cyclically oxidized low S superalloys do not spall as much as the regular S superalloys, water vapor has access to the oxide/substrate interface in both cases.
- Low S superalloys have increased spallation resistance because of a higher Al_2O_3/substrate interfacial toughness.
- A crack that forms propagates until it is large enough to result in failure. Water vapor has access to the oxide/substrate interface through cracks in the oxide and, combined with the stress, can cause spalling of the scale by interfacial stress corrosion cracking.

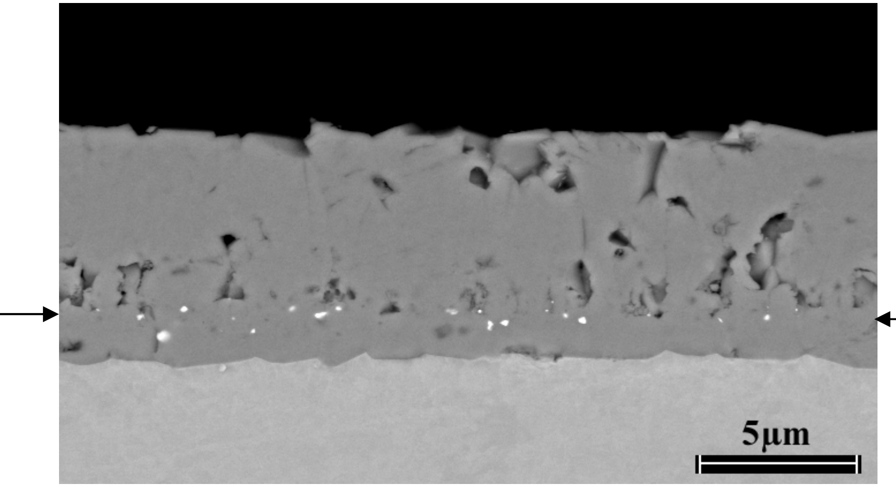


Water Vapor Adversely Affects the Selective Oxidation of Aluminum in Alloys

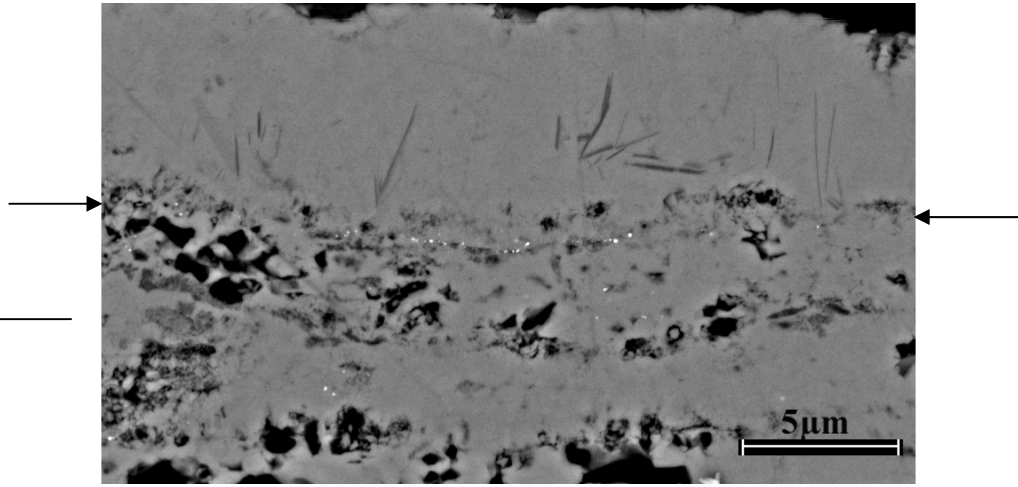


Cross-section of Ni-8Cr–6Al oxidized for 1 h at 1100ºC
(a) in dry air, and (b) in air with water vapor (0.1 atm).

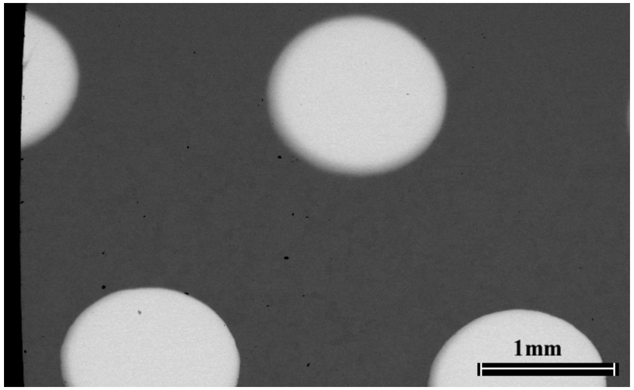
Cross-sections of Ni specimens exposed for 1hr@1100°C in dry air/air with water vapor showing position of Pt markers in the scale (see arrows);



dry air



air with water vapor (0.1atm)



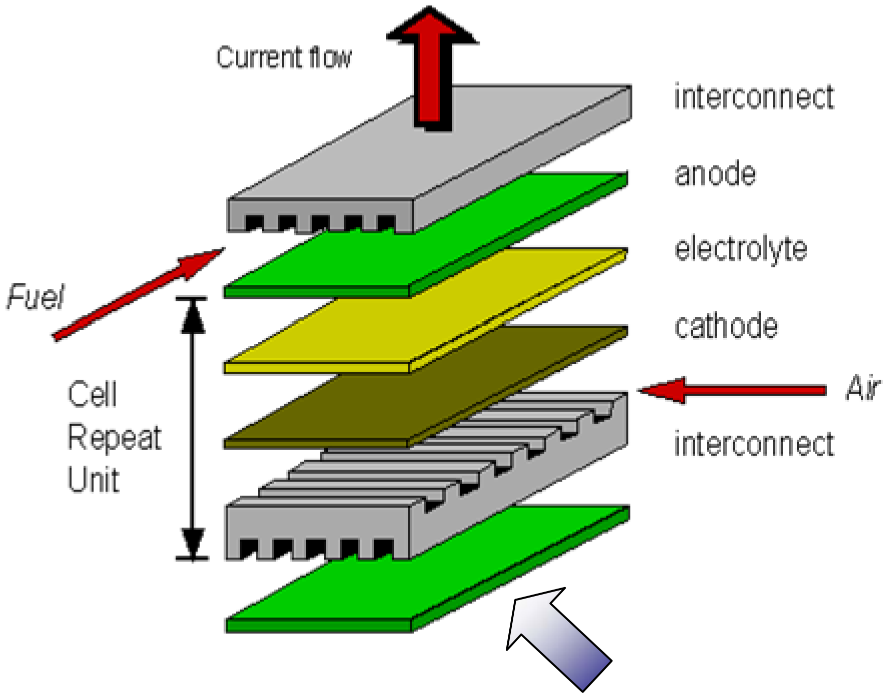
Pt mesh deposited in dots of 1mm diameter by sputtering

