

ELECTRICALLY CONDUCTIVE COATINGS FOR METALLIC INTERCONNECTS: ROLE OF DEFECT CHEMISTRY

DE-PS26-04NT42074-1B

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SECA Program Review
April 18-21, 2005

Project Objectives

- To identify materials with **low oxygen ion conductivity** but **high electronic conductivity** for application as coatings.
- To synthesize and characterize materials with very low oxygen ion conductivity through **site-specific doping**.
- To **deposit coatings** on **stainless steels** and **nickel-based alloys**.
- To investigate **oxidation kinetics** – **electrical resistance**.
- To develop **low-cost methods** for the deposition of coatings.

Approach

- Identify prospective candidates through literature search and prior work. **Perovskites, spinels, TiO_2 .**
- **Doping** to suppress oxygen ion transport. **Fabrication of sintered parts** for DC conductivity measurements, Hebb-Wagner DC polarization measurements, **sputtering targets.**
- Measurement of **DC conductivity**, ionic conductivity by **Hebb-Wagner (electron) blocking electrode** method.
- Deposition of **coatings on stainless steels and nickel-based alloy** foils by sputtering; studies on **oxidation kinetics.**
- Estimation of kinetic parameters through ex-situ measurements; comparison with **oxidation studies** – comparison with an **analytical model.**

Background

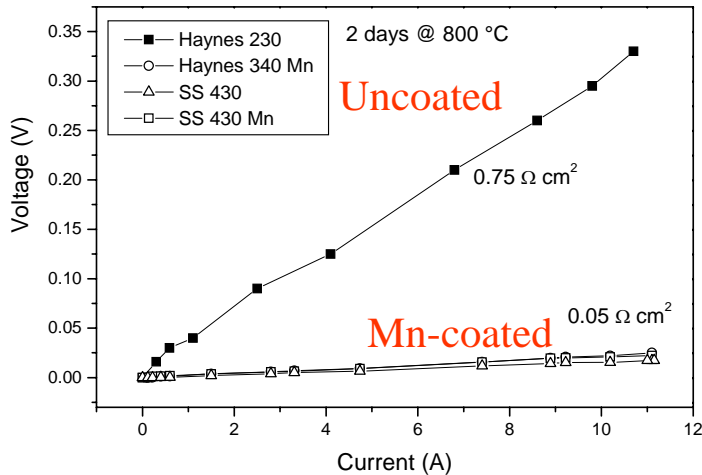
- Many prospective alloys contain **chromium** – formation of **chromia** as oxidation product (or Cr-containing spinels).
- Oxidation occurs in both **air and fuel** atmosphere.
- Oxide scales formed exhibit relatively **high electronic resistance**, or **spall easily**, or both.
- While electronic conductivity of the oxide scale is low, it is higher than ionic conductivity – ion transport determines oxidation kinetics.
- Kinetics of oxidation is usually **parabolic**.
- Kinetics of oxidation is relatively rapid at 800°C and higher, so that uncoated materials are not satisfactory – 40,000 hr life is difficult with the currently available materials.

