Overview Of Conductive Scale Growth

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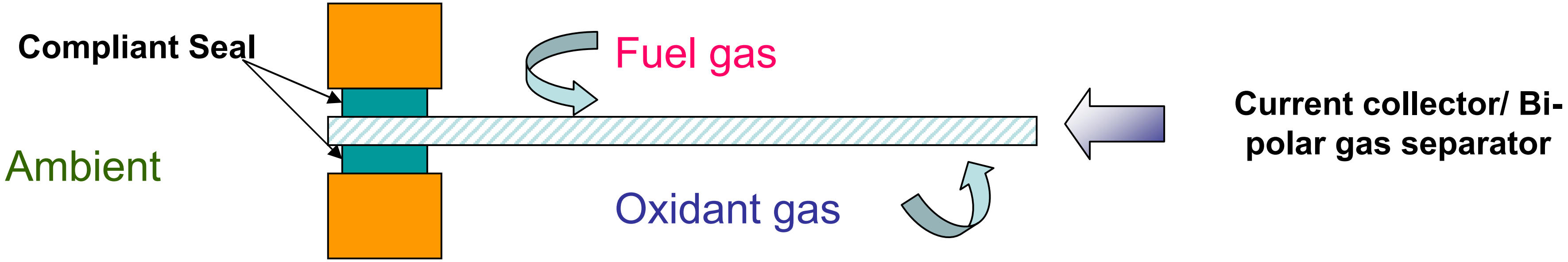
Outline

- Interconnect Requirements
- Selective Oxidation
- Oxide Growth Rates
- Oxide Electrical Properties
- Oxide Volatility
- Alloy Stability
- Summary

Current Collector (Interconnect) Exposure Conditions

T = 600 – 800°C



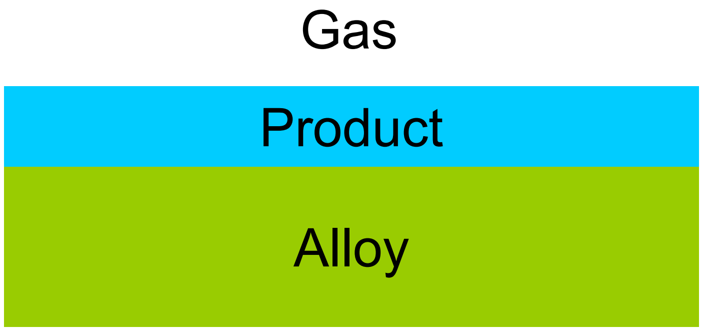
Interconnect Functional Requirements

- Long Term Chemical Stability: 40,000Hrs.
    - High-temperature Corrosion / Oxidation Resistance
    - Resistance to Thermal Cycling
    - Oxide Compatibility with Cell Components
- Electrical Performance Stability: ~ 0.1% Voltage reduction
    - Conducting Scale formation
    - Oxide Stability
- Mechanical / Structural Stability
    - Thermal expansion coefficient match
    - Weld / Joint Stability
    - Microstructural Stability

Material	TEC
YSZ	$10\text{-}11 \times 10^{-6}$/ºC
Cr-based alloys	$11\text{-}12 \times 10^{-6}$/ºC
400-series stainless steel alloys (Fe-Cr)	$12\text{-}13 \times 10^{-6}$/ºC
X10Cr alloys (Fe-Cr-1Al)	$13\text{-}14 \times 10^{-6}$/ºC
Ni-based alloys (Ni>60%)	$13\text{-}16 \times 10^{-6}$/ºC
Ni-based alloys (Ni<60%)	$16\text{-}19 \times 10^{-6}$/ºC
Other stainless steel alloys (Fe-Cr-5Al)	$15\text{-}18 \times 10^{-6}$/ºC

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.

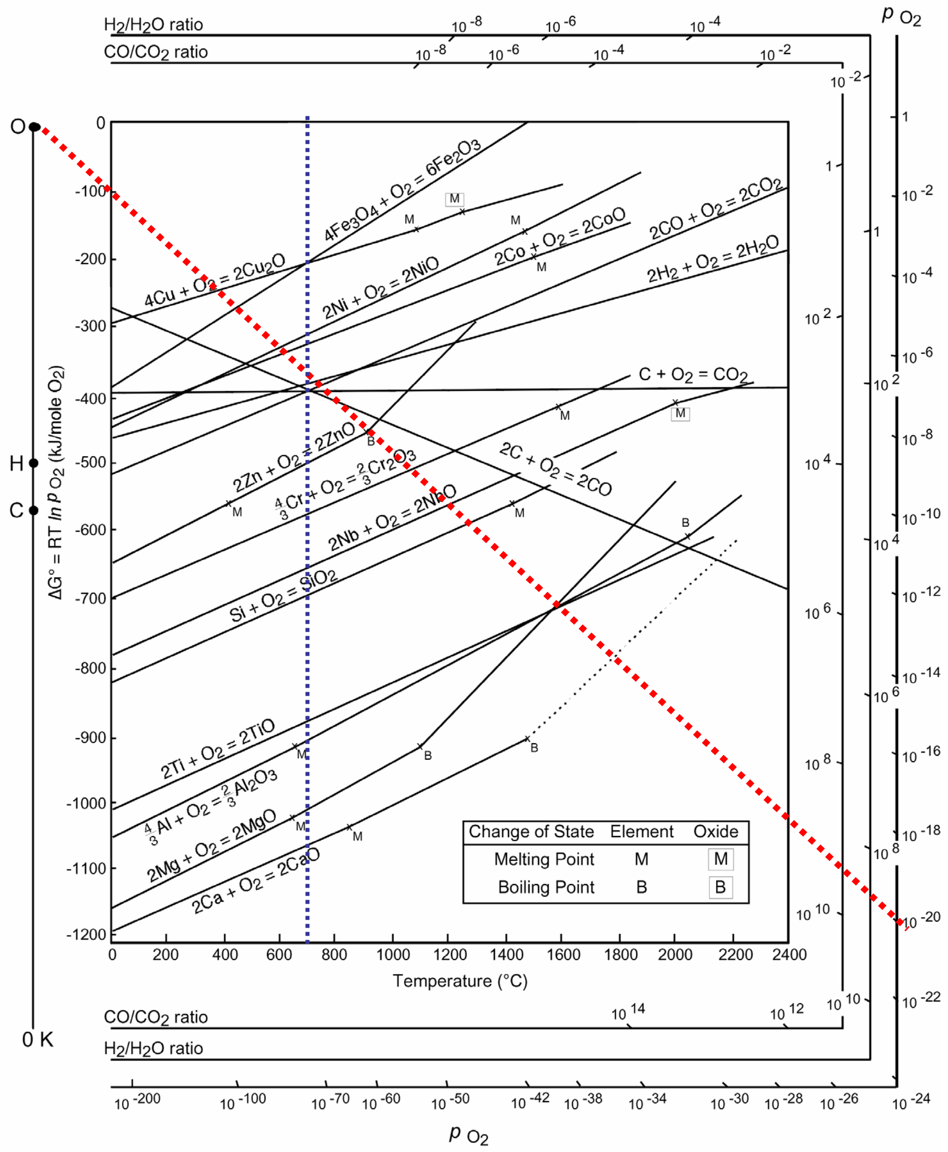


$ASR = \rho_{ox} h_{ox}$

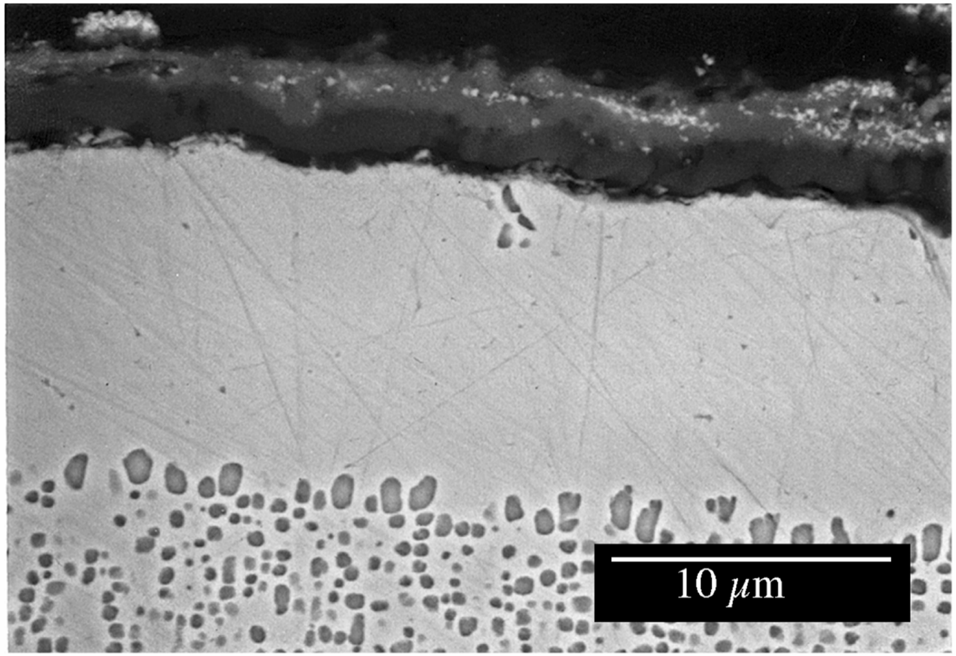
Most environments encountered in practice contain some oxygen, hence protective barriers are usually α-Al_2O_3, Cr_2O_3 and SiO_2.

For SOFC-ICs one wants to avoid the selective oxidation of Si and Al.

Ellingham Diagram



PWA 1484 oxidized at 1100°C

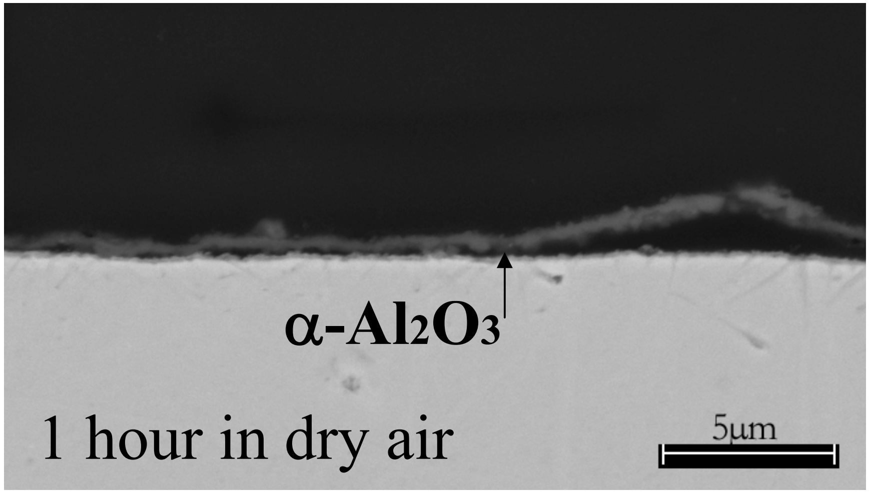


Transient Oxide

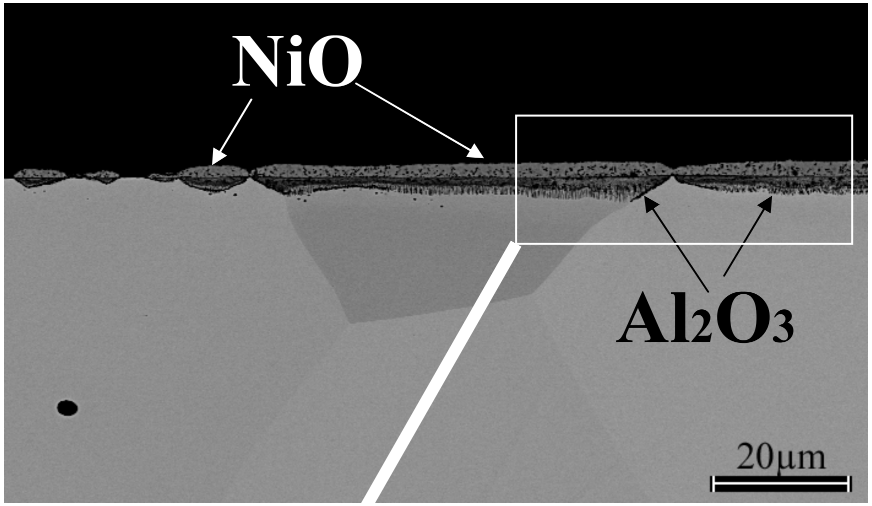
Alumina

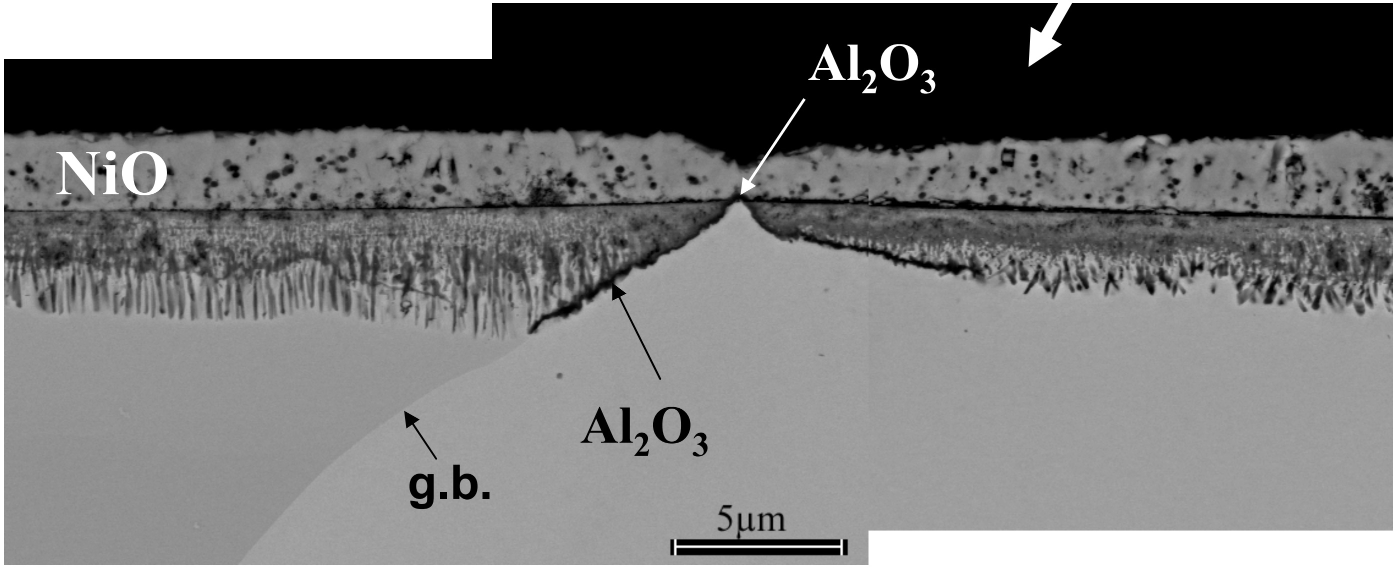
Al Depletion

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



1 hour in dry air

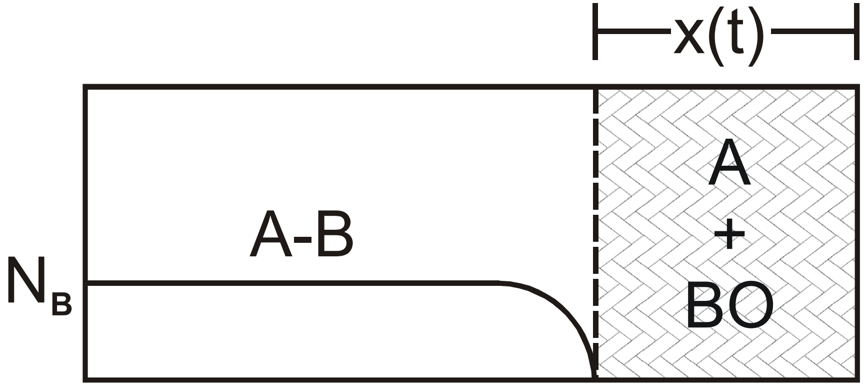




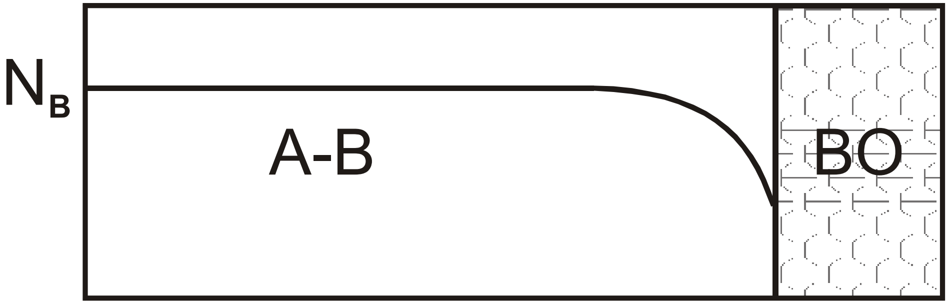
1 min in air with water vapor (0.1atm)

Transition to Extenal Scale Formation

a.



b.