Highlights of important results:

- the initial stages of oxidation are affected by water vapor
  - more extensive transient oxidation stage
  - enhanced internal oxidation
  - inhibition of selective oxidation of Al

- NiO grows more rapidly during the transient period in water vapor
  - enhanced inward transport of oxygen-containing species along the oxide grain boundaries promotes growth of NiO
  - smaller grain size oxide

Planar SOFC Configuration



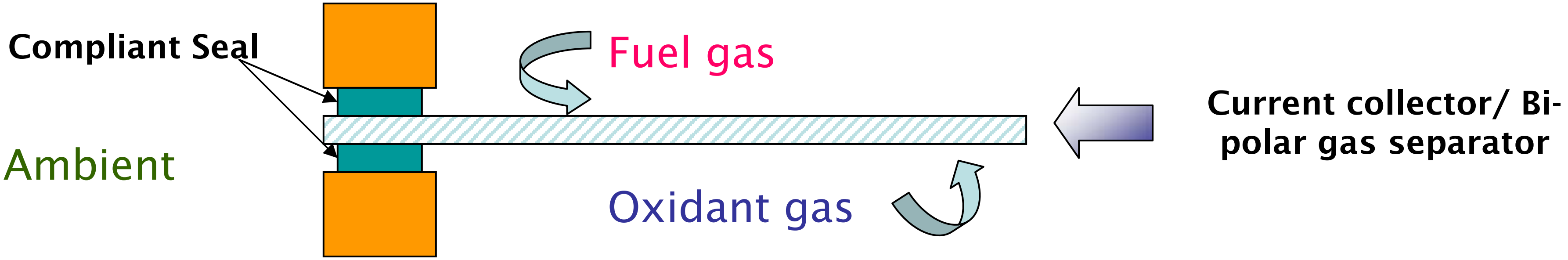
Repeat Components

Electrolyte – YSZ Cathode – La/Sr-Manganite (LSM)
Anode – Ni/YSZ Interconnect – Metallic

SOFC Current Collector (Interconnect)

Exposure Conditions

T = 600 – 800°C



Requirements

Low ASR

Surface Stability

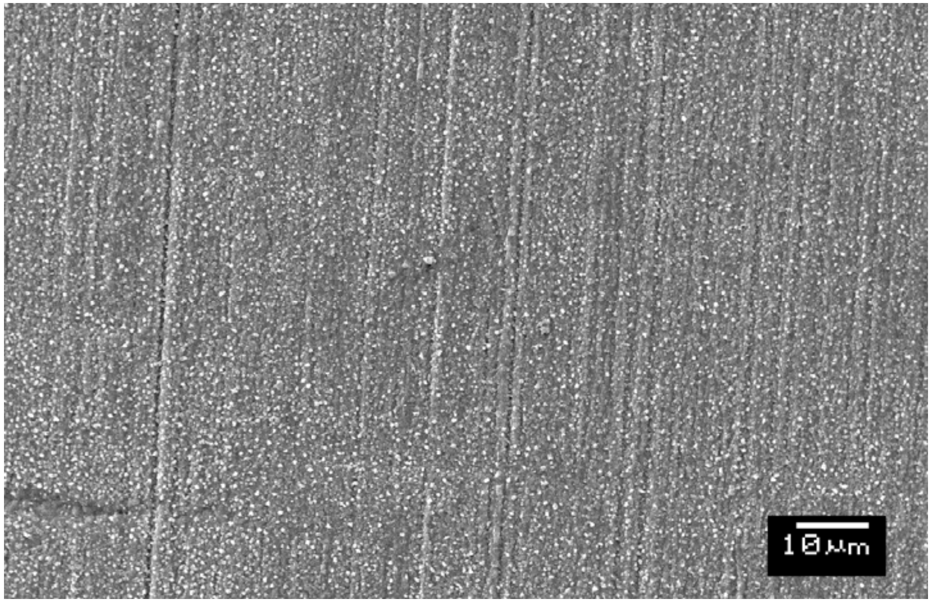
Air ± H_2O, Fuel + H_2O, Dual Atmospheres

No Contamination of Other Components

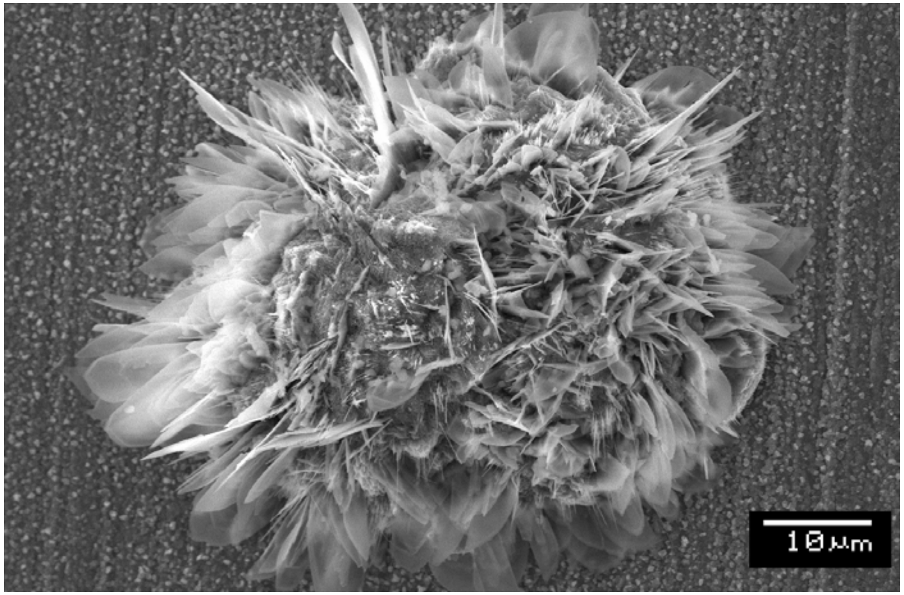
Metallurgical Stability

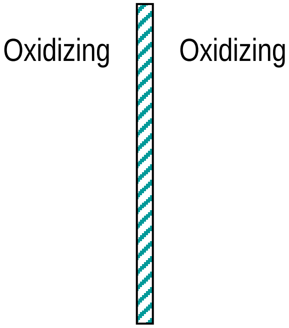
Dual Atmosphere Effect – 304 Stainless Steel