Two approaches: (a) Protective coatings, (b) Alloy development

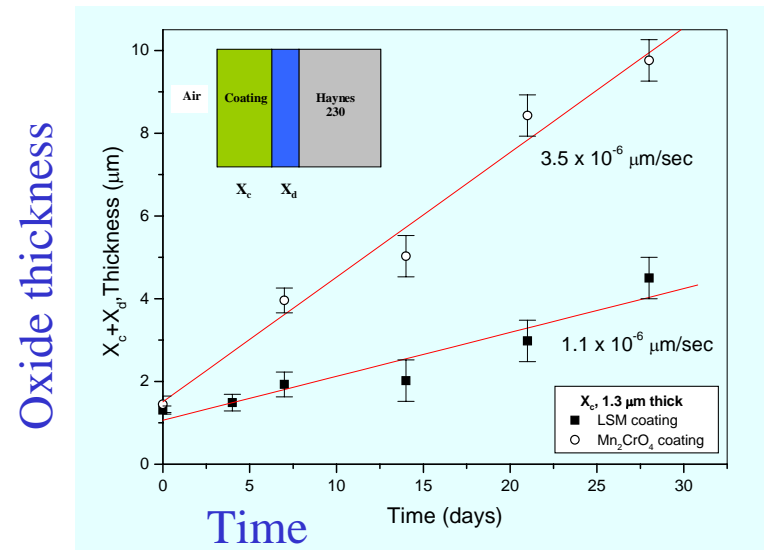
Our Prior Work

- Investigation of **oxidation kinetics** (up to **10,000** hr) and **ASR** of Haynes 230, Inconel 718, Inconel 600 series, Hastelloy X in air and fuel (hydrogen).
- Demonstration of the role of **Mn-Cr-spinels** formed in-situ in suppressing oxidation kinetics.
- Investigation of oxidation kinetics of **Haynes 230 coated with LSM and Mn-Cr-spinel**. Both coatings found to be protective – **LSM better** than Mn-Cr-spinel.
- Simple **parametric model** for oxidation of coated materials.
- Investigation of Mn-coated interconnects in **short term stack** tests – coated interconnects perform better.