Transition to Extenal Scale Formation

Equating the molar fluxes of solute B and oxygen

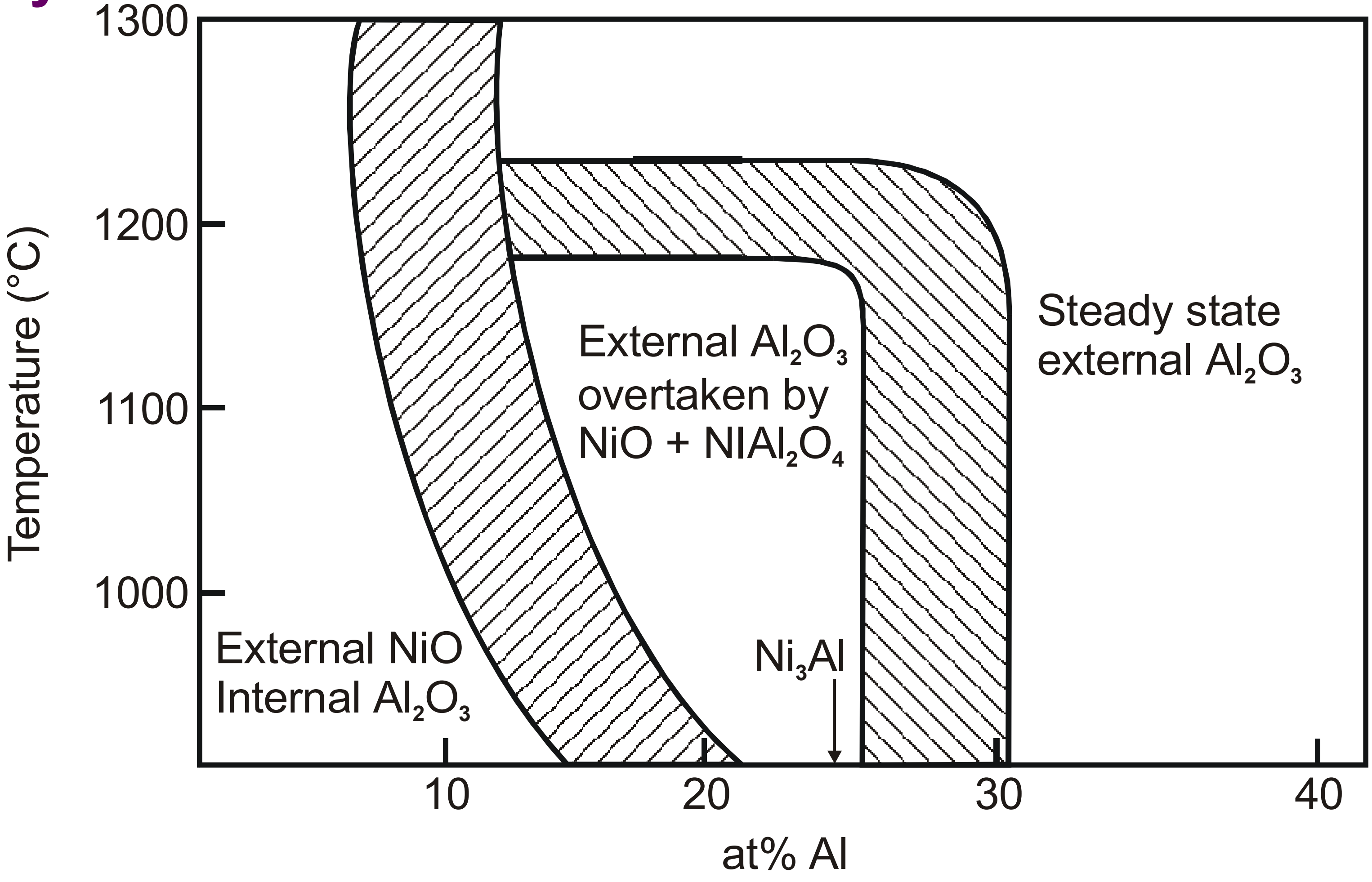
$$N_B^{(o)} > \left[\frac{\pi g^*}{2\nu} N_O^{(S)} \frac{D_O V_m}{D_B V_{ox}} \right]^{1/2}$$

Maintaining the Growth of an External Scale

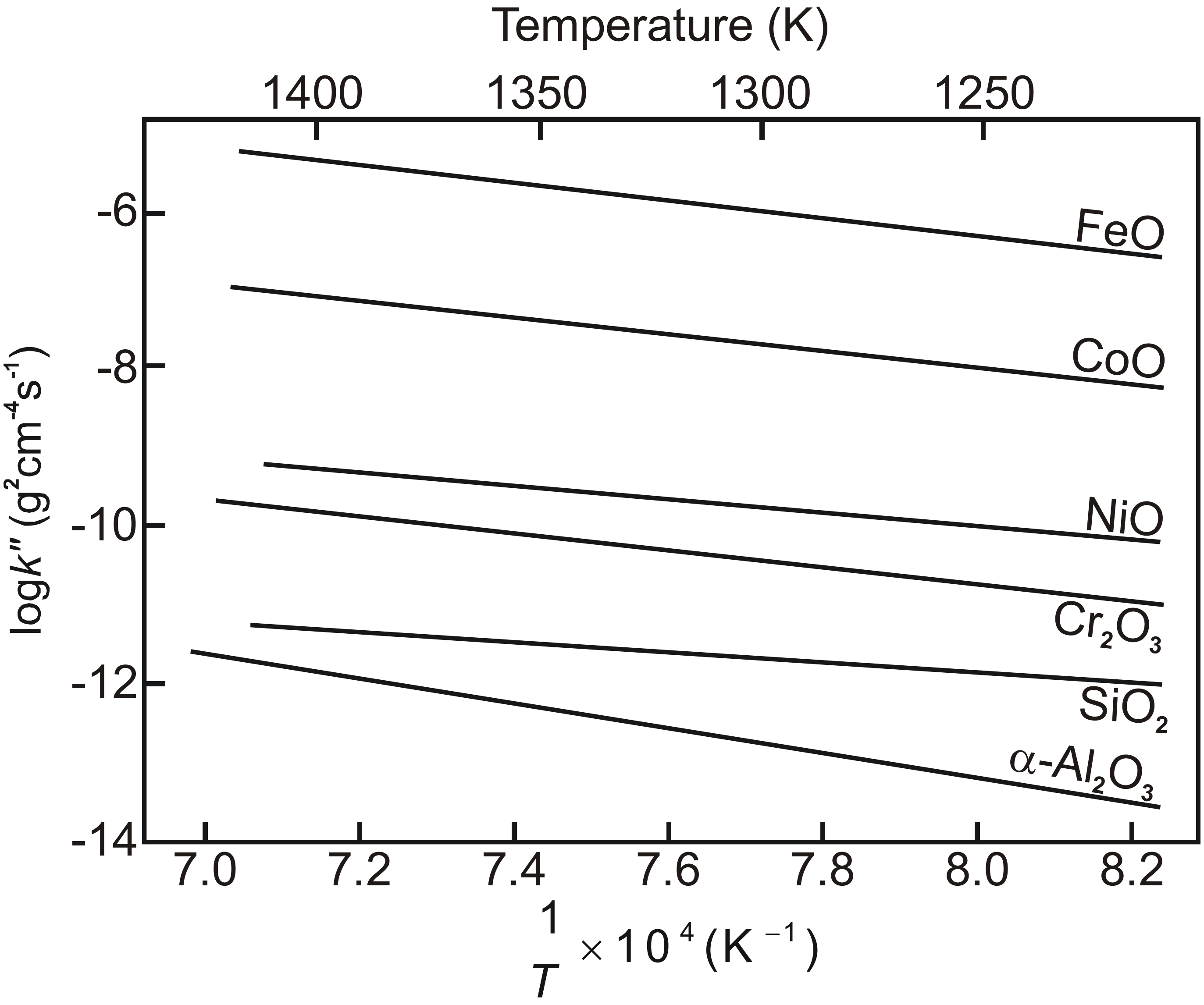
Equating the molar flux of solute B to that being required for oxide growth

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

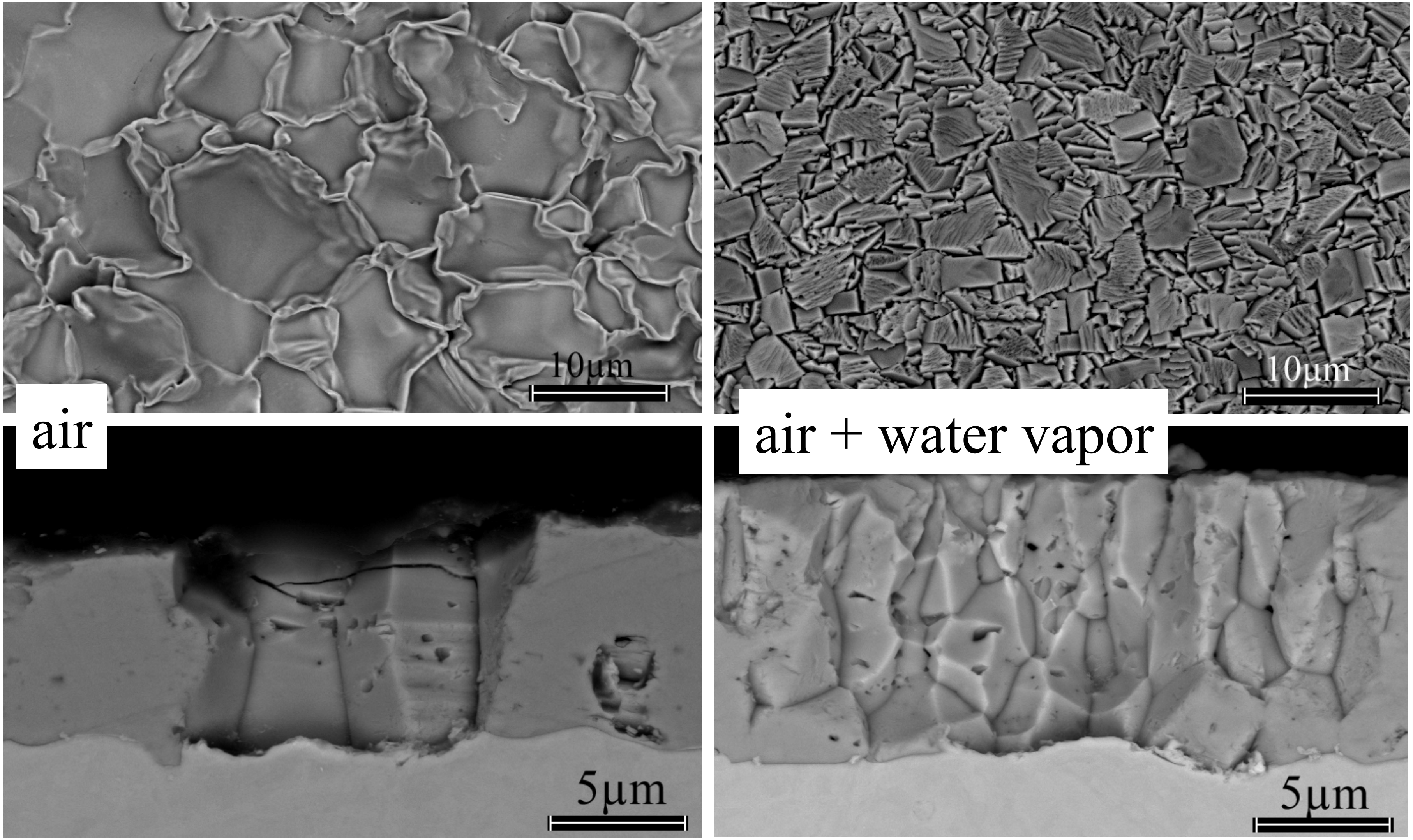
Effect of Temperature and Al Content on the Formation and Continued Growth of External Alumina on Ni-Al Alloys



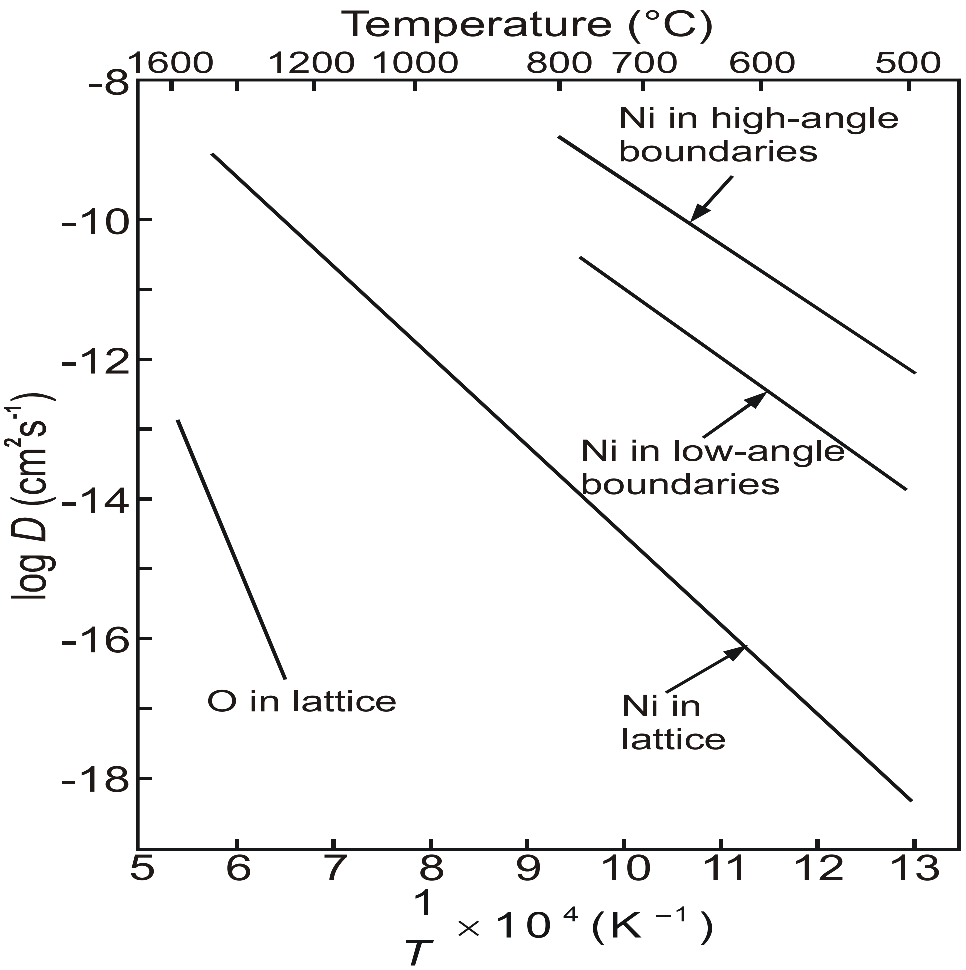
Relative Growth Rates of Several Oxides



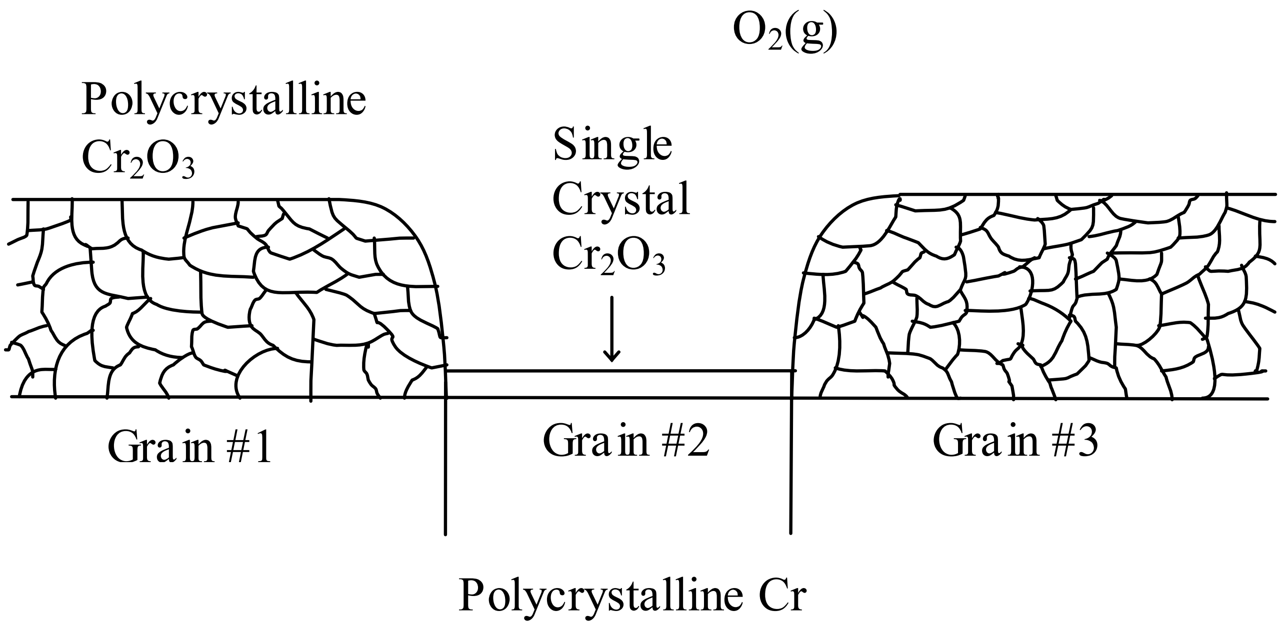
Ni 99.999+% pure, exposed for 1 hour @ 1100°C