Air – Air Exposure

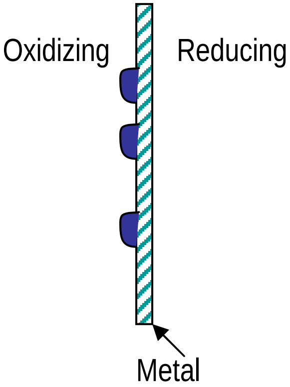


Air Side – Dual Atmosphere Exposure





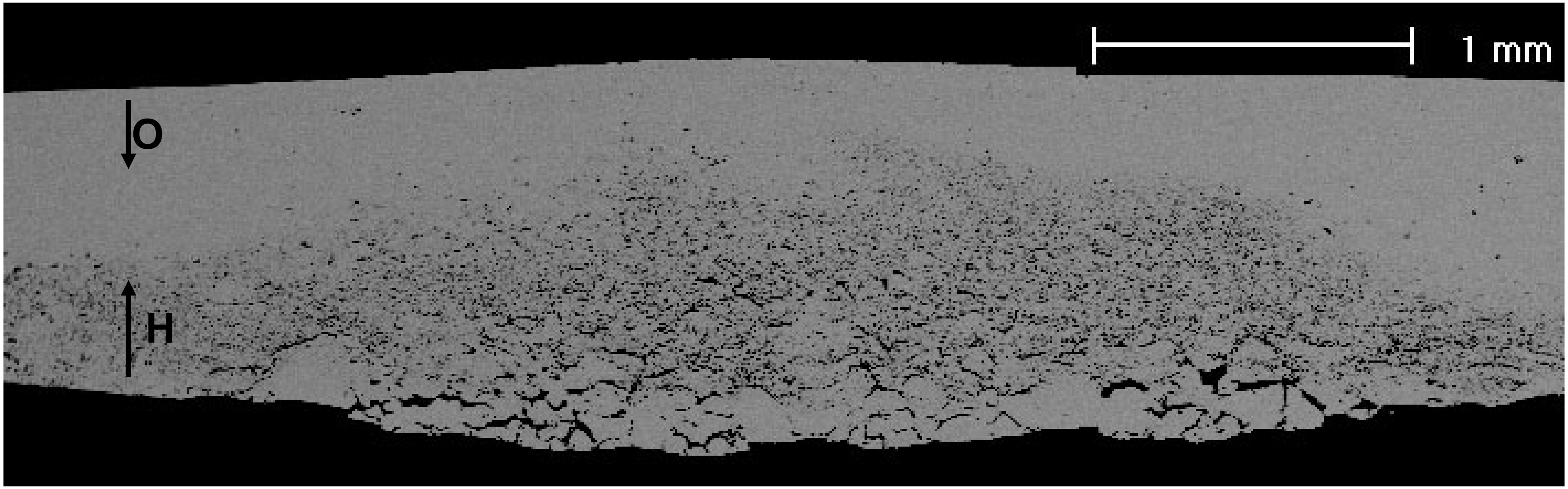
Uniform Cr_2O_3



Fe-rich Oxide Nodules

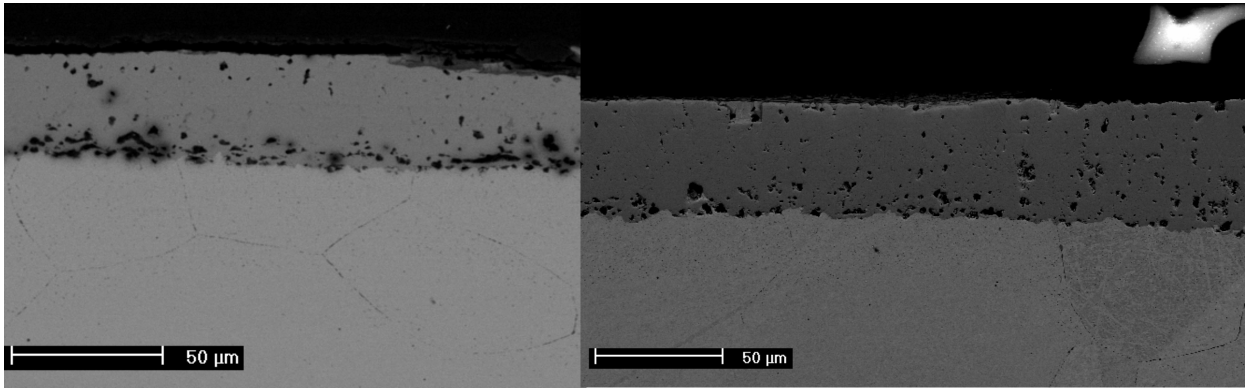
Silver Exposed Under Dual Atmosphere Conditions for 24 h at 800°C