Transport Paths - NiO

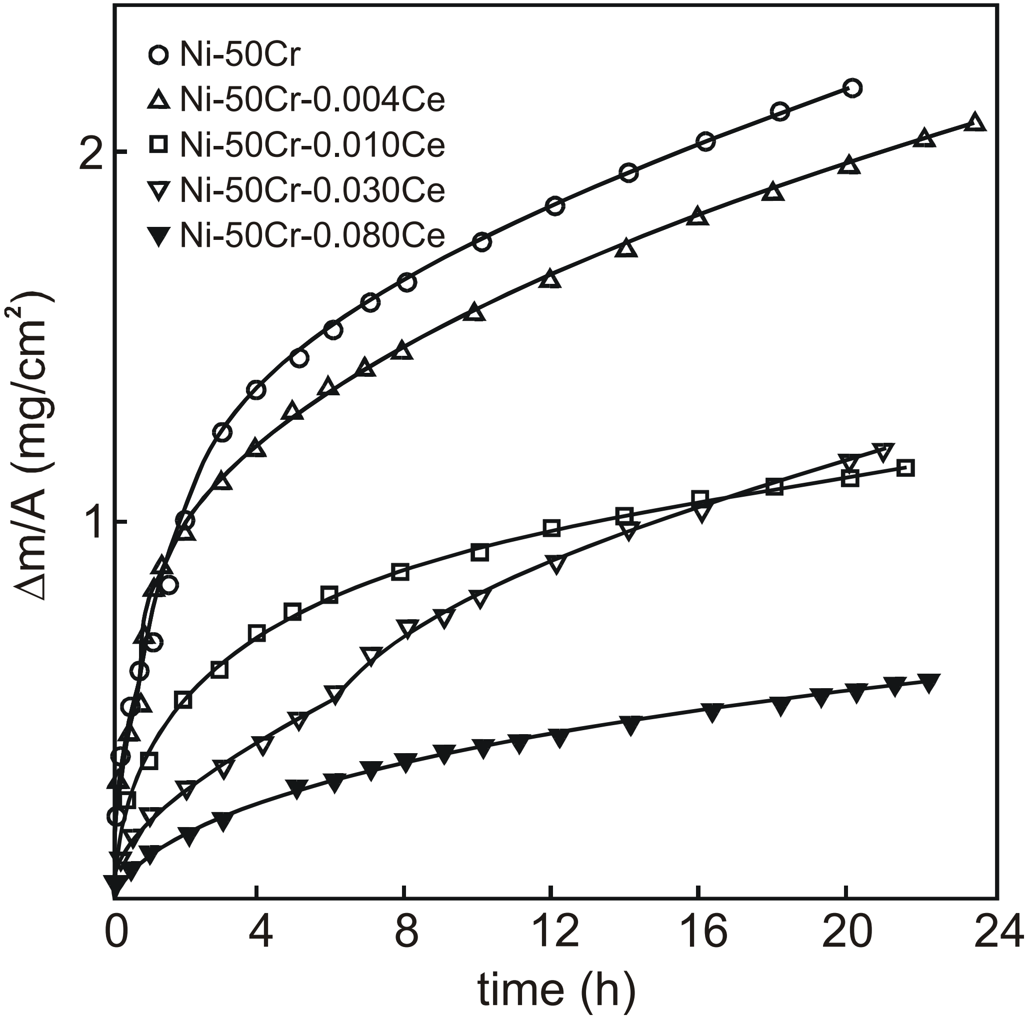


Oxidation of Chromia-forming Alloys



Caplan and Sproule, Oxid. Of Metals, 1975

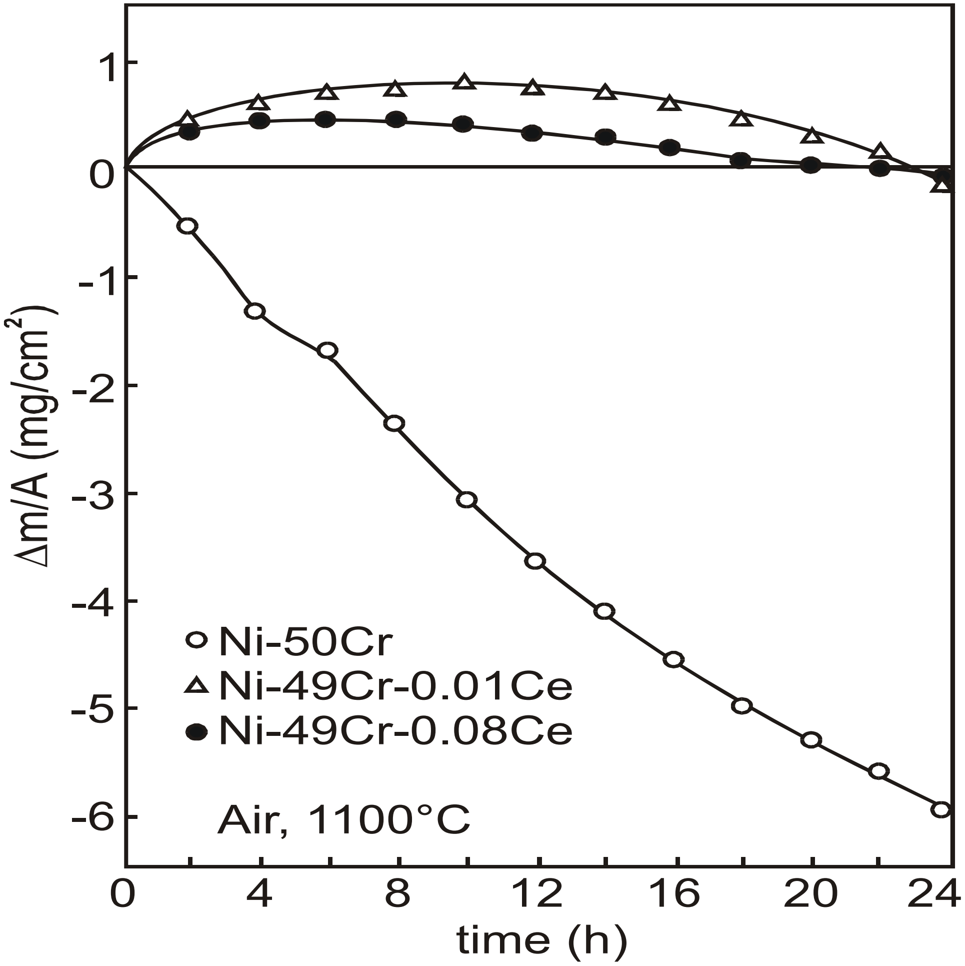
Isothermal Oxidation – RE Effect



Ecer, and Meier, Oxid. Of Metals, 1979

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

Cyclic Oxidation – RE Effect



Cyclic Oxidation

Oxidation of Ferritic Alloys

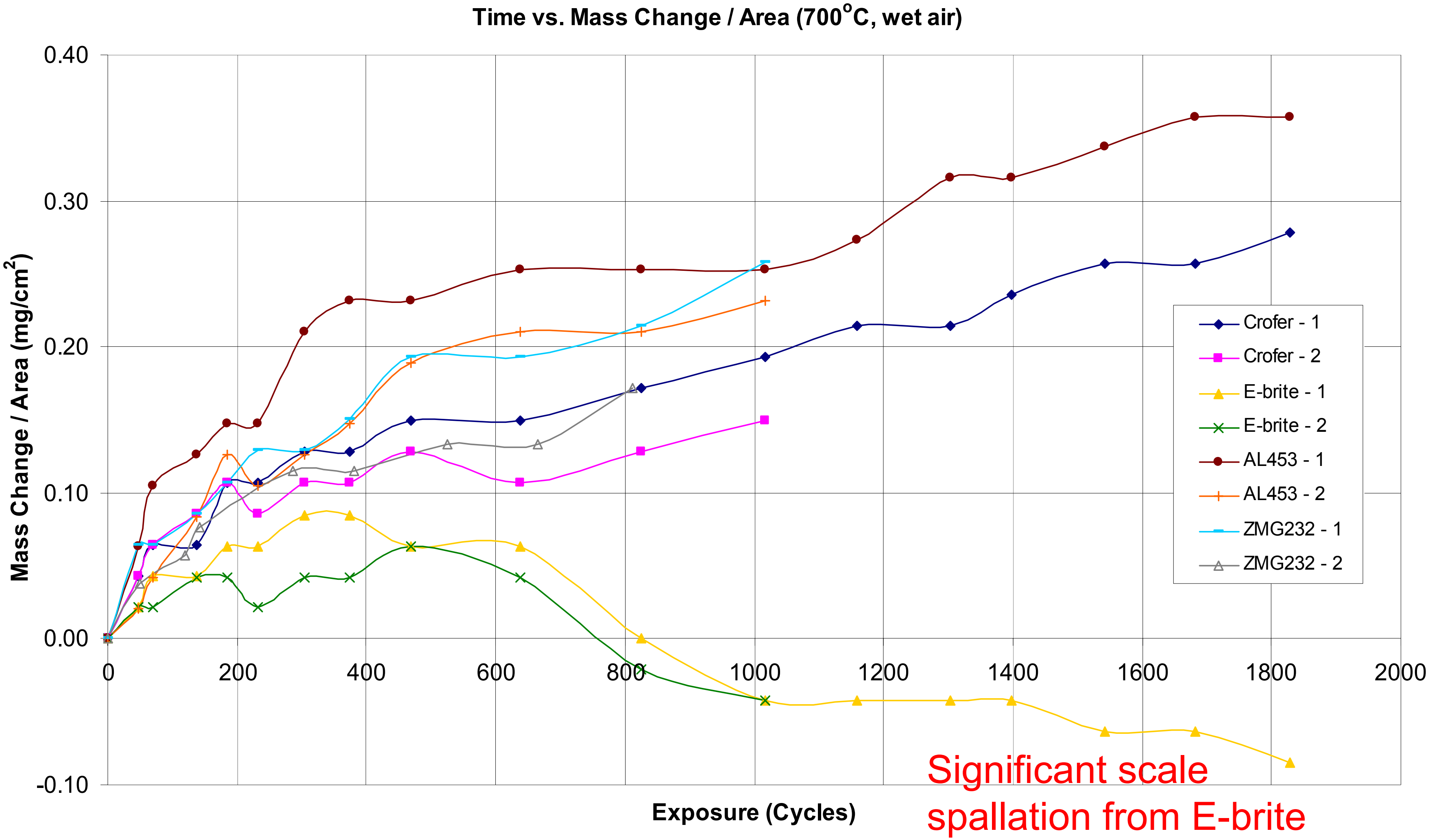
Alloys

- E-BRITE (26 Cr-1 Mo+Si)
- AL 453 (22 Cr +0.5Al+ Ce/La)
- Crofer (22 Cr +0.5Mn+ La)
- ZMG232 (22 Cr + La/Zr)

Exposure Conditions

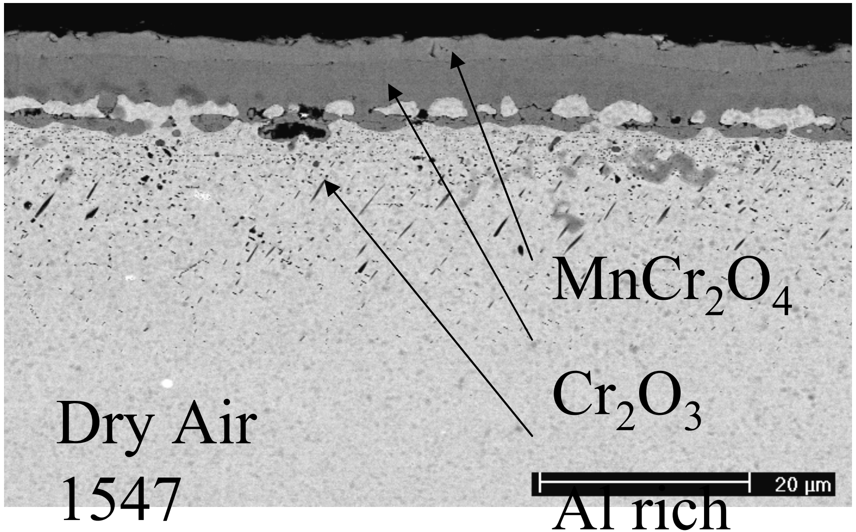
- T = 700°C, 900°C
- One-Hour Cycles
- Atmospheres
  - Dry Air (SCG)
  - Air + 0.1 atm H_2O
  - $Ar/H_2/H_2O$ (SAG) ($p_{O2} = 10^{-20}$ atm at 700°C and 10^{-17} atm at 900°C)

Wet Air (0.1 atm H_2O) Exposures - 700°C



Significant scale spallation from E-brite

Microstructural and Phase Identification
Crofer 900°C

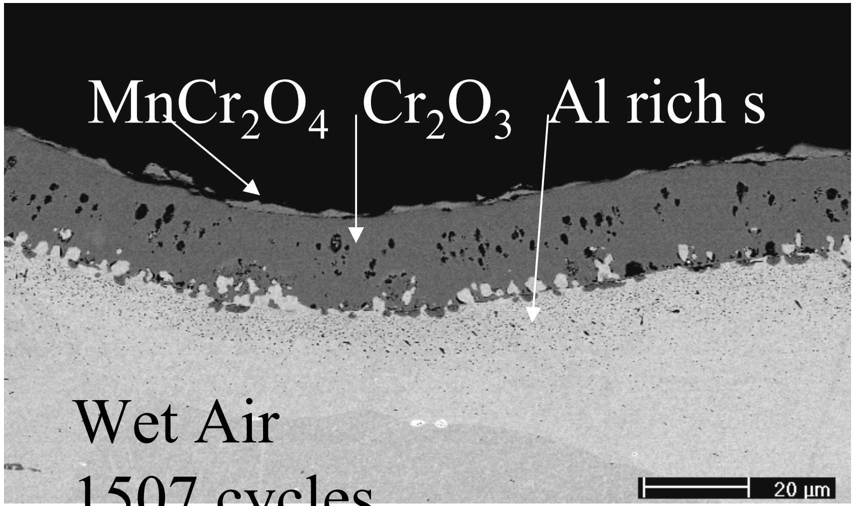


$MnCr_2O_4$

Cr_2O_3

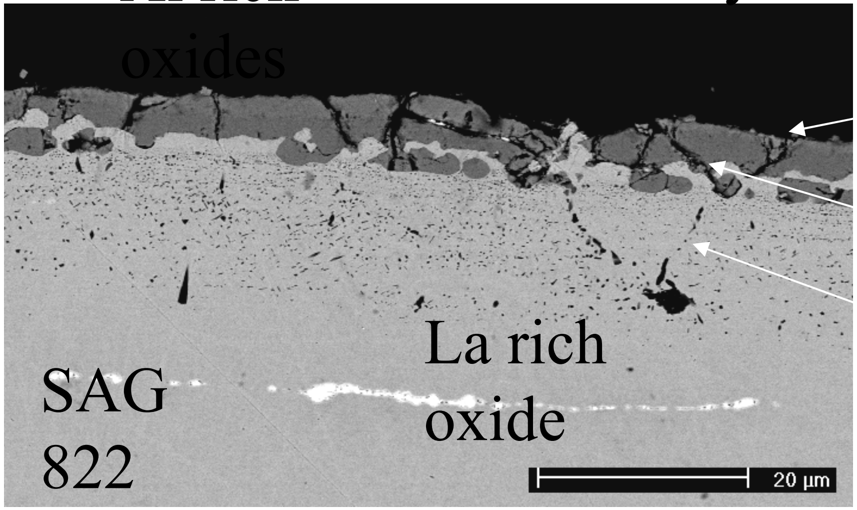
Al rich oxides

Dry Air
1547 cycles



$MnCr_2O_4$ Cr_2O_3 Al rich s

Wet Air
1507 cycles



$MnCr_2O_4$

Cr_2O_3

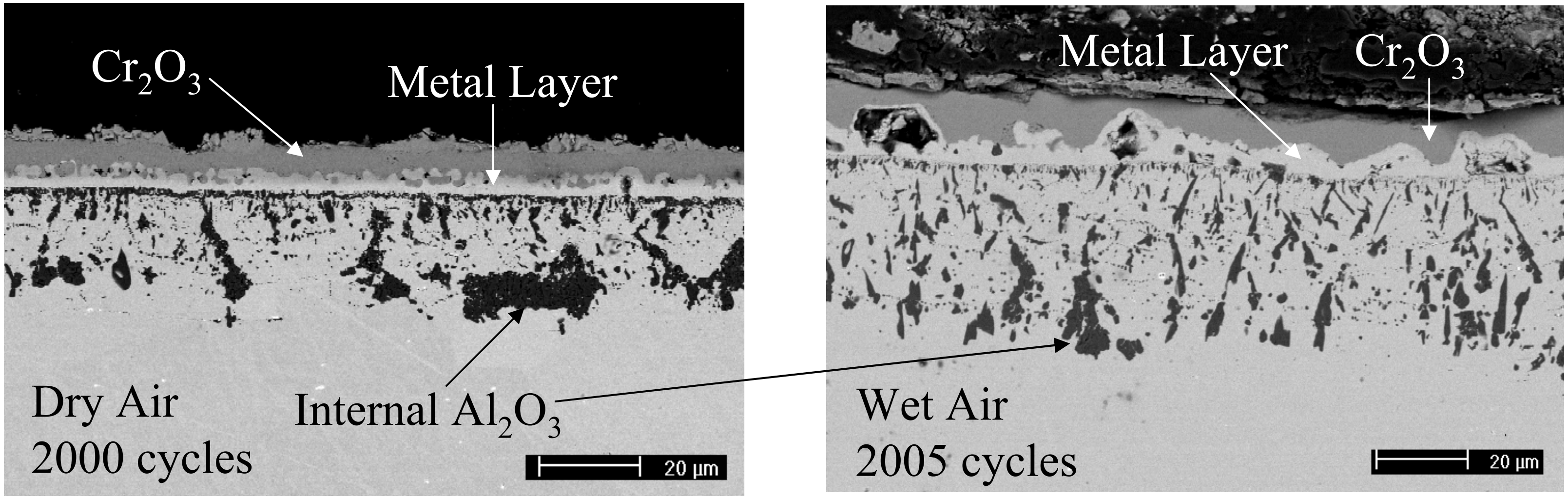
Al rich oxides

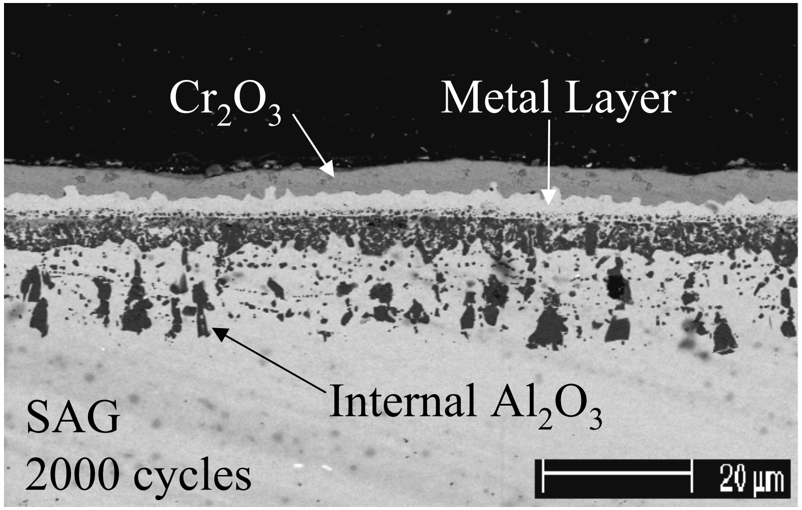
La rich oxide

SAG
822 cycles

0.5 wt% Mn results in an external layer of $MnCr_2O_4$

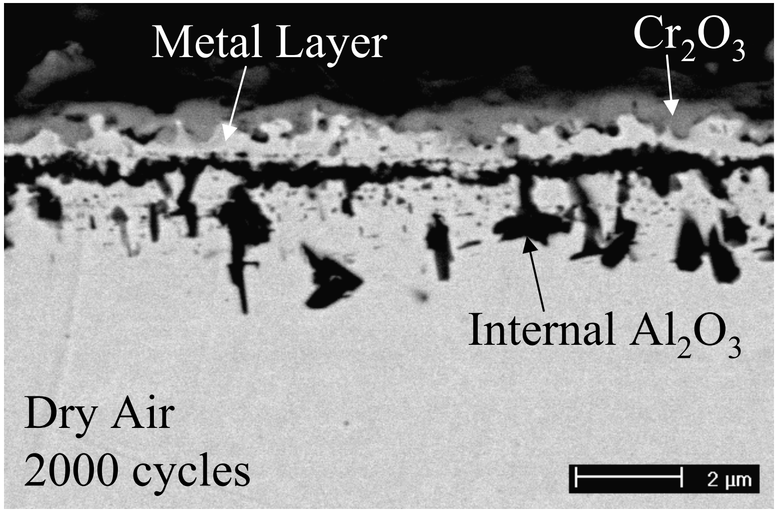
Microstructural and Phase Identification AL453 900°C

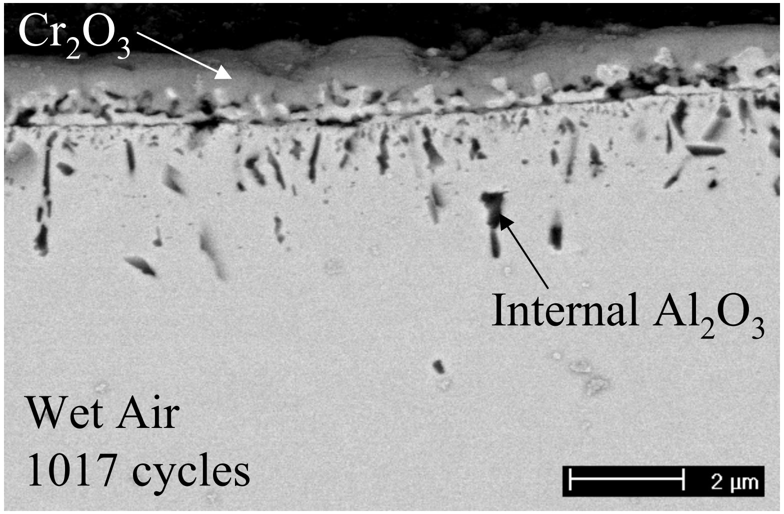


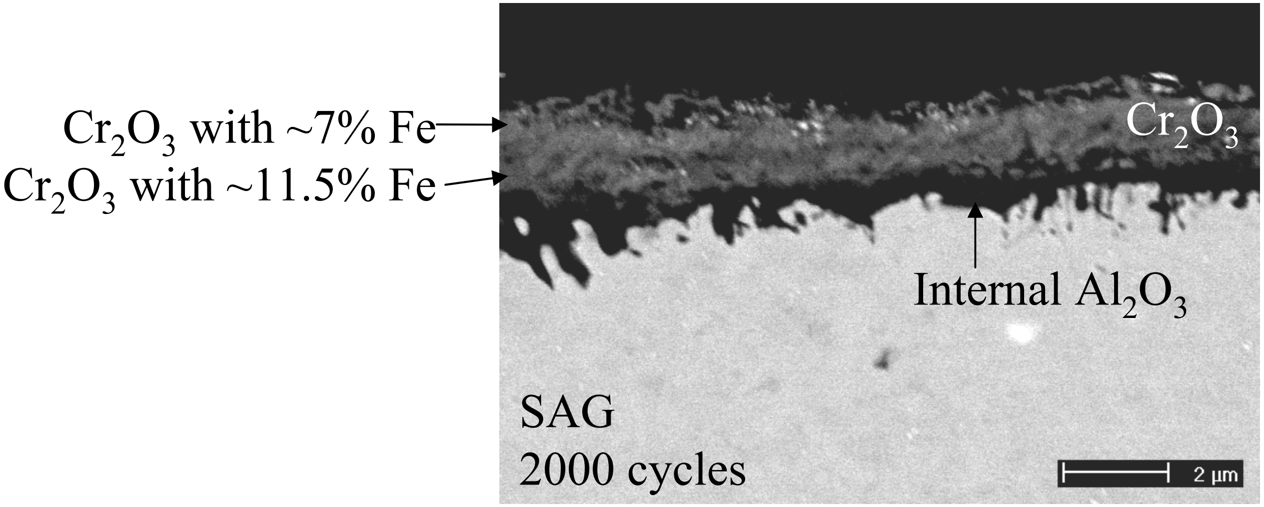


0.5 wt% Al results in internal oxidation

Microstructural and Phase Identification
AL453 700°C







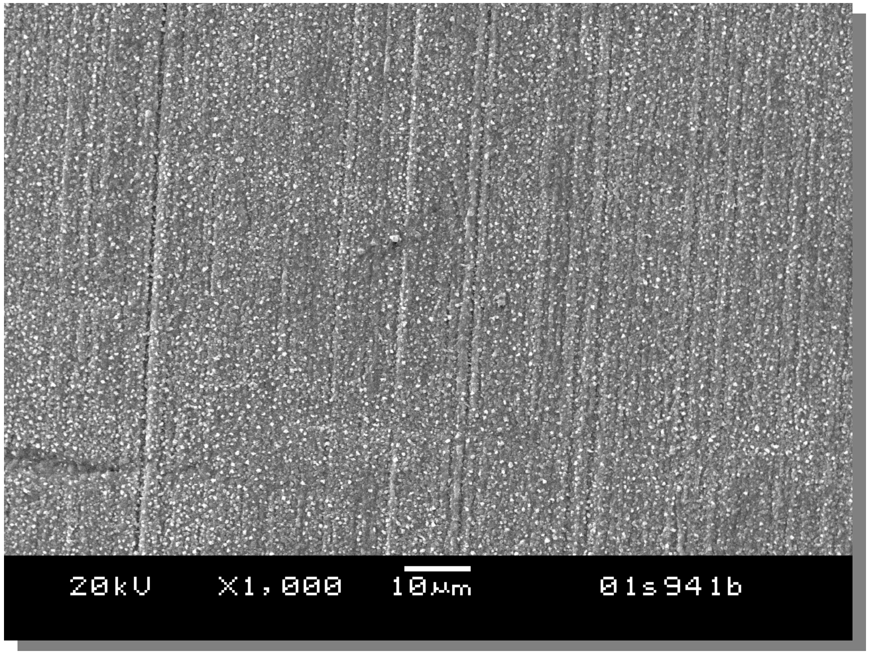
Dual Atmosphere Effects

Interconnects are simultaneously exposed to:

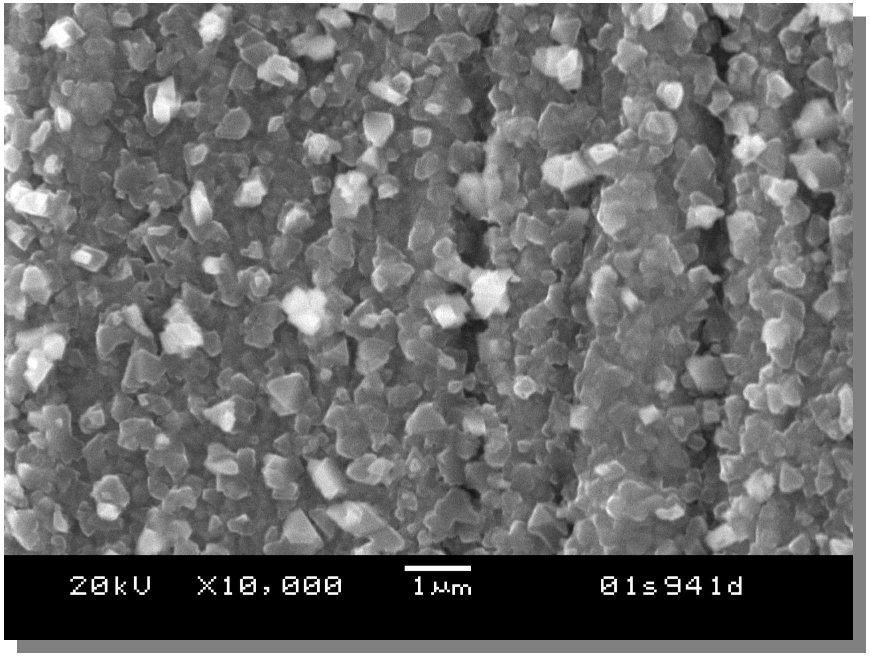
- Cathode gas – air – high oxygen potential
- Anode gas – fuel – low oxygen potential (high hydrogen potential)

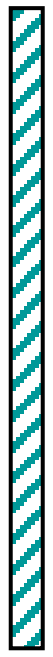
Oxide Formation on 304SS

– Simultaneous Ox / Ox atm.



Simulated oxidant side

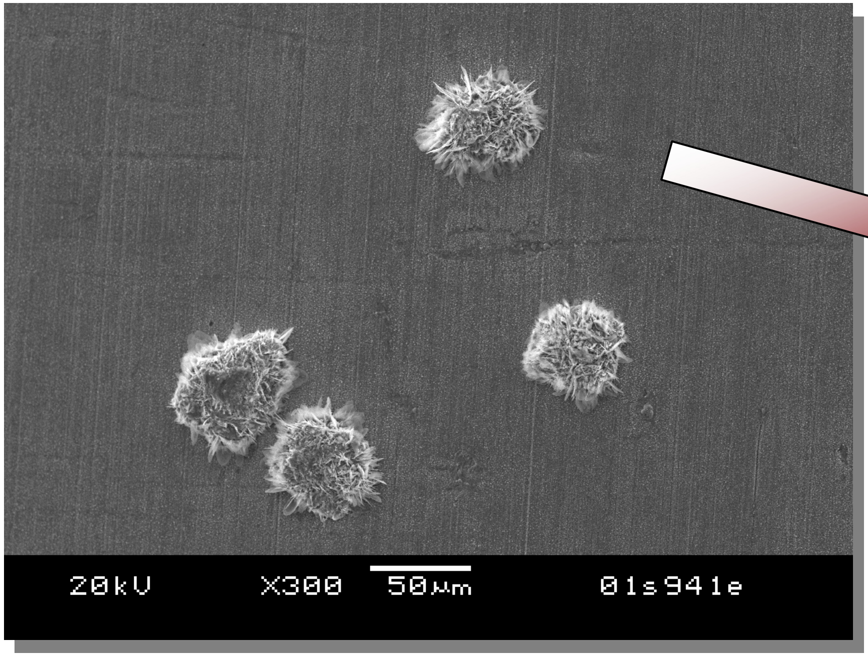




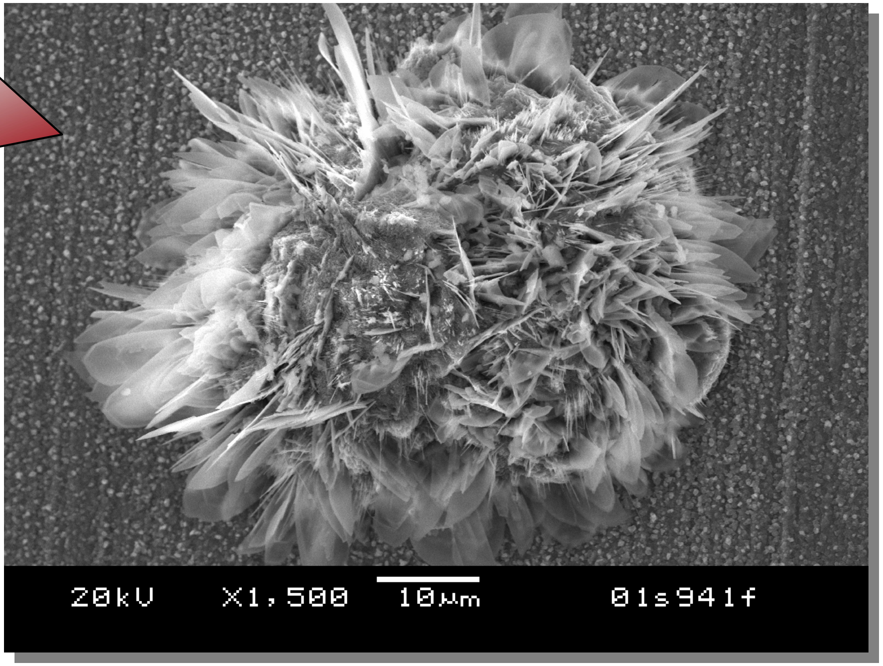
- Uniform Scale Growth – Cr_2O_3 Rich Oxide
- Crystalline Oxide

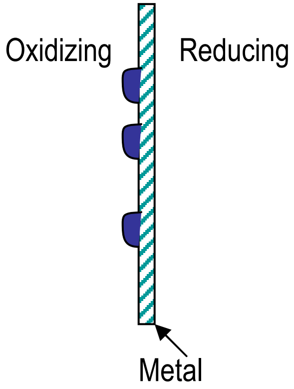
Courtesy of Dr. Prabhakar Singh, PNNL

Oxide Formation – Simultaneous Ox / Red atm.



Simulated oxidant side

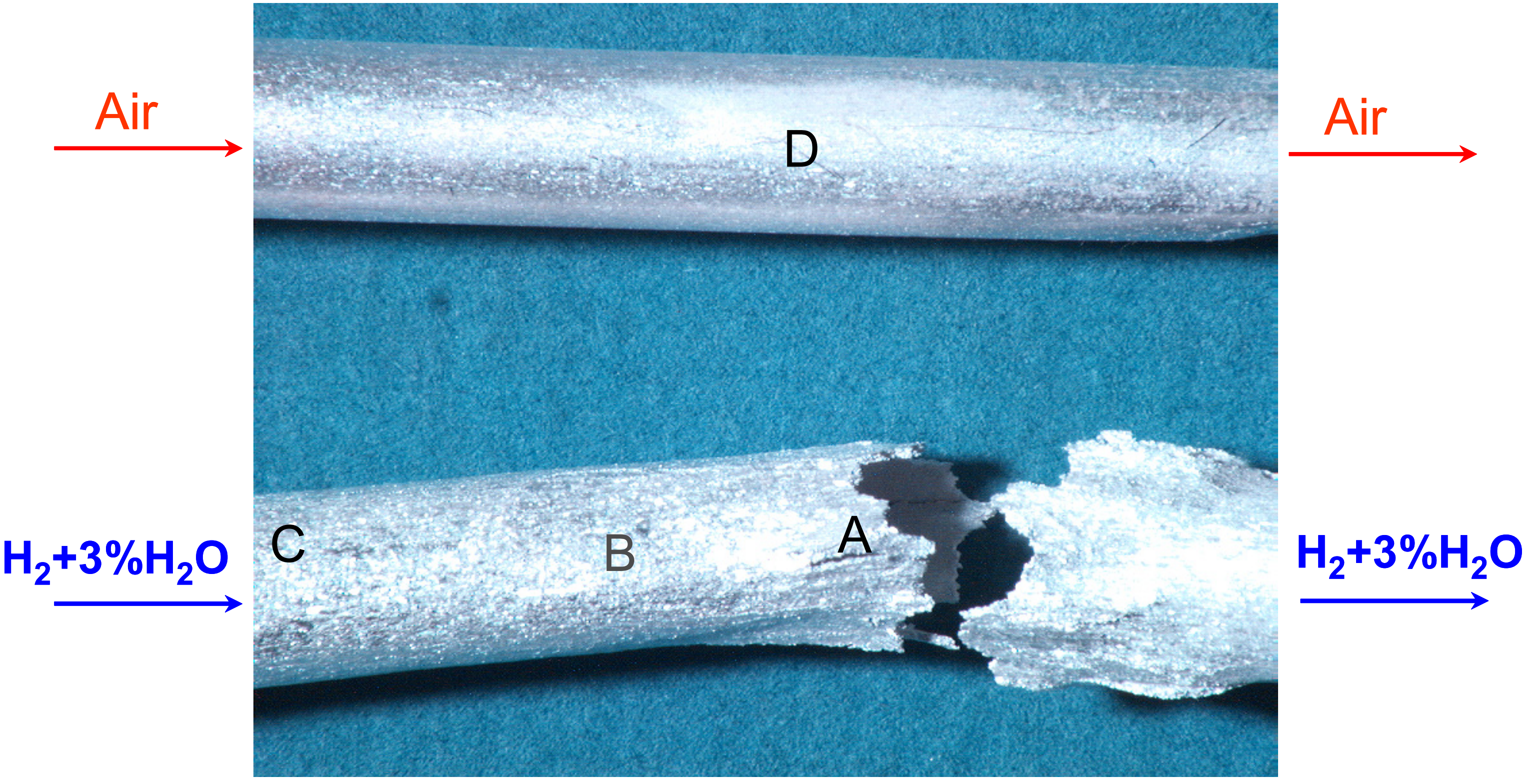




- Localized Scale Overgrowth – FeO Rich Oxide
- Platelets/ Whiskers Formation- Preferred Growth

Courtesy of Dr. Prabhakar Singh, PNNL

Observations



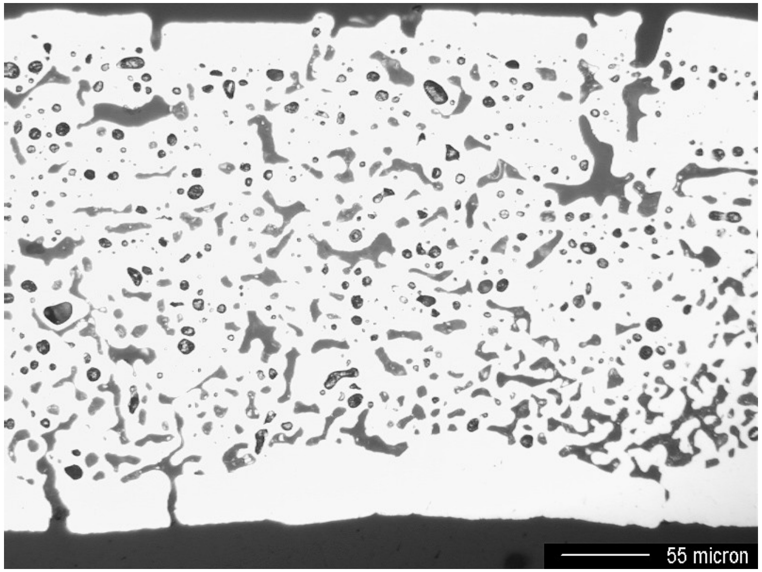
After 100 hours at 700°C.