Air Side



Ar-H_2-H_2O Side

Ni-200 - 600 Hours 800°C

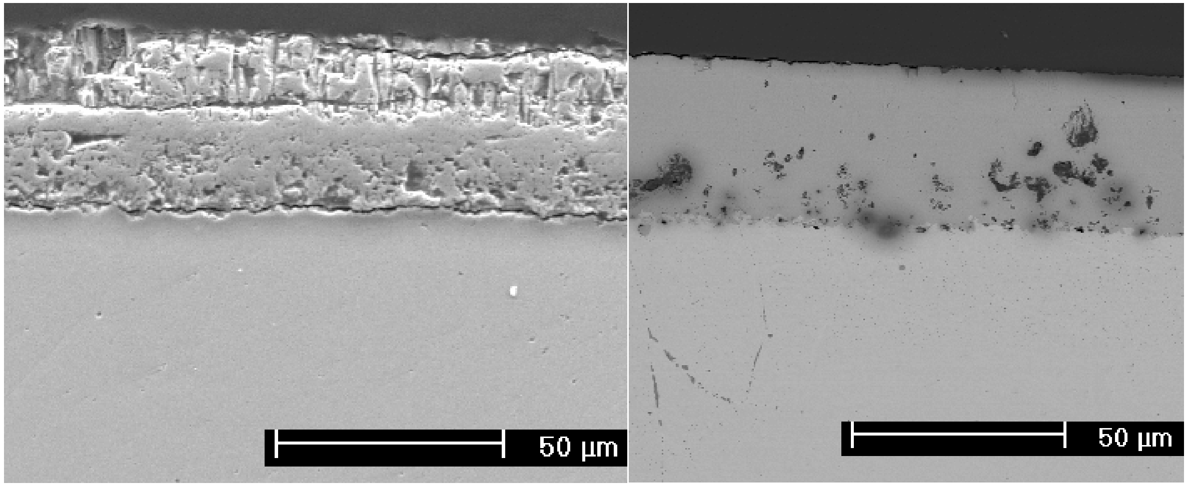


Air Side

Air/Air

400 Hours 800°C

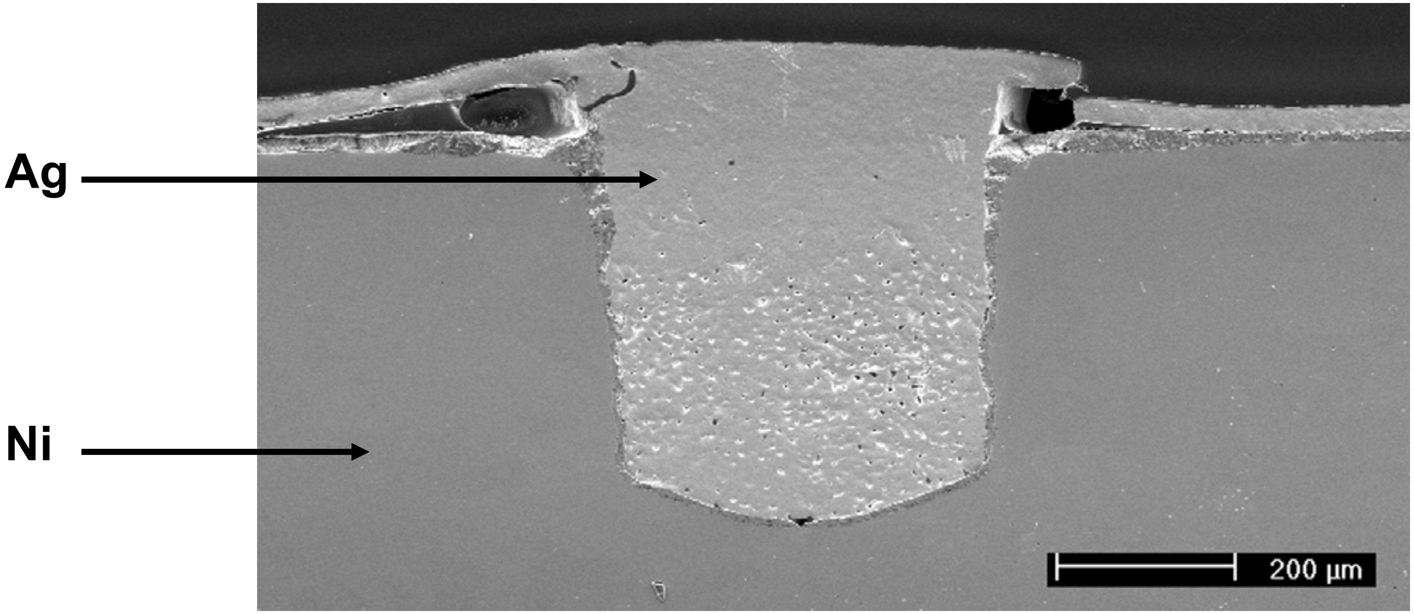
Ar-10%H$_2$0-4%H$_2$/Air



Air Side

Ar-4%H$_2$

High Conductivity Pathway

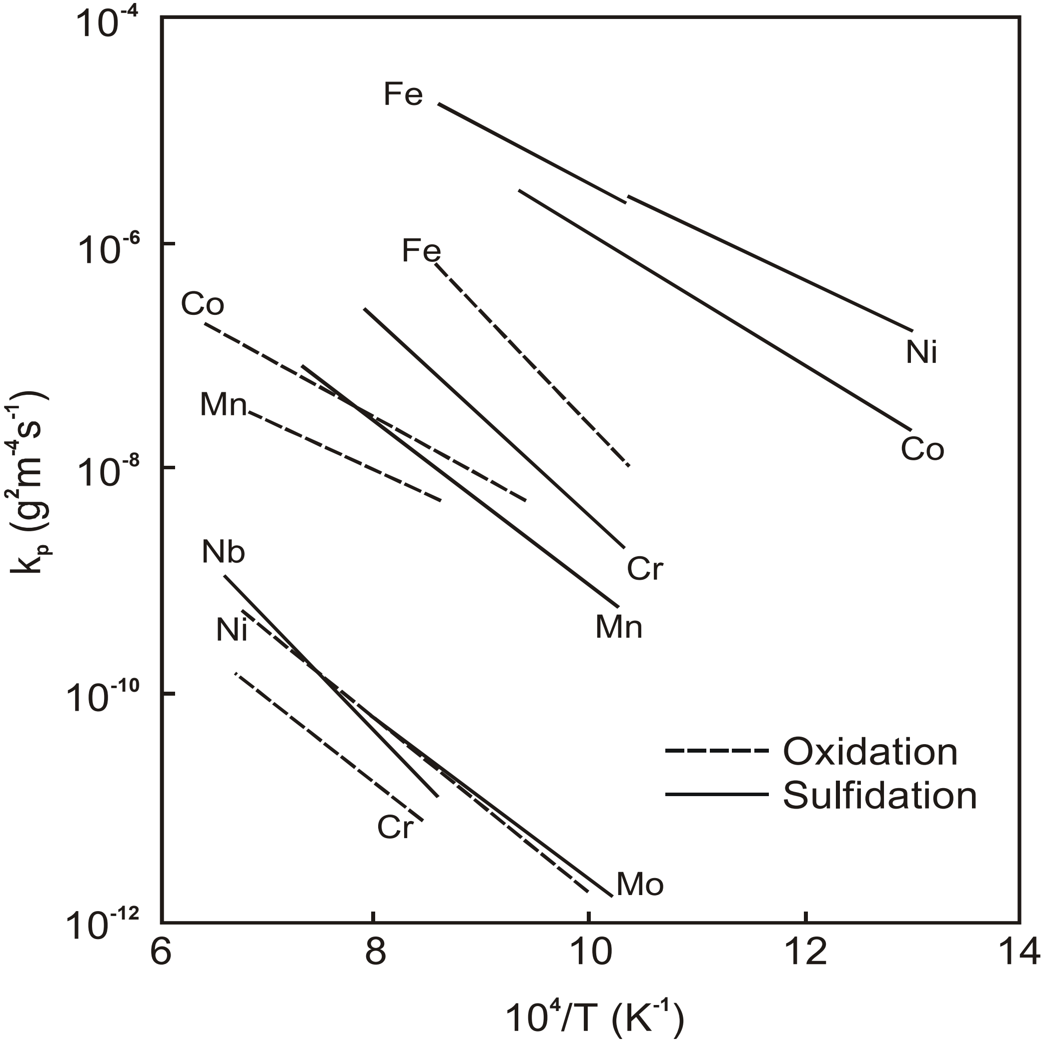


Silver Via, 800°C 100 Hours, exposed under dual atmospheric conditions. The upper surface was exposed to dry air while the lower surface was exposed to simulated anode gas of Ar-10%H_2O-4%H_2.