Outside surface exposed to flowing air

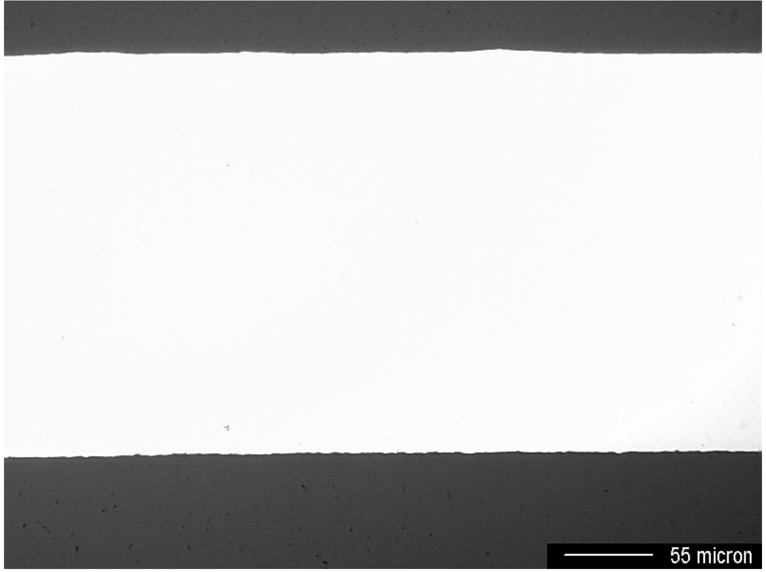
Courtesy of Dr. Prabhakar Singh, PNNL

Observations

Dual exposures



In air only



Metallurgical cross section of the metal shows elaborate porosity formation and grain boundary decoration during dual atmosphere exposure.Single environment exposure does not affect the bulk

Courtesy of Dr. Prabhakar Singh, PNNL

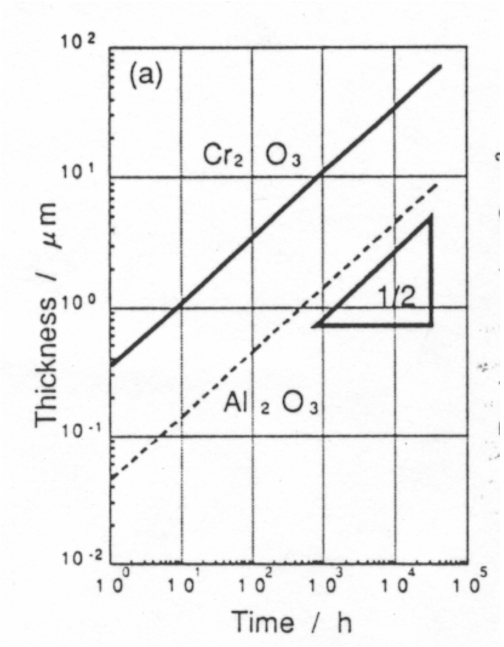
Oxide Electrical Properties

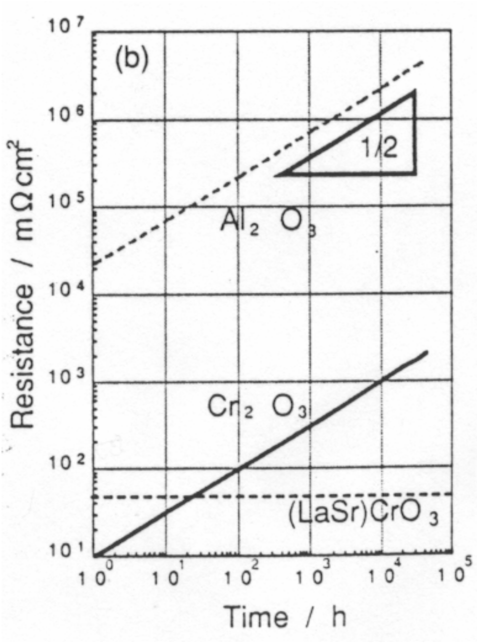
Oxide	ρ (ohm cm) in air
SiO_2	7×10^6 (600°C)
Al_2O_3	5×10^8 (700°C)
Cr_2O_3	1×10^2 (800°C)
NiO	5 (900°C)
CoO	1 (950°C)
TiO_2*	3×10^2 (1000°C)

* Note: $\rho_{TiO2} = 5 \times 10^{-1}$ ohm cm at $p_{O2} = 10^{-16}$ atm

Cr_2O_3 vs. Al_2O_3 Scale Formation

- All of the metal alloy candidates form Cr_2O_3 or Al_2O_3 protective layers.
- In general, Cr_2O_3 forms a thicker, but more conductive scale than Al_2O_3.
- Calculated trends based on published parabolic rate constants.





Note: Rate constants taken from referenced work. Base materials identified only as “heat-resisting alloys” and exposure temp. not specified. Resistance of LSC assumed to be 25 mΩ cm^2

Ref: Kadowaki et al., 1993 (Japan)

Doping Effects

Doping of p-type NiO

$$Cu_2O + V''_{Ni} = 2Cu'_{Ni} + O_O^X$$

$D_{Ni}\downarrow, \rho\downarrow$

$$H_2O = 2H_i^{\bullet} + O_O^X + V''_{Ni}$$

$D_{Ni}\uparrow, \rho\uparrow$

$$Cr_2O_3 = 2Cr_{Ni}^{\bullet} + 3O_O^X + V''_{NI}$$

$D_{Ni}\uparrow, \rho\uparrow$

Effect of Impressed Current

The effect of the current density across the interconnect may be significant.

This effect will be negligible for a predominantly electronically conducting oxide, e.g. NiO.

Some conductivity measurements indicate that chromia has a significant ionic transference number at fuel cell temperatures. This would lead to acceleration of the chromia growth on the anode side and decrease of the growth rate on the cathode side and, beyond a limiting oxide thickness, no further growth on the cathode side.

Oxide Evaporation

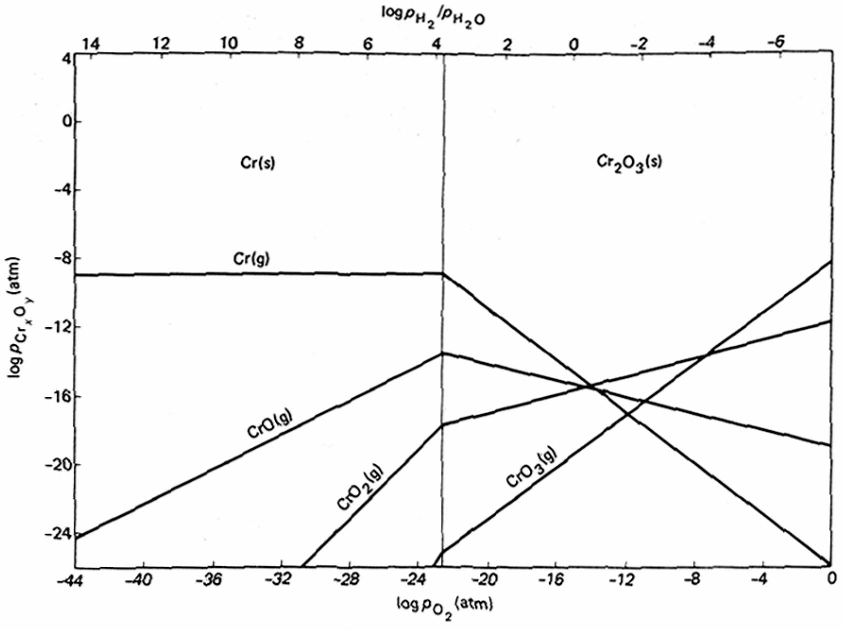
CHROMIA

- At high T and high PO_2 volatile oxides develop

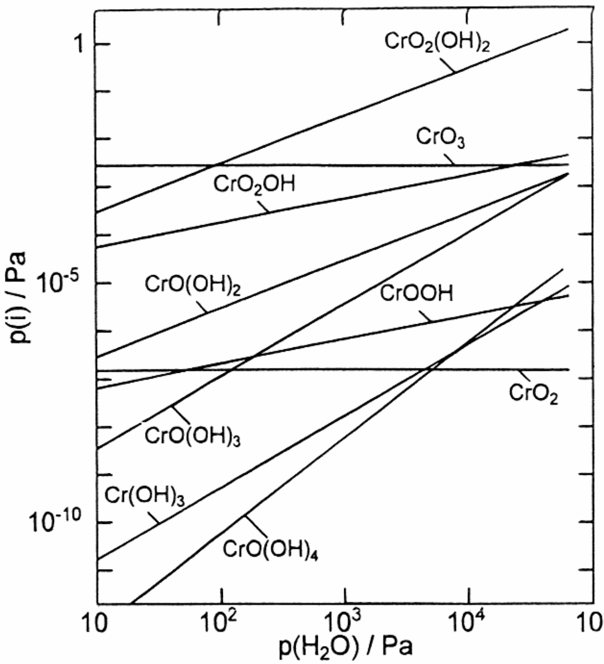
$$Cr_2O_3 + 3/2\ O_2 \rightarrow 2\ CrO_3(g)$$

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

Even small amounts of evaporation of CrO_3 or $CrO_2(OH)_2$ will poison cathode materials e.g. LSM

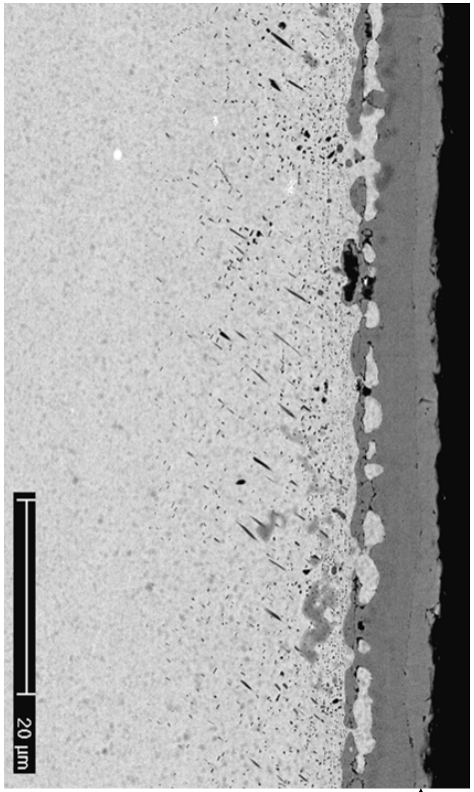


Cr-O volatile species at 1250K



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

Chromia Evaporation



Crofer

MnCr$_2$O$_4$

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

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

$$MnO(s) + Cr_2O_3(s) = MnCr_2O_4(s)$$

$$\Delta G^o_{1100K} \approx -89KJ/mole$$

Chromia Saturation $a_{Cr_2O_3} = 1$ $p_{CrO_3} = 4x10^{-11} atm$

MnO Saturation

$a_{Cr_2O_3} = 6x10^{-5}$ $p_{CrO_3} = 3x10^{-13} atm$

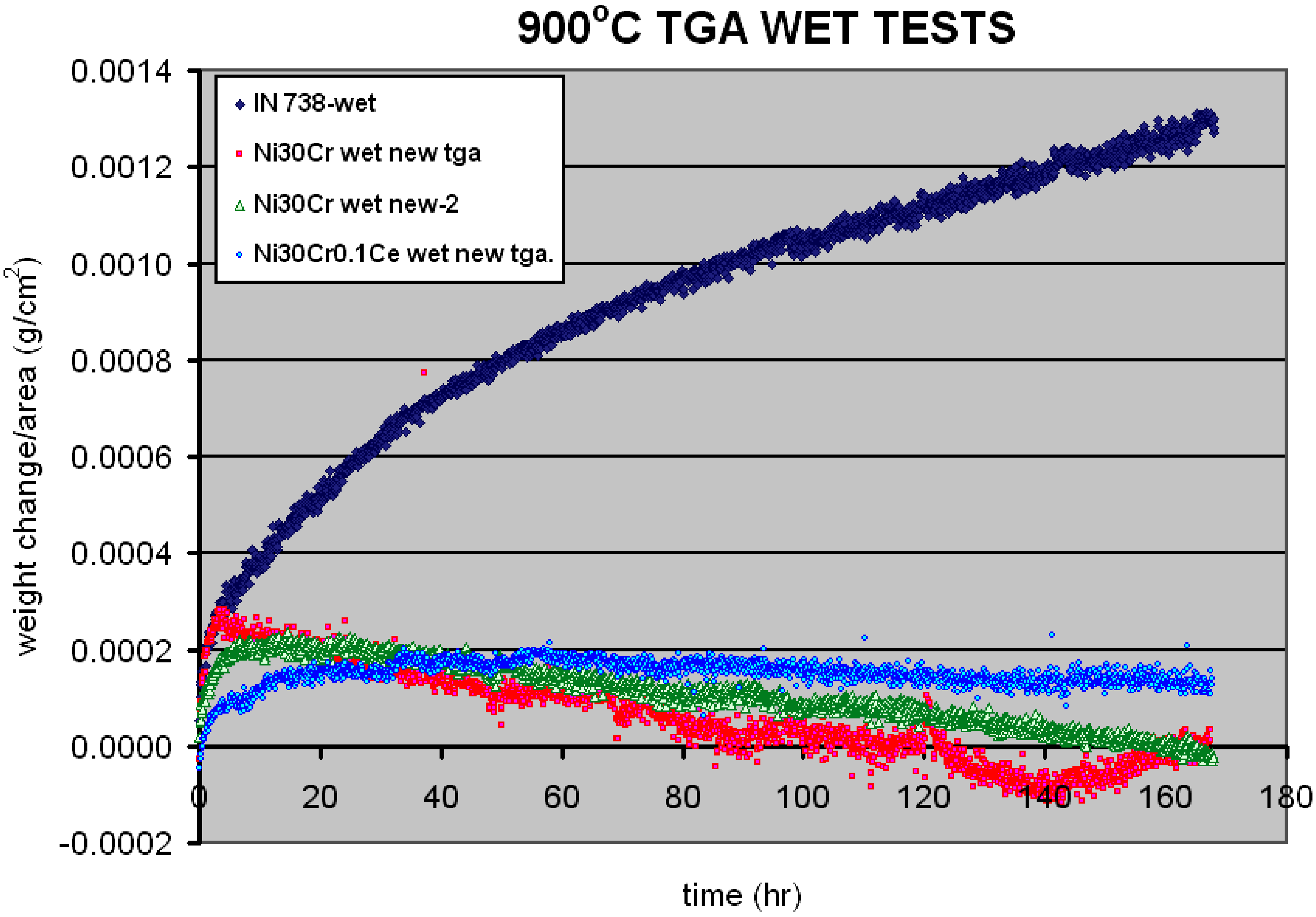
LaCrO$_3$ (Activity data from Hilpert et al)

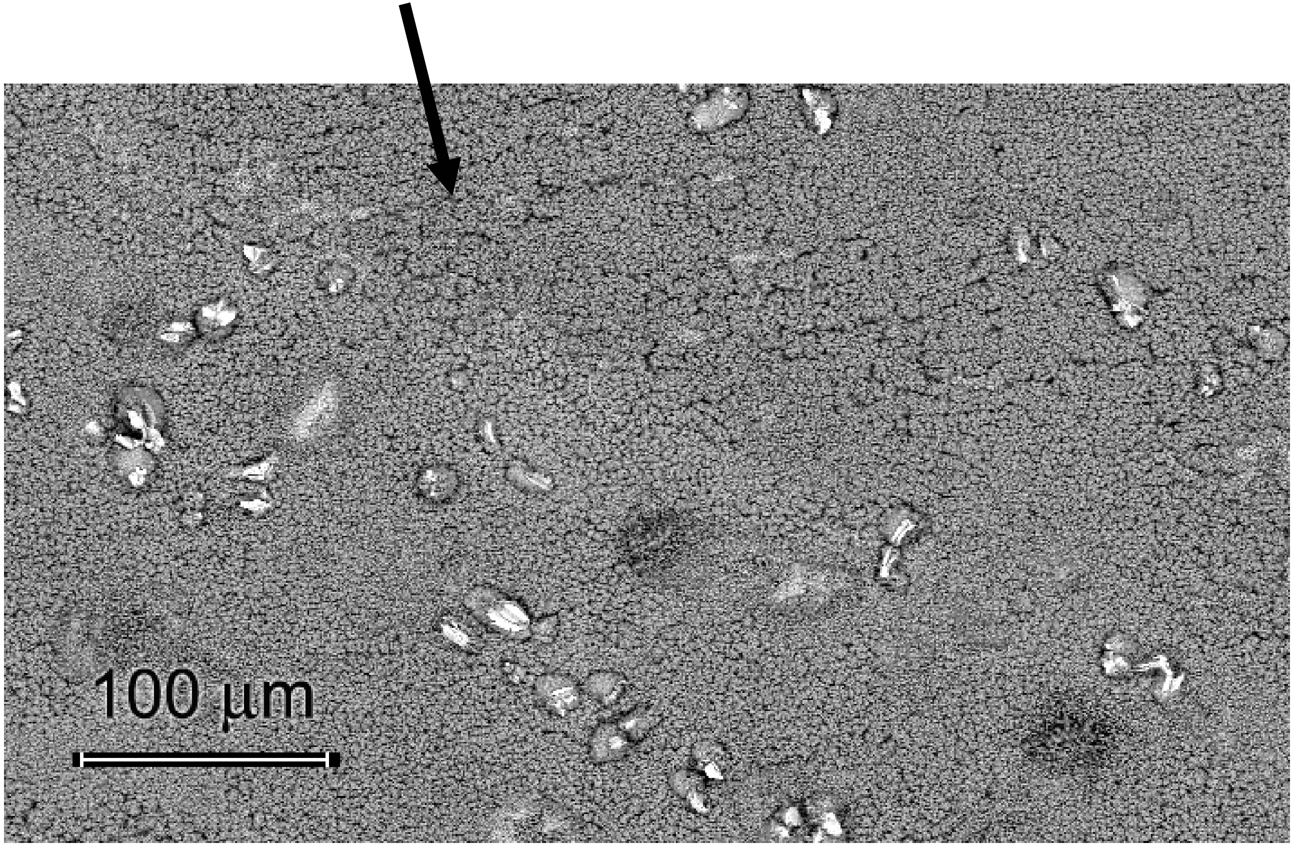
$a_{Cr_2O_3} = 10^{-7}$ $p_{CrO_3} = 1x10^{-14} atm$

Solutions to the Evaporation Problem

- Overgrowth of Low-Volatility Oxide
- Use of Coatings
- Development of Cr-free Interconnects.

Oxide Evaporation from Ni-Cr Alloys

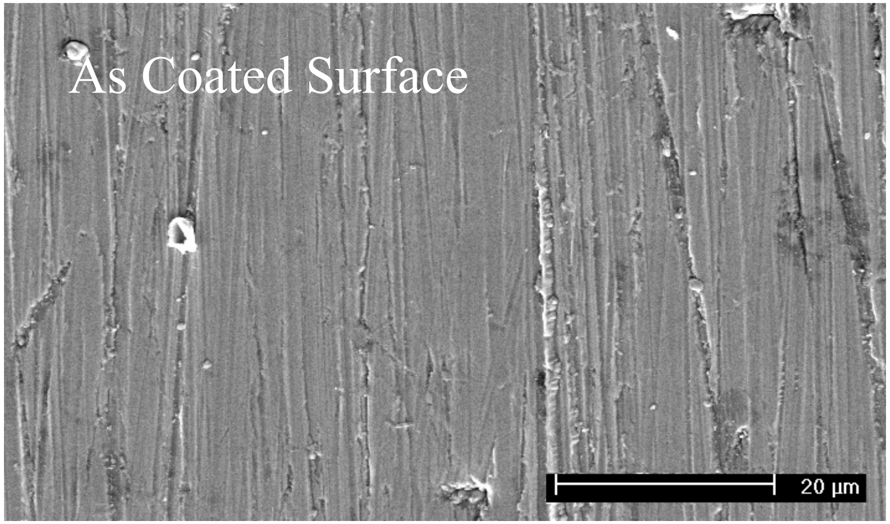


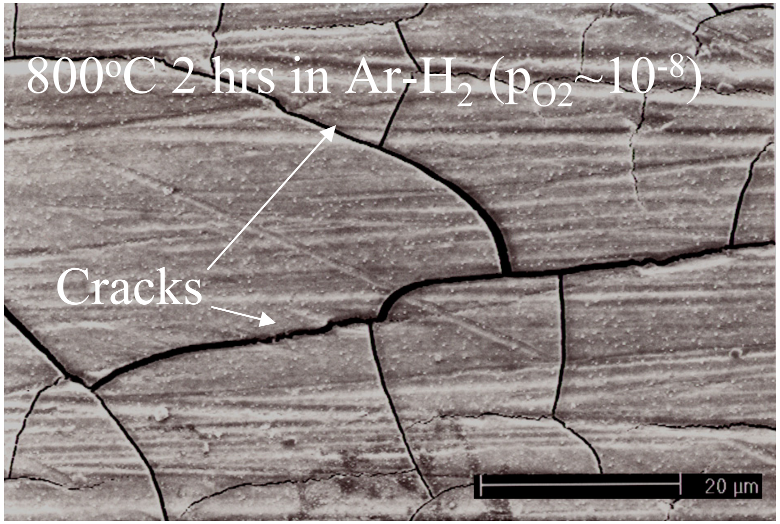


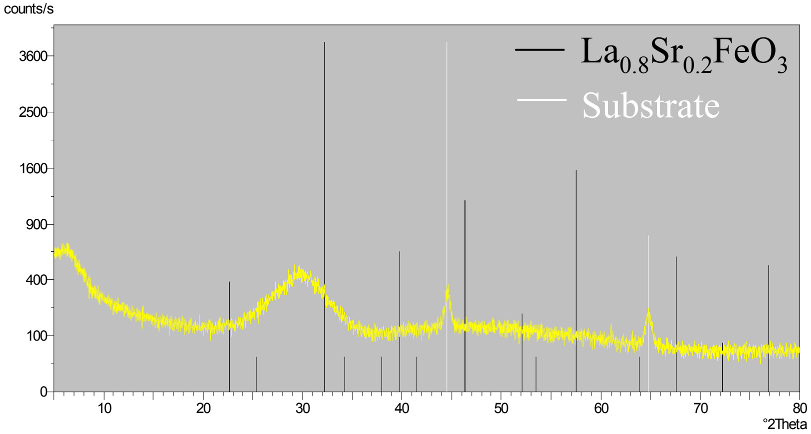
Continuous TiO_2 Overgrowth

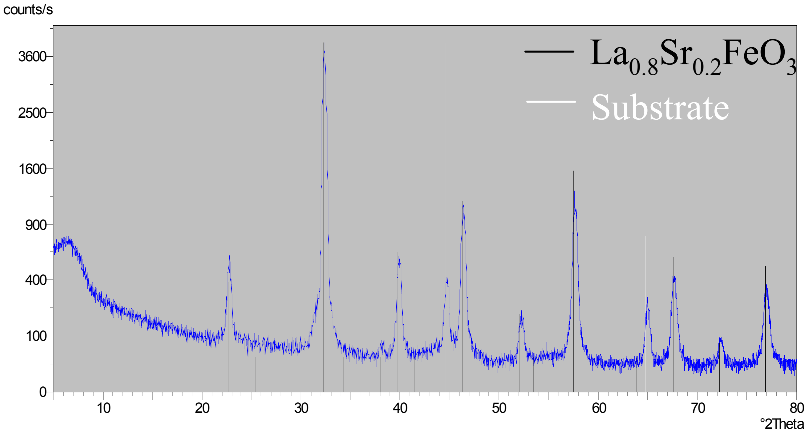
IN 738 at 900°C in wet air (0.1 atm) isothermal-168 hr

$La_{0.8}Sr_{0.2}FeO_3$ Coated E-Brite (~5mm thick)

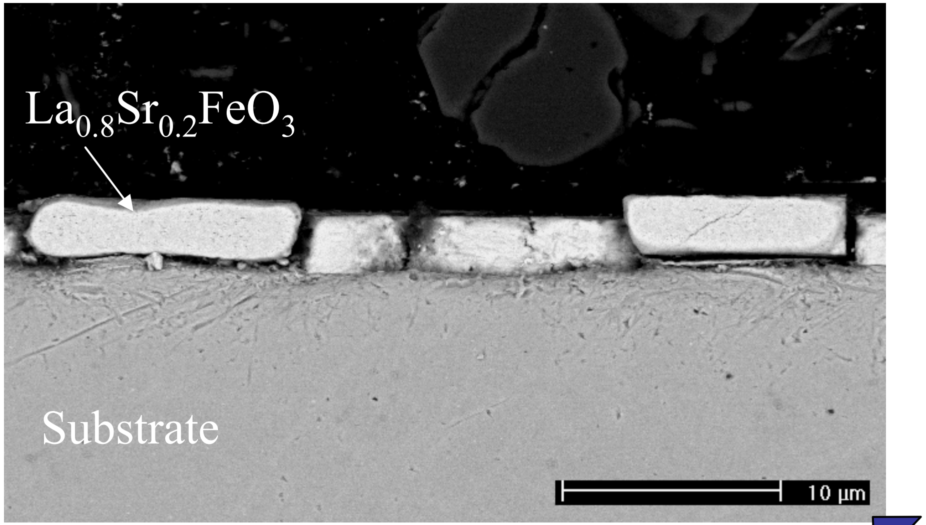

As Coated Surface

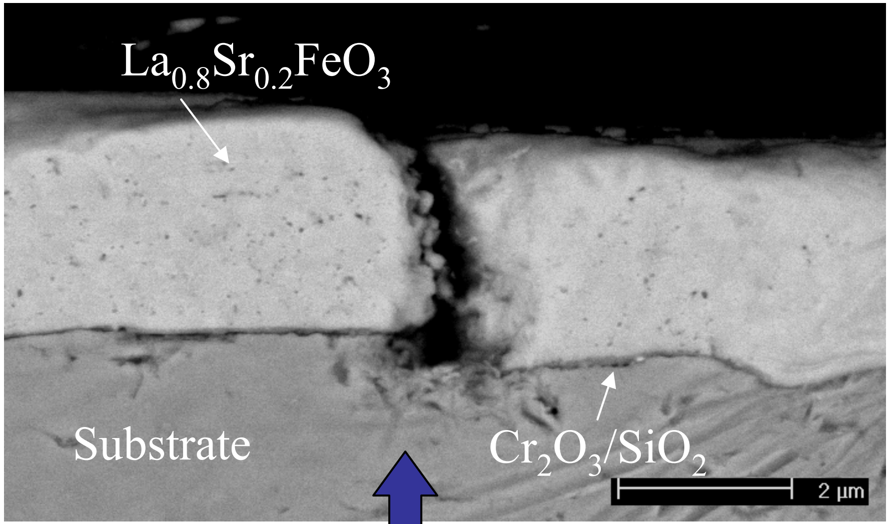

800°C 2 hrs in Ar-H_2 (p_{O2}~10^{-8})



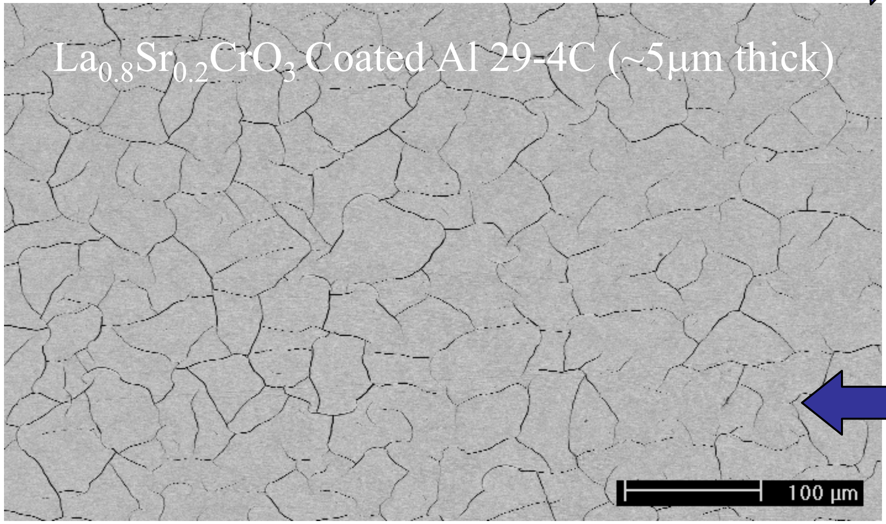


$La_{0.8}Sr_{0.2}FeO_3$ Coated E-Brite (~5mm thick)





Cross sections show the coating to be much more dense, but also confirms the cracks seen from the surface

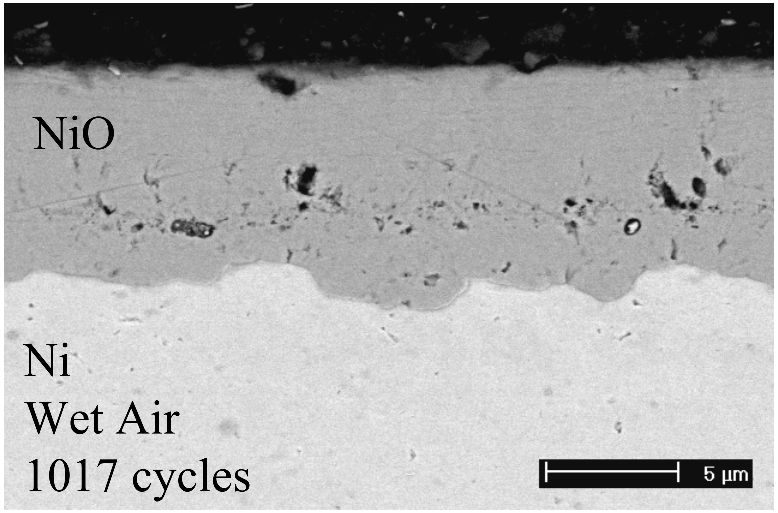

$La_{0.8}Sr_{0.2}CrO_3$ Coated Al 29-4C (~5µm thick)

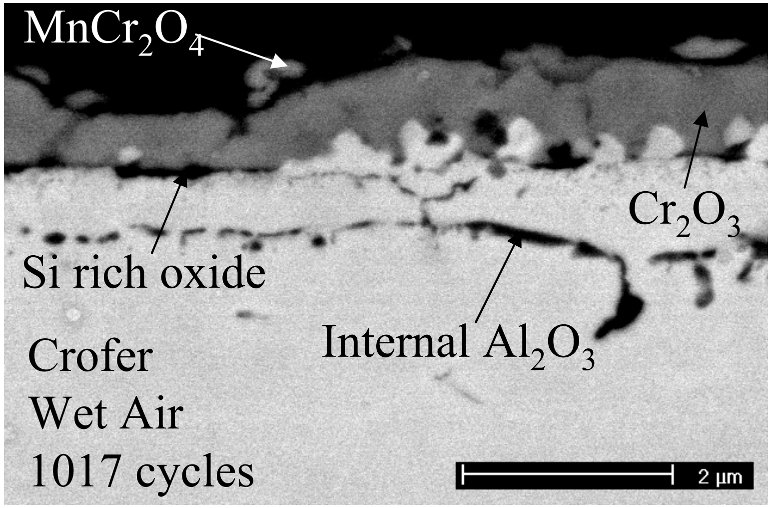
Chromite coating cracked as well after same exposure conditions

Vapor Pressures – 1100 K

Metal	**p_M (atm)**	**p_{O2}-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}

Comparison of Oxide Thickness for NiO and Cr_2O_3 -700°C



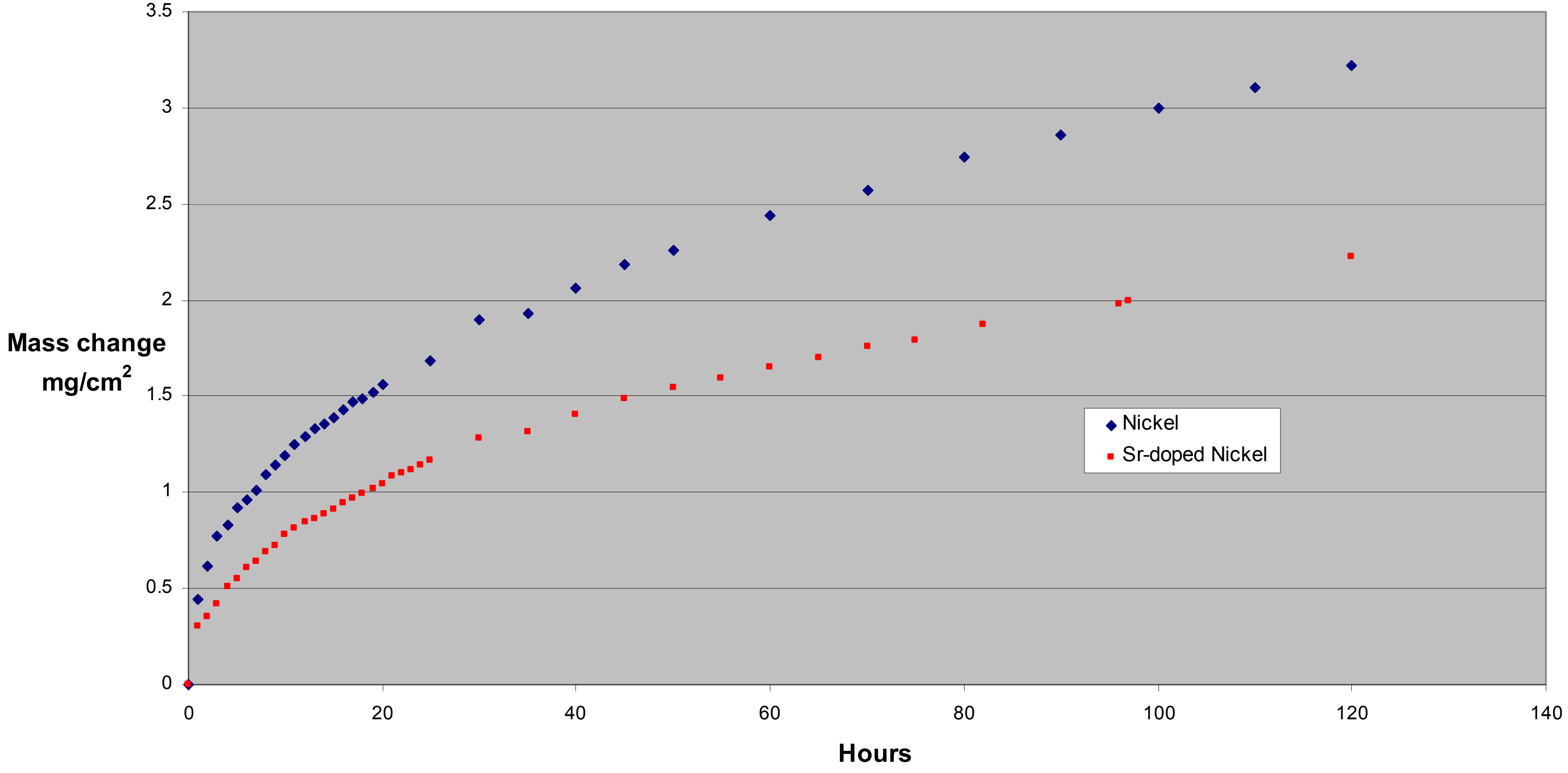


Estimated ASR is approximately the same for Ni and Crofer after oxidation

Doping of metal-deficit NaCl-structure oxides (NiO, CoO) with univalent cations can decrease oxide growth rate and increase electrical conductivity.

Doping with large cations Ca^{2+}, Sr^{2+}, La^{3+}, etc can slow oxide growth rate.

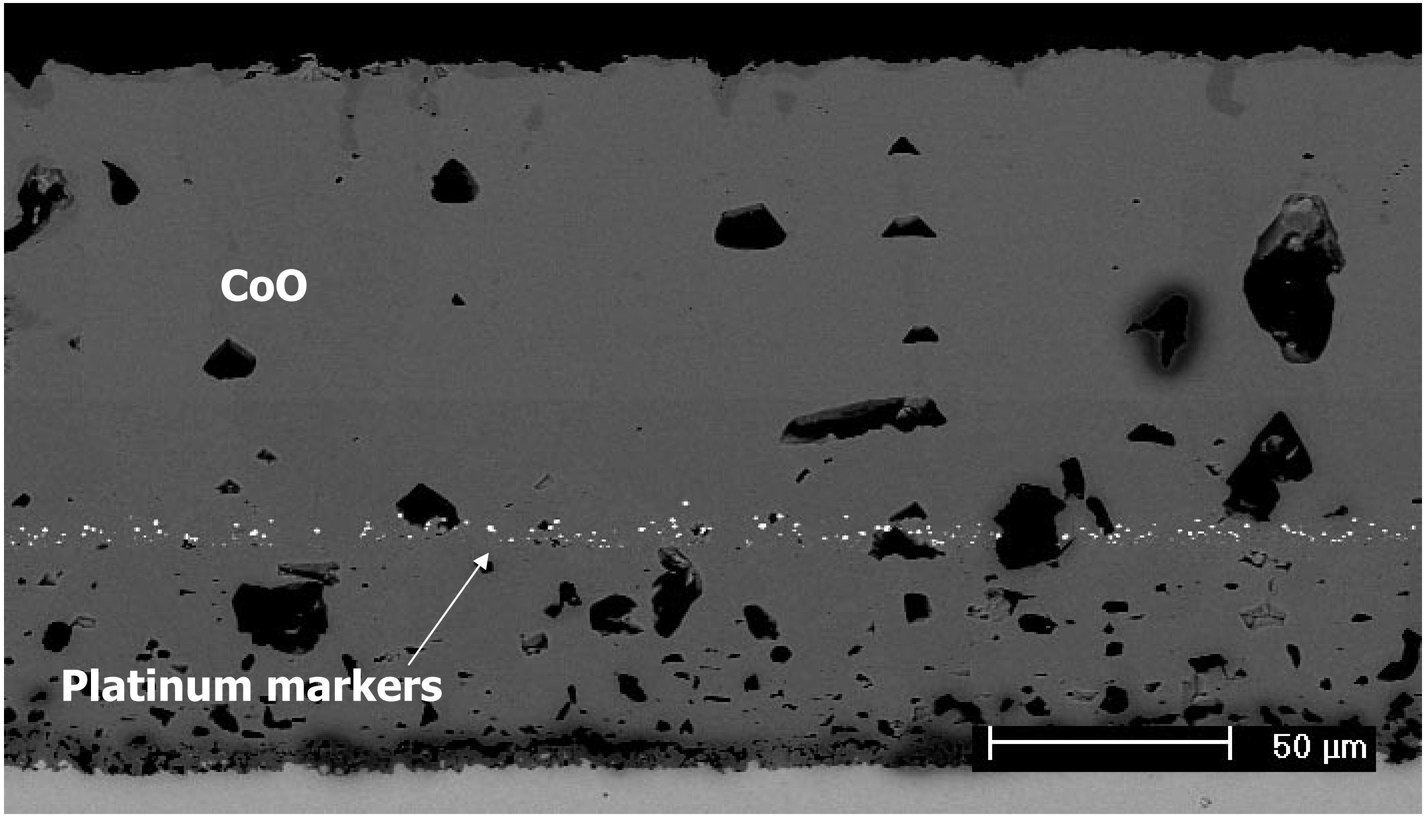
Thermogravimetric Analysis - Ni Oxidized at 900°C in Dry Air