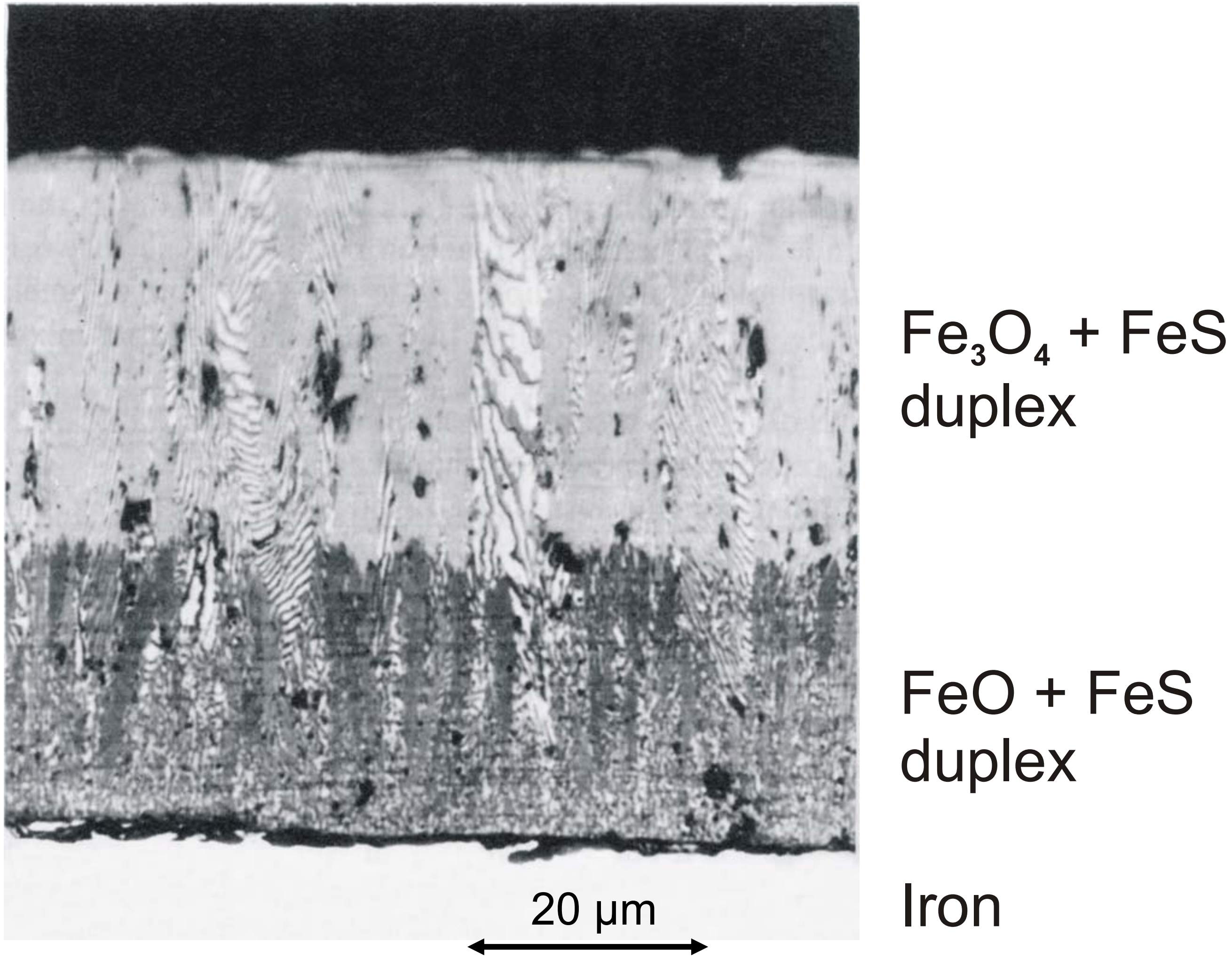
Mixed Oxidant Corrosion

The phases formed from other oxidants generally grow faster than the respective oxides (with some notable exceptions).