Ionic Radii

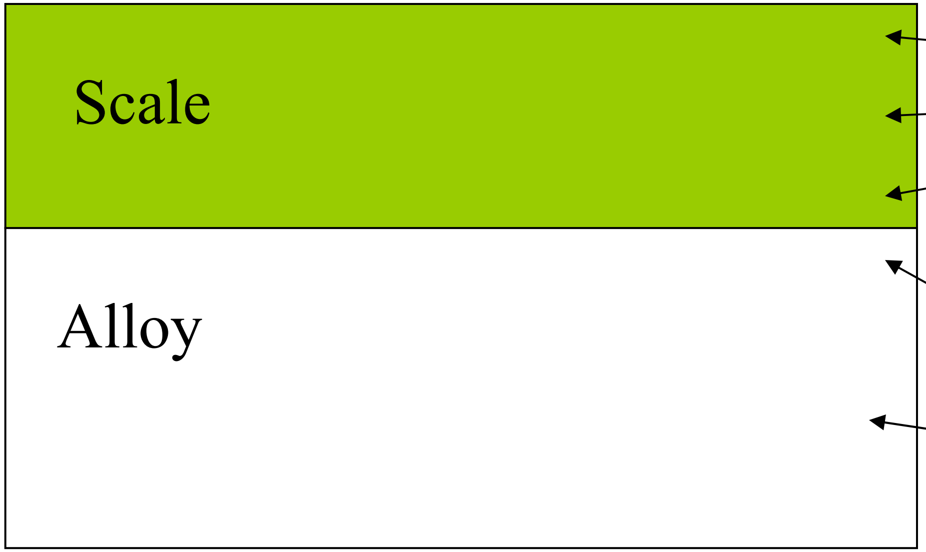
ION	Radius (nm)
Cr^{3+}	0.064
Ni^{2+}	0.078
Co^{2+}	0.082
Cu	0.128
Cu^{1+}	0.096
Cu^{2+}	0.072
Sr^{2+}	0.127
Ca^{2+}	0.106
Mg^{2+}	0.079
La^{3+}	0.122
Ce^{4+}	0.094

Co-8 wt% Cu - 900ºC Dry Air - 28 hours



Pt markers observed above scale/alloy interface

Copper Concentrations
125 hr Exposure

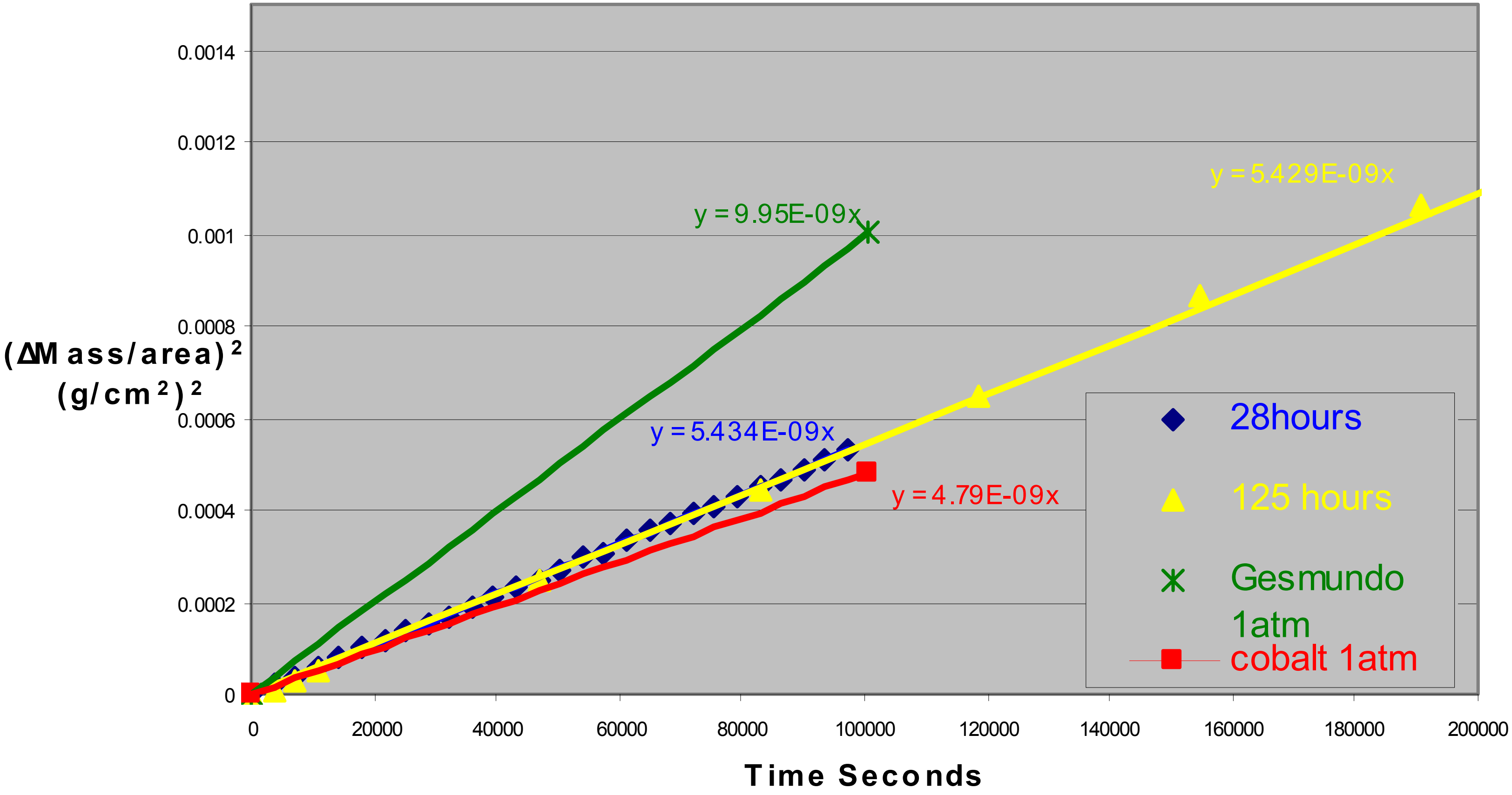


Copper to Cobalt ratio		Position
12.51	±1.06	5 µm from gas/scale interface
7.01	±0.95	midway through scale
2.55	±1.05	5 µm above scale/alloy interface

Copper Concentration		Position
6.38%	±0.83%	5 µm below scale/alloy interface
8.40%	±1.17%	midway through alloy

Note significant "uphill diffusion" of Cu in CoO.

Parabolic Rate Constants at 900ºC

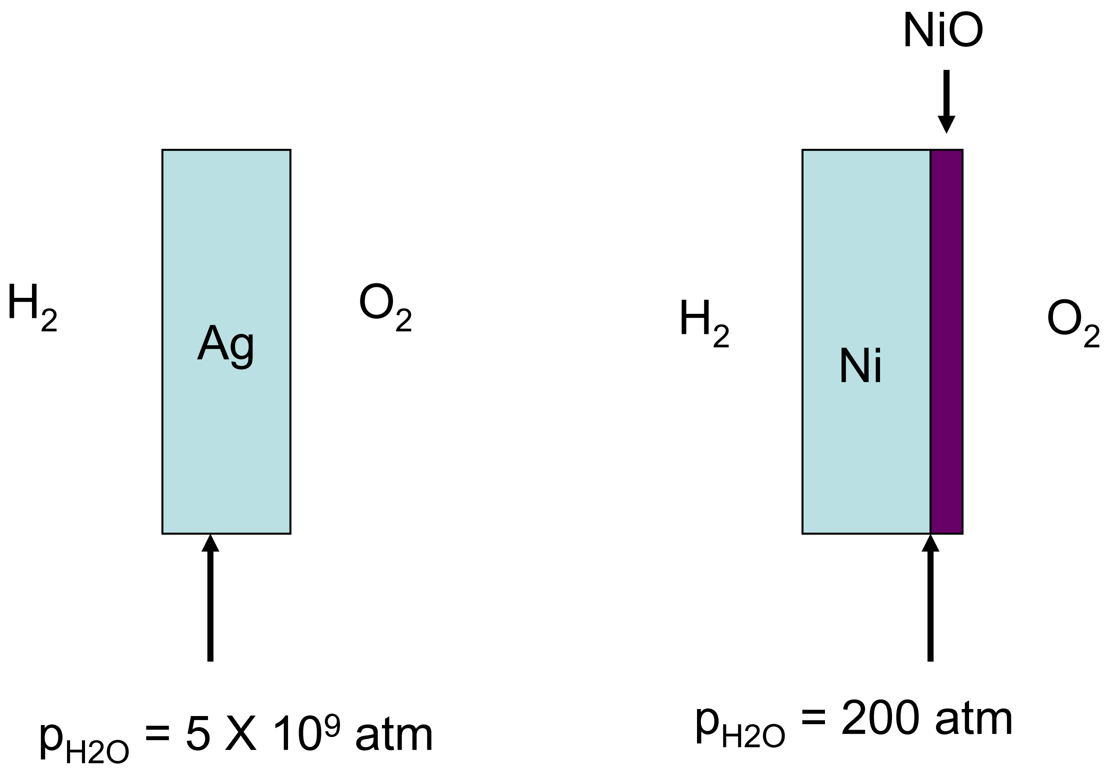


Summary: Cu was successfully doped into CoO but growth rate was not decreased.

Experiments are underway with Ni-Cu alloys.

Dual Atmosphere Effects

1000K



H_2 Ag O_2

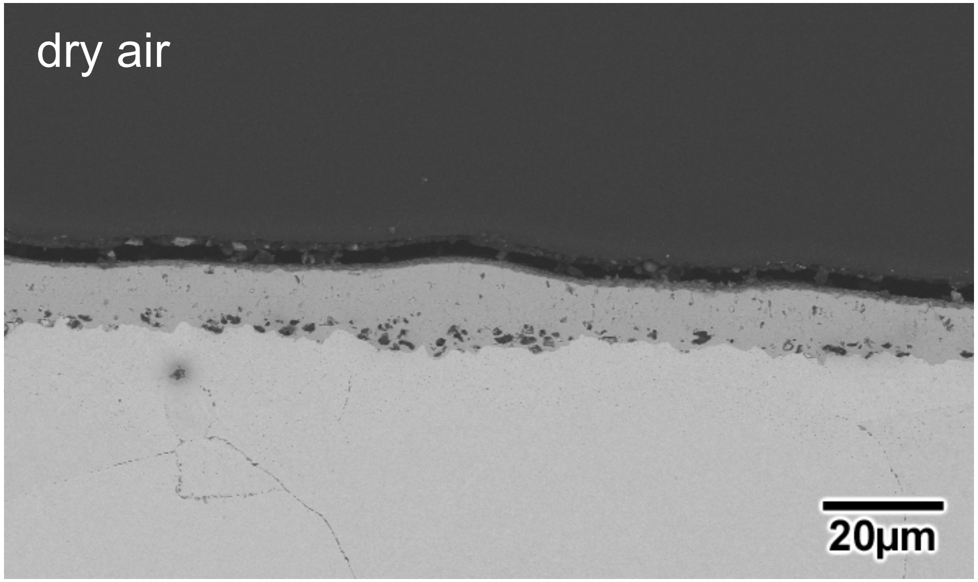
p_{H2O} = 5 X 10^9 atm

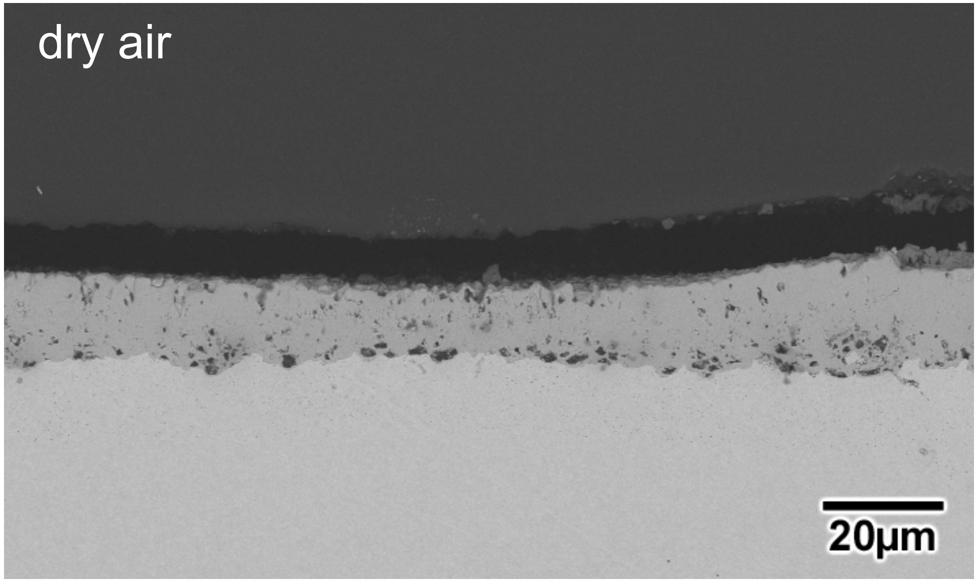
NiO

H_2 Ni O_2

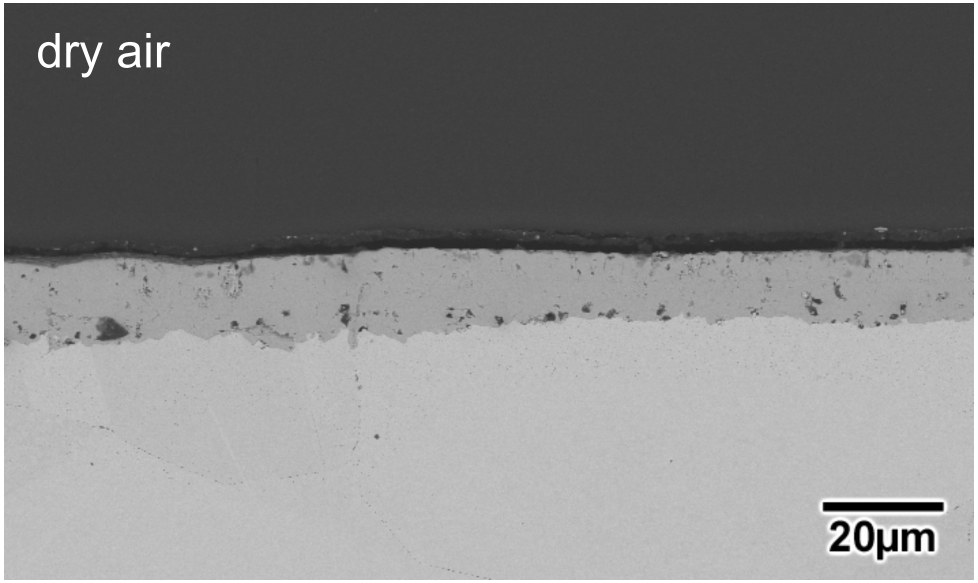
p_{H2O} = 200 atm

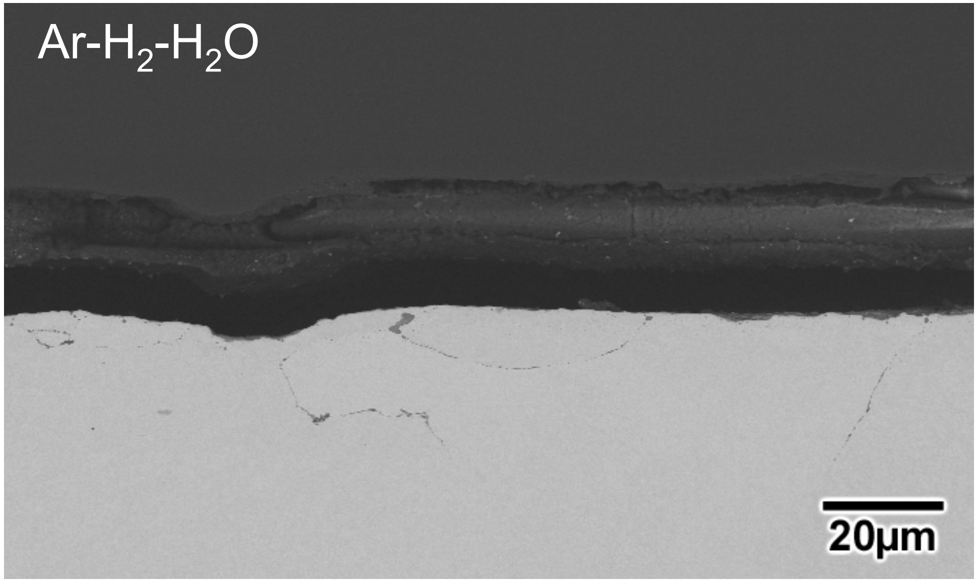
Ni: 72h, 800°C, dry air/dry air



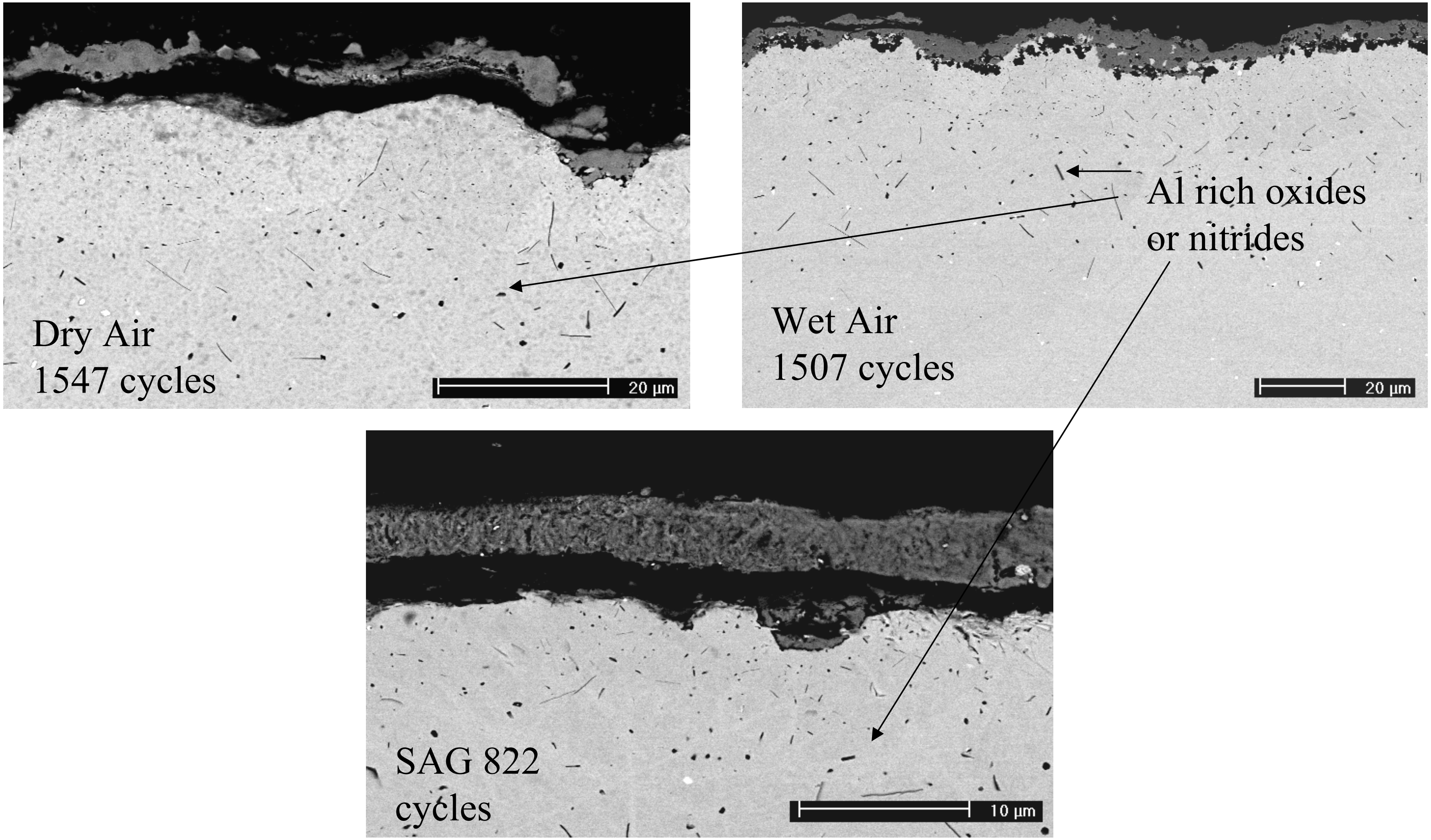


Ni: 72h, 800°C, dry air/wet Ar-H_2





Microstructural and Phase Identification E-brite 900°C



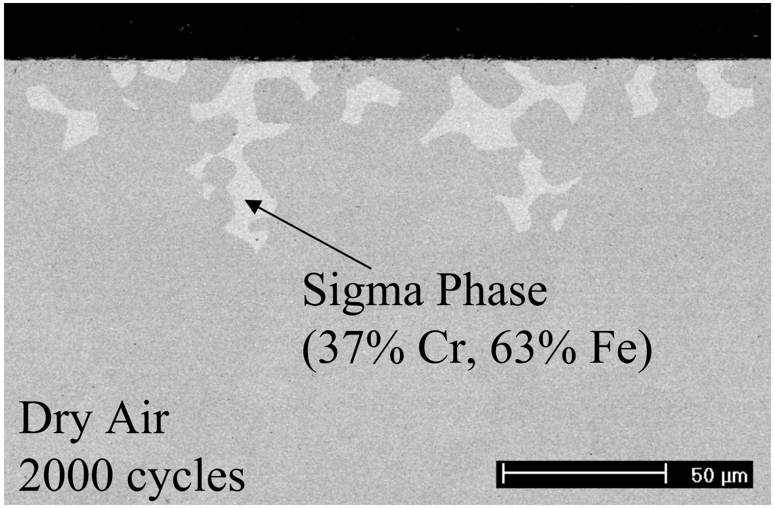
Dry Air
1547 cycles

Wet Air
1507 cycles

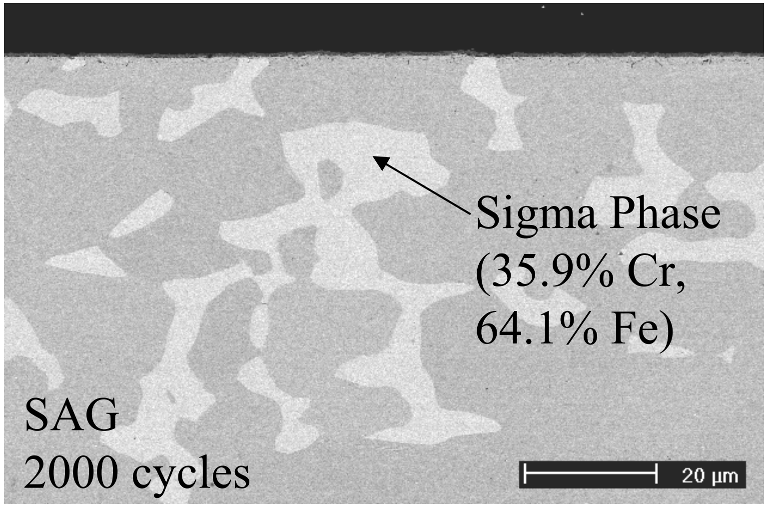
SAG 822
cycles

Al rich oxides
or nitrides

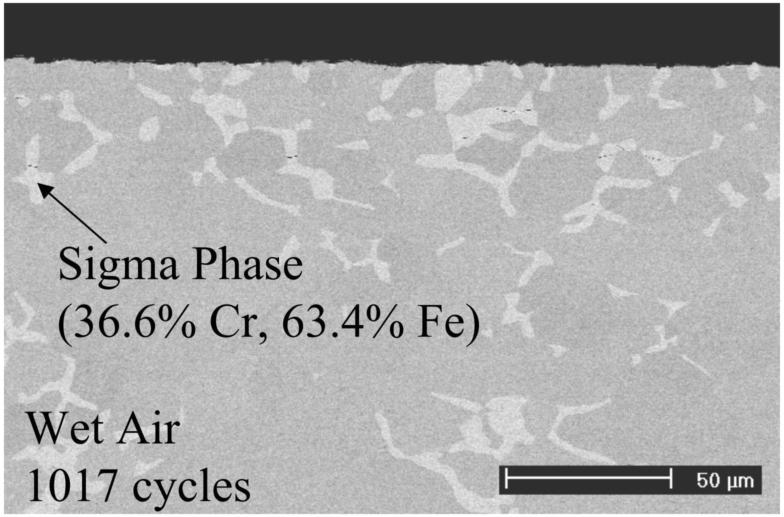
Sigma Phase in E-brite at 700°C


Sigma Phase
(37% Cr, 63% Fe)

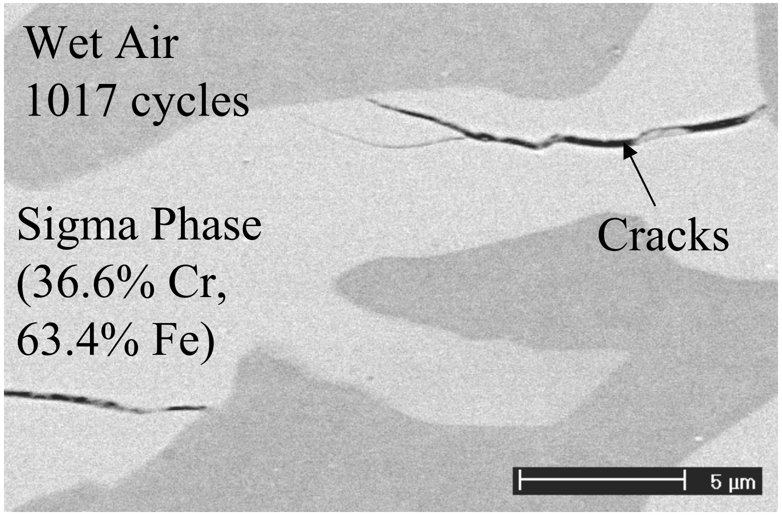
Dry Air
2000 cycles


Sigma Phase
(35.9% Cr,
64.1% Fe)

SAG
2000 cycles

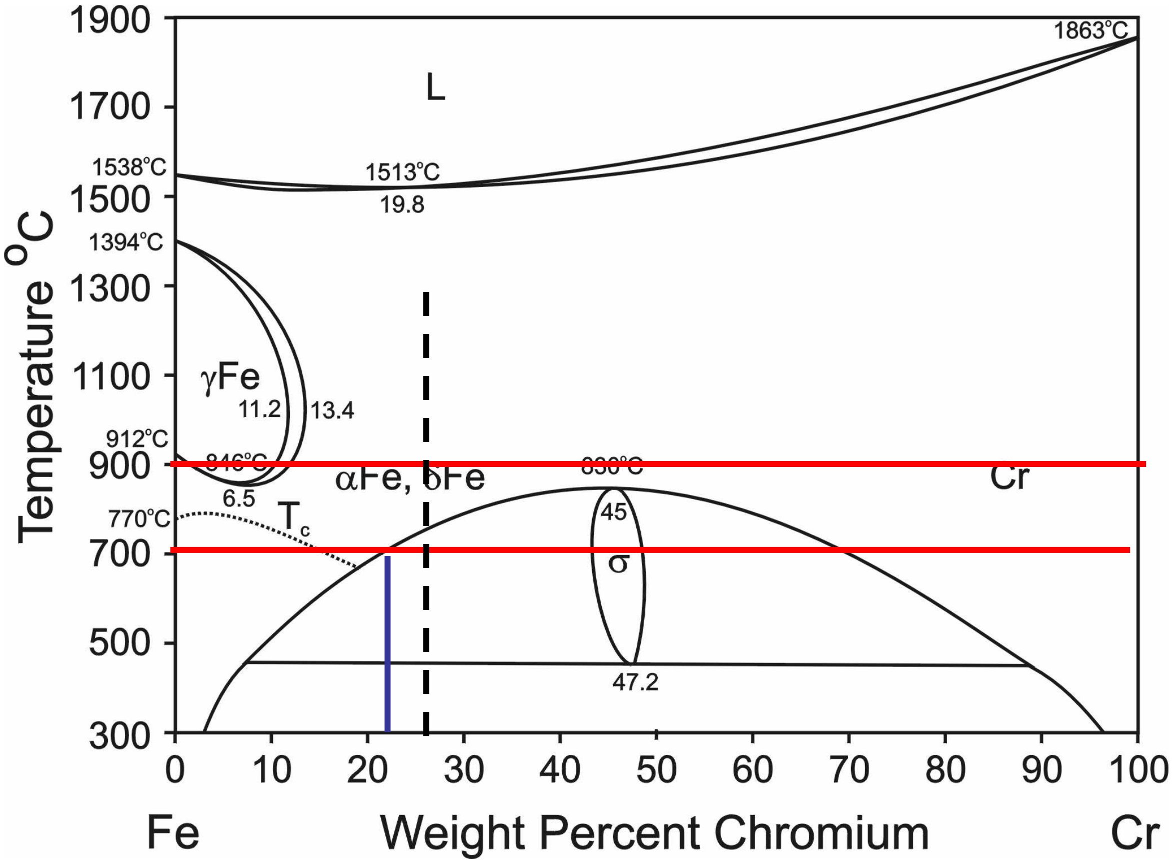

Sigma Phase
(36.6% Cr, 63.4% Fe)

Wet Air
1017 cycles


Wet Air
1017 cycles

Sigma Phase
(36.6% Cr,
63.4% Fe)

Cracks


1900
1700
1500
1300
1100
900
700
500
300
Temperature °C
1863°C
L
1538°C
1513°C
19.8
1394°C
γFe
11.2
13.4
912°C
846°C
830°C
αFe, δFe
Cr
6.5
770°C
T_c
45
σ
47.2
0
10
20
30
40
50
60
70
80
90
100
Fe
Weight Percent Chromium
Cr

Sigma-Phase Formation

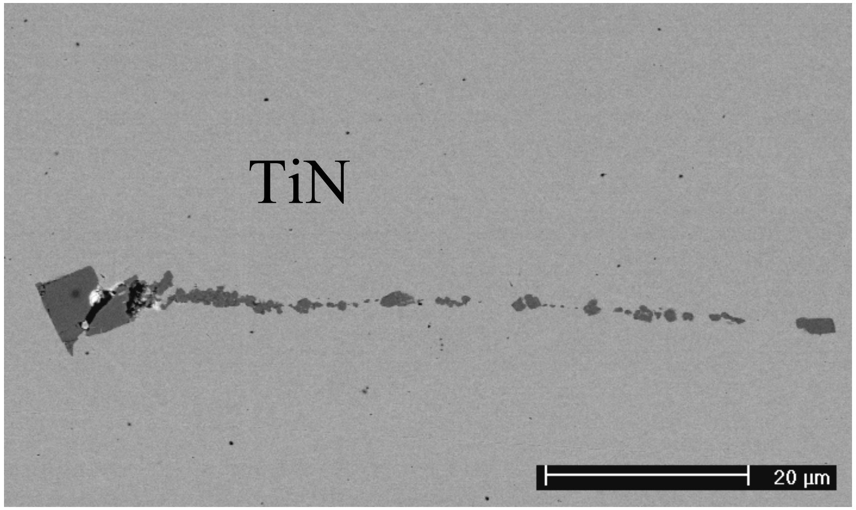
Known for 75 years:

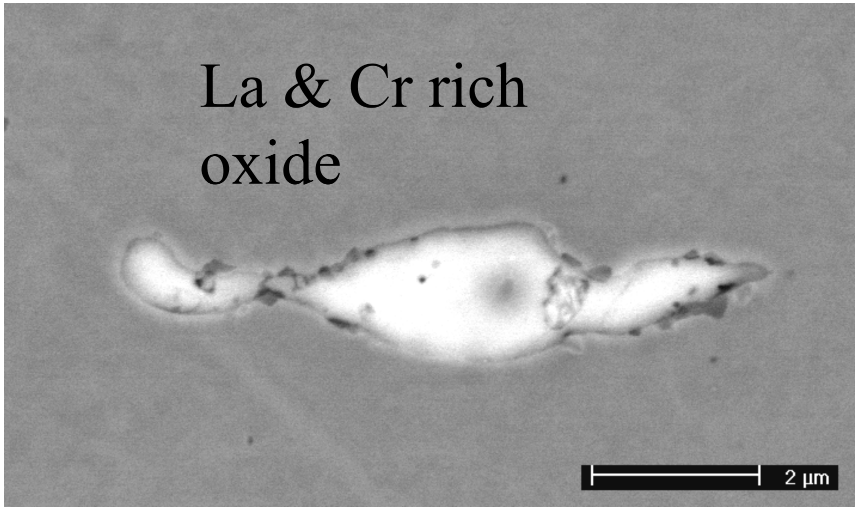
- Tetragonal crystal structure 30 atoms/unit cell
- Nucleates at grain boundaries in α – usually starting from a free surface
- Slow transformation – retarded by high purity (e.g. absence of Si)

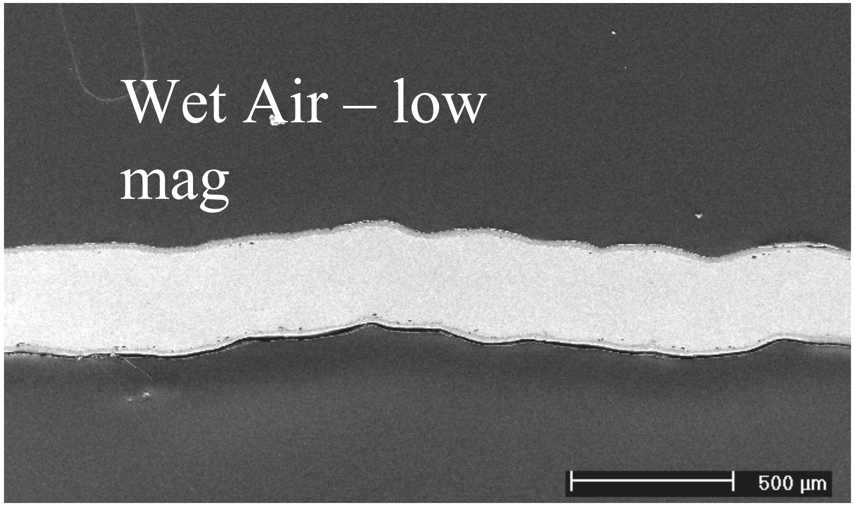
New observation:

- Transformation seems to be affected by environment
- Thermal cycling may have an effect???

Microstructural and Phase Identification Crofer 900°C







Concluding Remarks

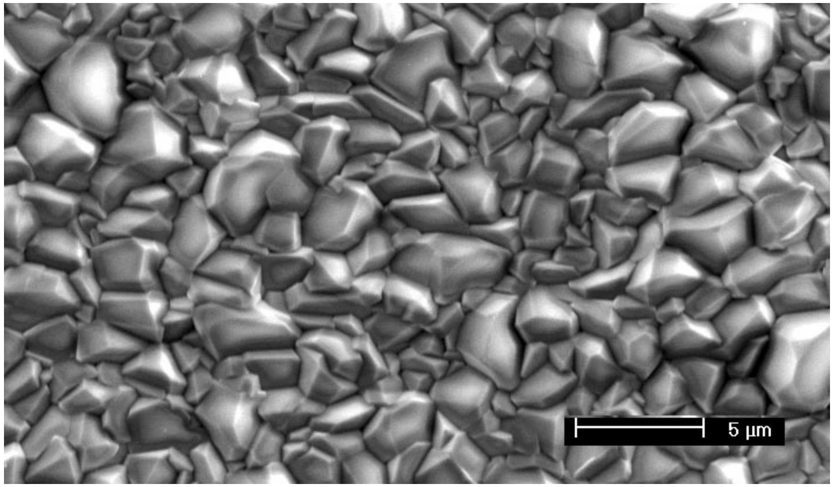
Alloys which form silica or alumina scales are not viable interconnect materials because of the high electrical resistivity of silica and alumina.

Chromia scales have lower resistivities than silica or alumina and can be formed on a variety of of alloys by selective oxidation.

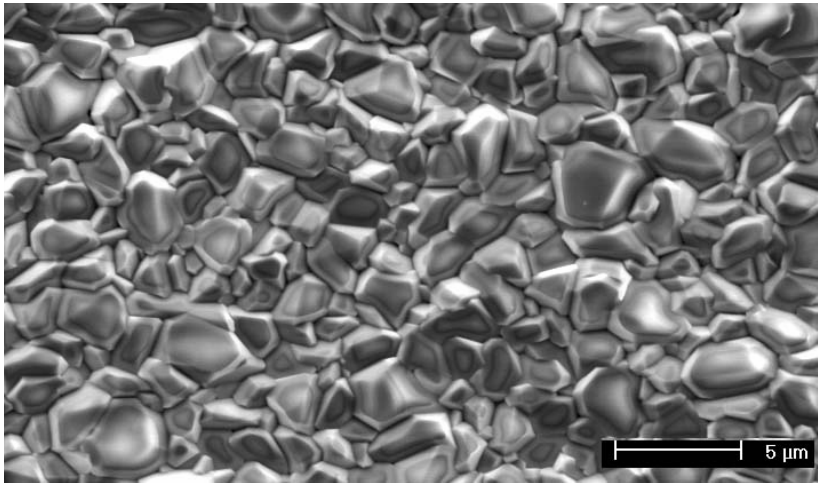
Problems with oxide evaporation from chromia and, in some cases, metallurgical stability make it desirable to explore the possibility of a Cr-free interconnect material.

Engineering interconnect systems, based on Ni, provides one interesting alternative.

Surface Micrographs



Nickel 900^{o}C



Sr-doped Nickel 900^{o}C