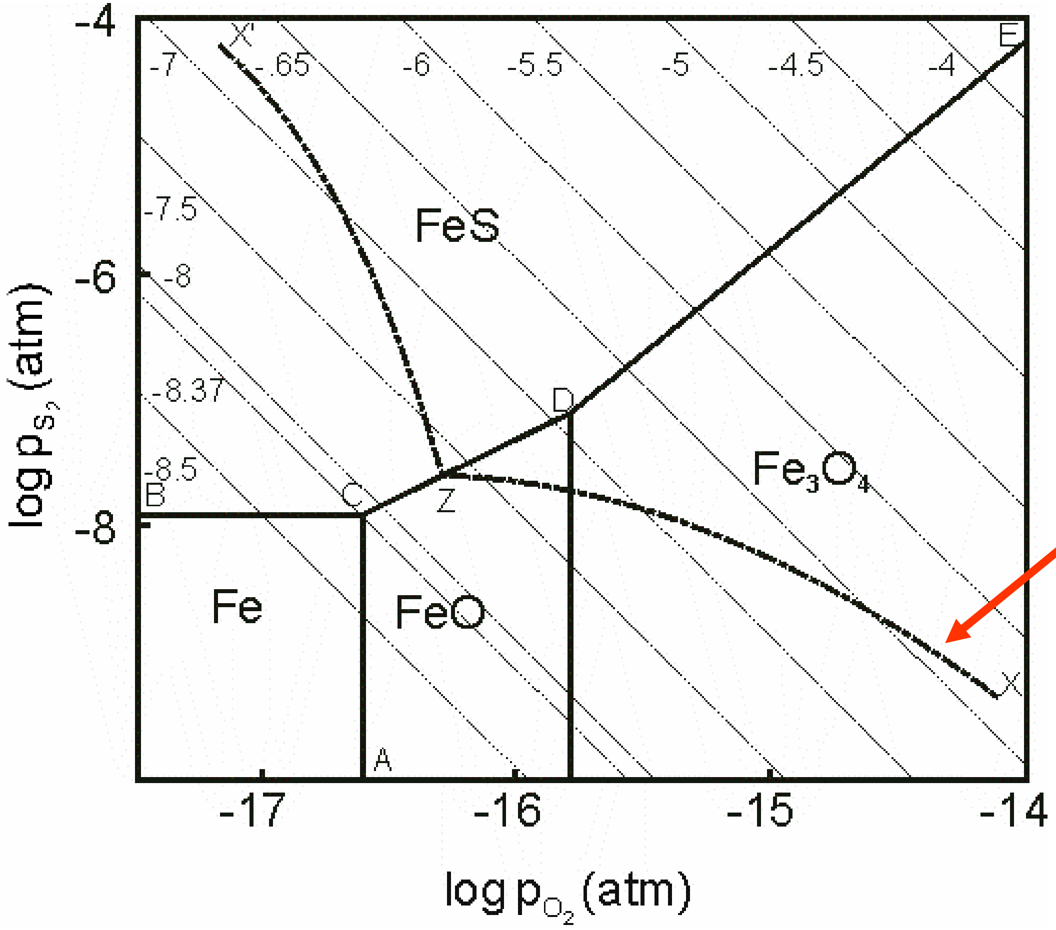
Growth of Oxides and Sulfides



Duplex Sulfide/Oxide Scale on Iron in Ar-1%SO_2 at 900°C

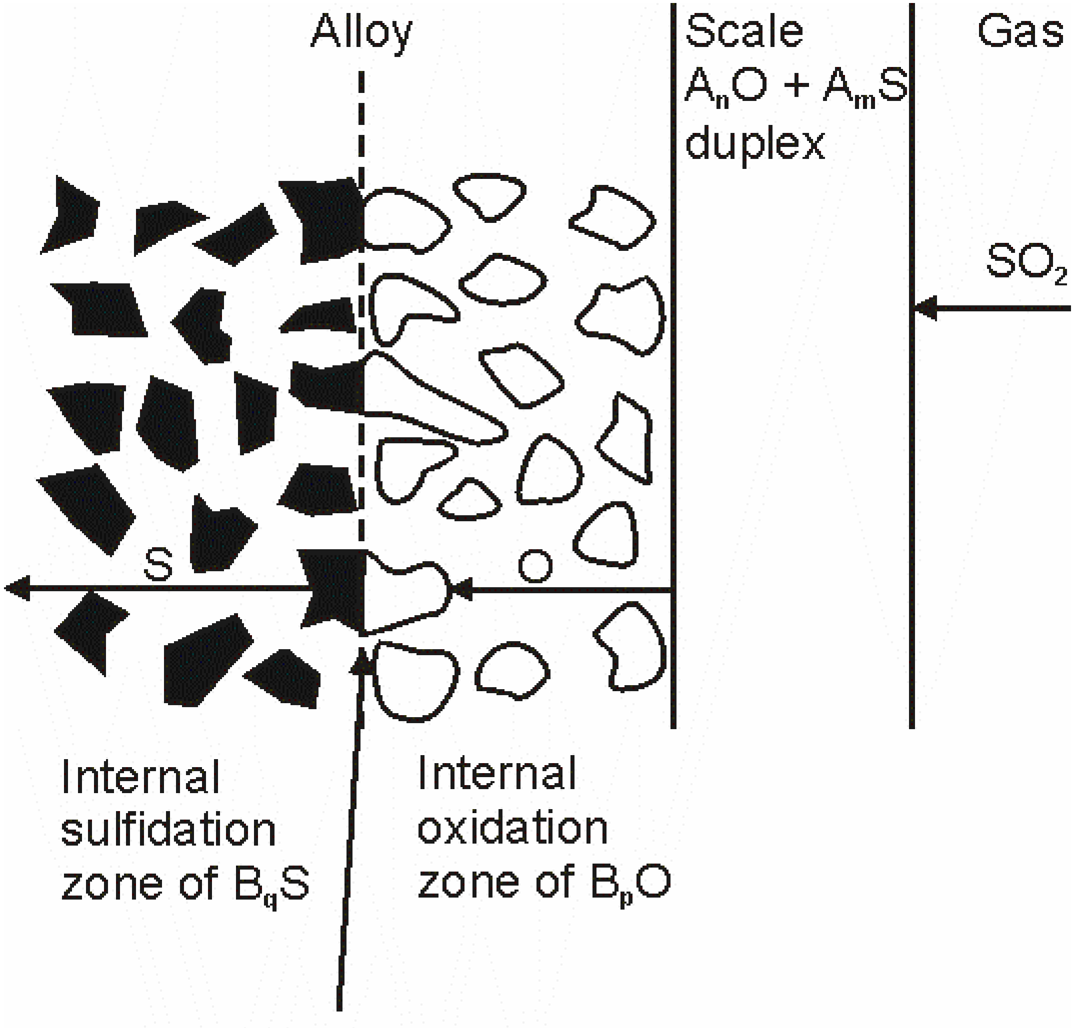


Reaction Path



Reaction Path

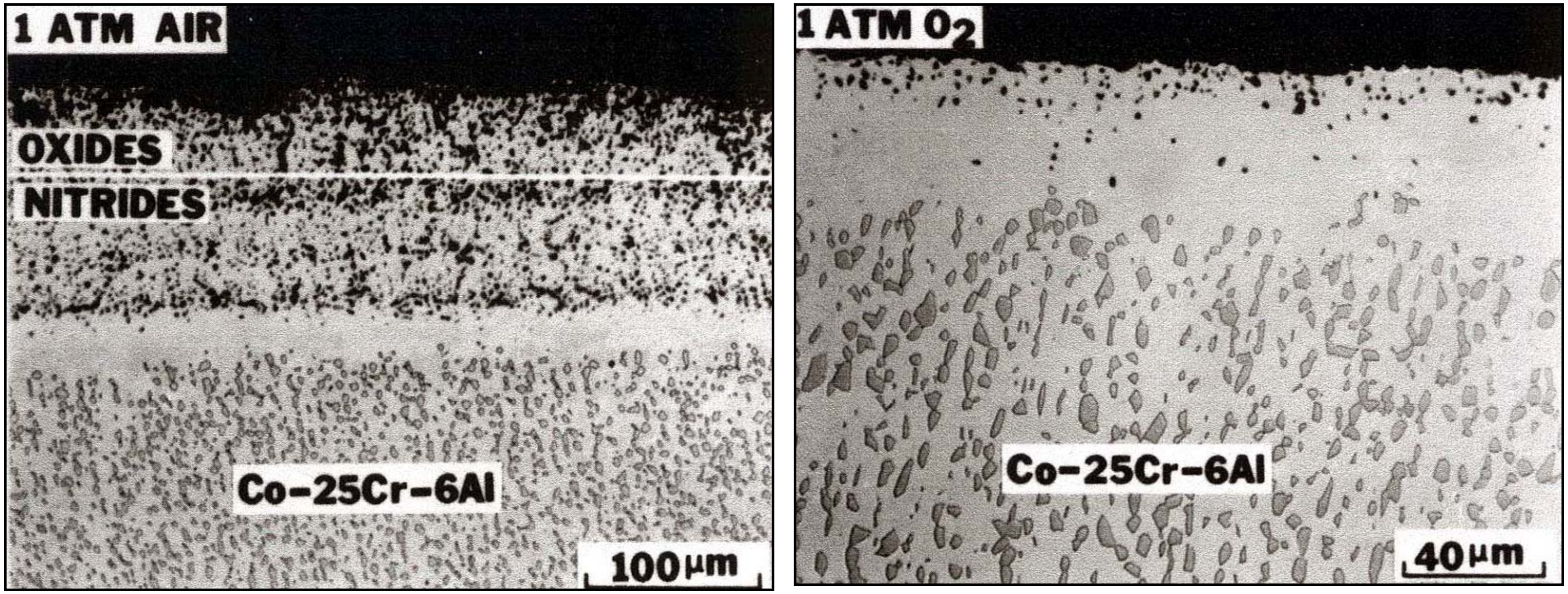
Sulfidation/Oxidation of an Alloy



$$\underline{O} + B_qO = B_pO + \underline{S}$$

Other Reactants in Gas Affecting Cyclic Oxidation of Alumina Formers

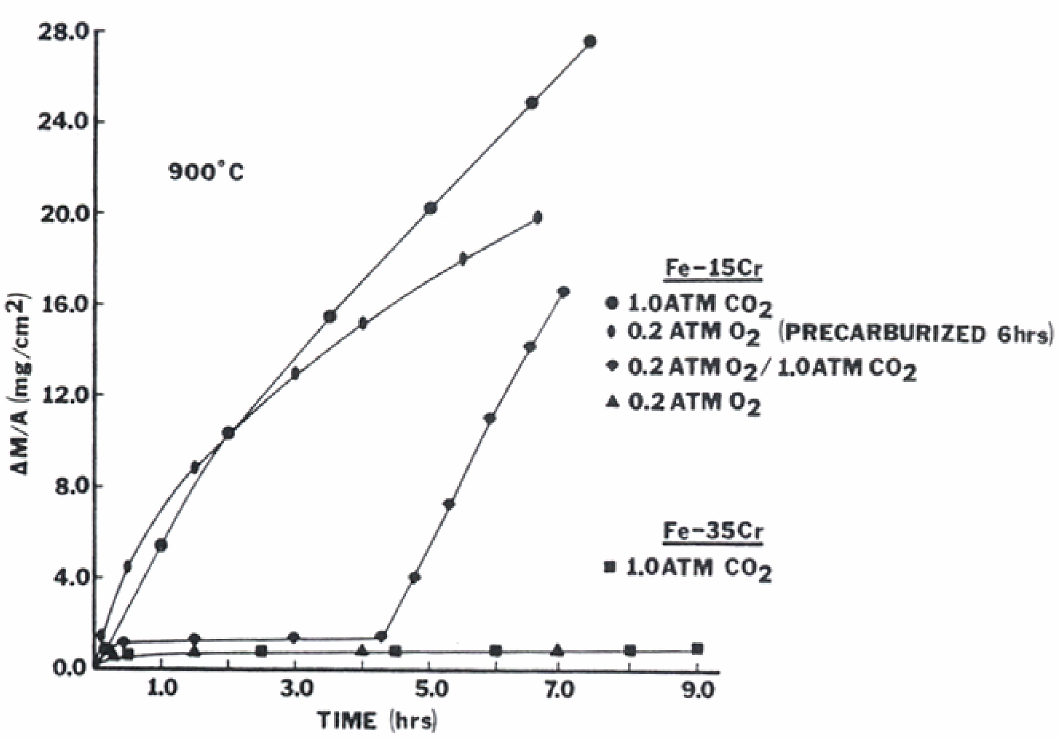
The second reactant causes alumina formation to stop at shorter times

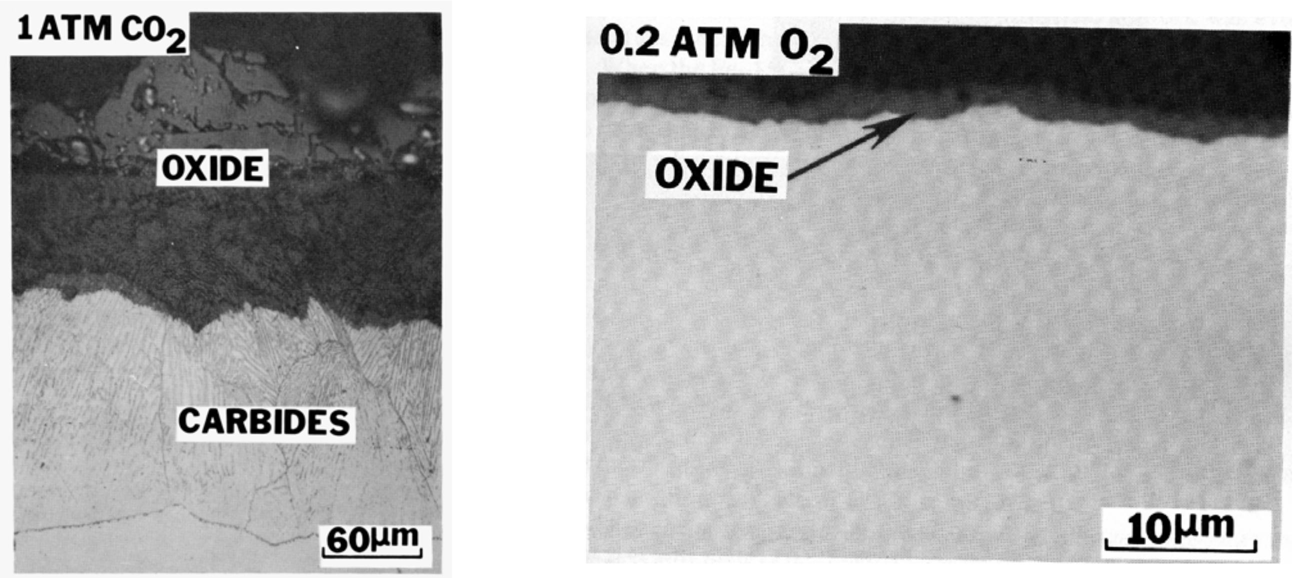


Effects of Carbon on the High Temperature Corrosion of Fe-Base and Ni-Base Alloys

- Gases with low carbon activities can disrupt the selective oxidation process.
- Gases with high carbon activities ($a_C>1$) can result in coking and metal dusting. (T range for dusting 400-850^oC)

Effect of CO_2 on the Oxidation of Fe-Cr Alloys

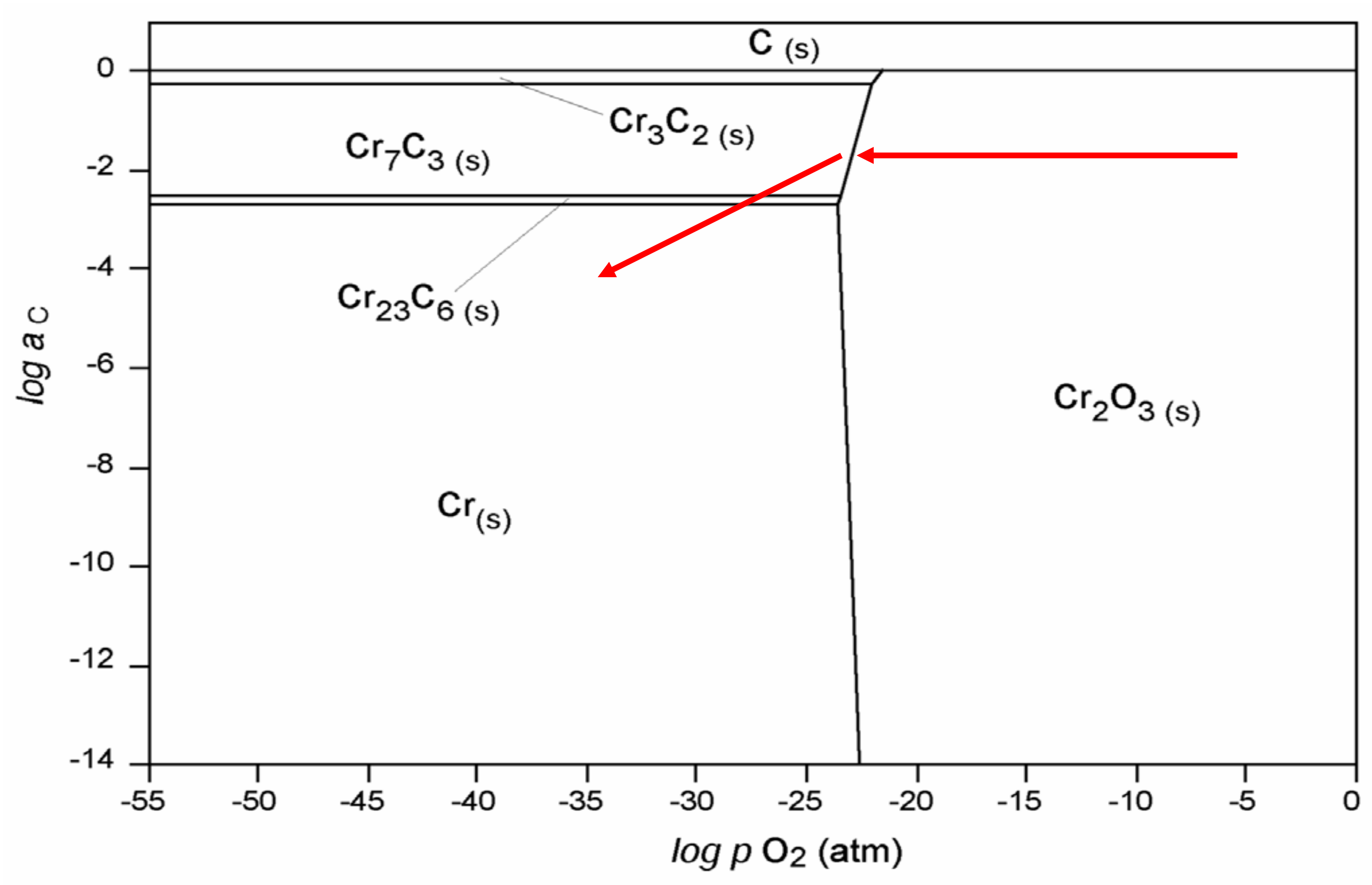




Cross-sections of Fe-15wt%Cr Oxidized at 900°C

Alloy on the left was exposed for 4 h in CO_2

Alloy on the right was exposed for 16.6 h in 0.2 atm O_2



Isothermal Stability Diagram for the Cr-C-O System at 1250K

Carbon Activity in Gaseous Mixtures

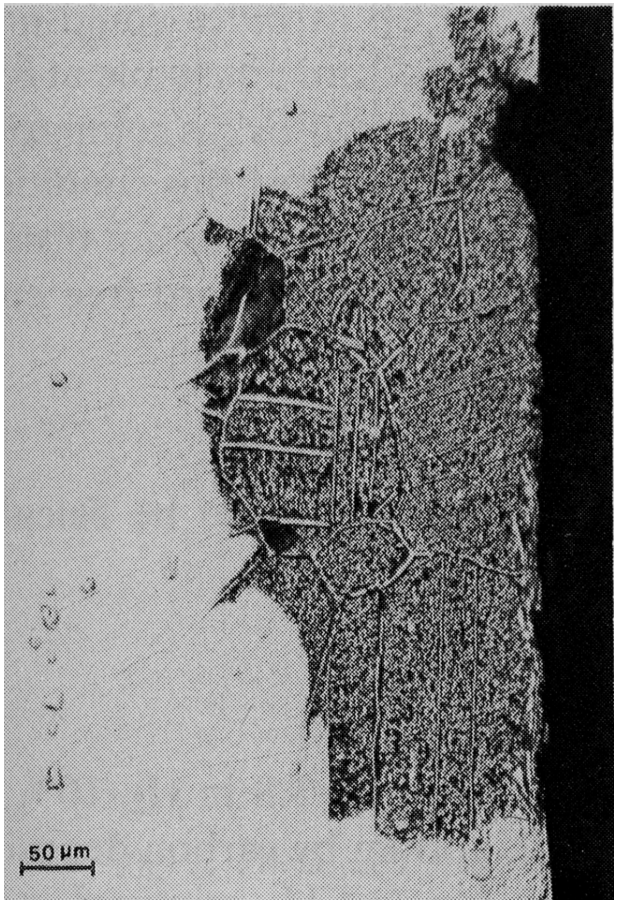
Consider a gas consisting initially of 99%CO and 1% CO_2 at P = 1 atm entering a system at 1100K

$$2CO(g) = C(s) + CO_2(g)$$

$$K = \frac{a_C \, p_{CO_2}}{p_{CO}^2}$$

$$a_C = \frac{K p_{CO}^2}{p_{CO_2}}$$

$K_{1100} = 0.0885$ → $a_c = 8.7$ i.e. Gas is Supersaturated



Metal Dusting of Alloy 800 Exposed for 48 h at 850°C in Ar-10%CH_4