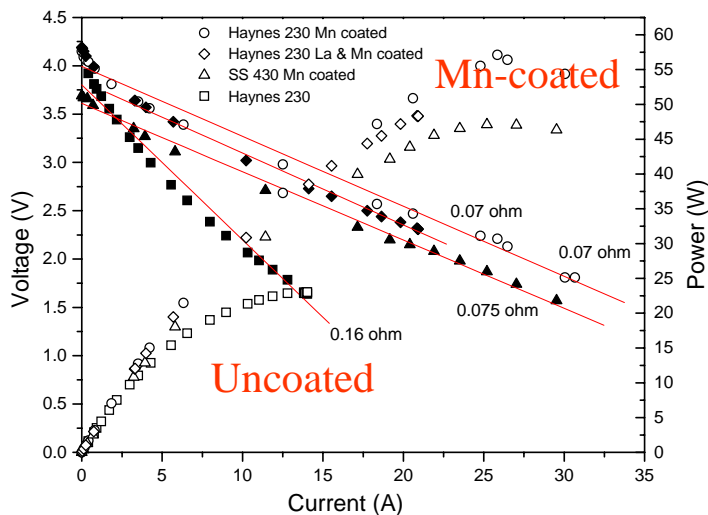
Some Prior Results



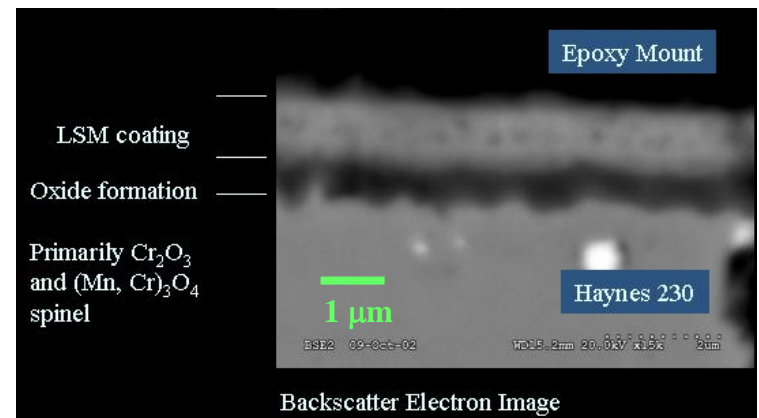
ASR of coated foils



Kinetics of coated H230 at 800°C in air



Stack tests with coated foils

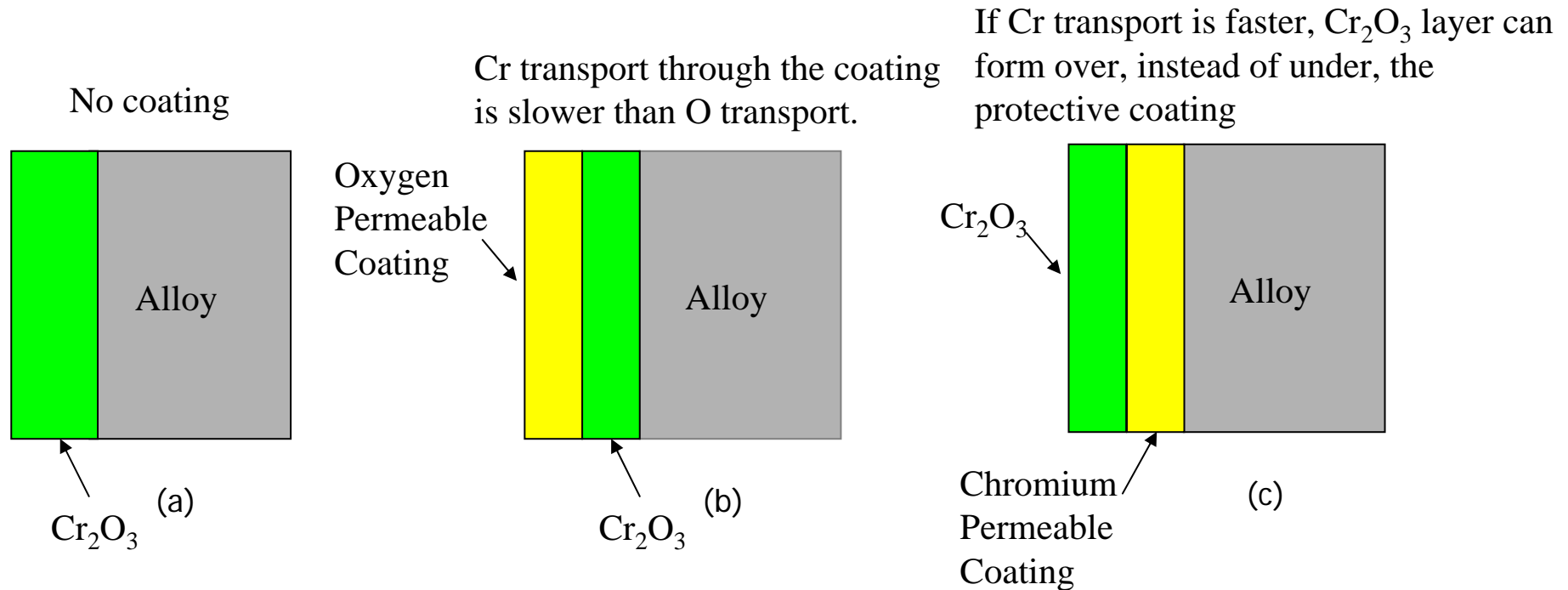


SEM of LSM-coated H230 at 800°C in air

Observations on Oxidation of Coated Foils

- With the coatings (perovskites and spinels) investigated so far, oxide (chromia) **scale forms under the coating**. This means oxygen transport through the coating is faster than chromium transport through the coating.
- **Electronic conductivities higher** in both the oxide scale and the deposited coating, compared to respective ionic conductivities.
- Predominantly cation transport through chromia, predominantly anion transport through the deposited coating.

Oxidation of Coated and Uncoated Foils: Schematics

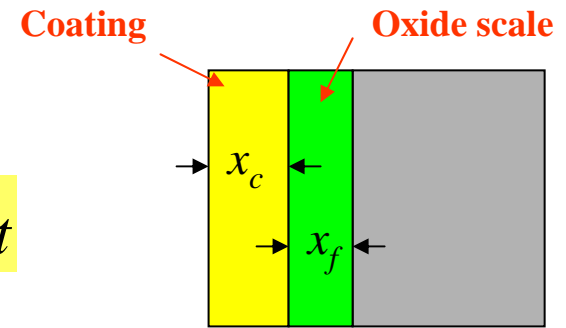


The coating should be such that $\text{ASR}(\text{coating}) \ll \text{ASR}(\text{Cr}_2\text{O}_3 \text{ scale})$

Required properties of the coating: (1) Should not readily transport oxygen.
(2) Should be a good ENOUGH electronic conductor.

Possible coatings: (1) Perovskites (ABO_3). (2) Spinel (AB_2O_4). (3) Donor-doped TiO_2 . (4) Other.

Model



A quadratic in x_f $k_c x_f^2 + 2k_f x_c x_f = k_f k_c t$

Base alloy rate constant

$$k_f \approx \frac{EV_M}{2F} \sigma_i^f$$

Coating permeation kinetic parameter

$$k_c \approx \frac{EV_M}{2F} \sigma_i^c$$

Ionic Conductivity
Of the Coating

Two limiting cases: (a) Coating un-protective, (b) Coating protective

(a) Un-Protective coating

$$k_c x_f \gg 2k_f x_c$$

$$x_f \approx \sqrt{k_f t}$$

Undesirable: Oxidation
Kinetics independent of
Coating: **PARABOLIC**

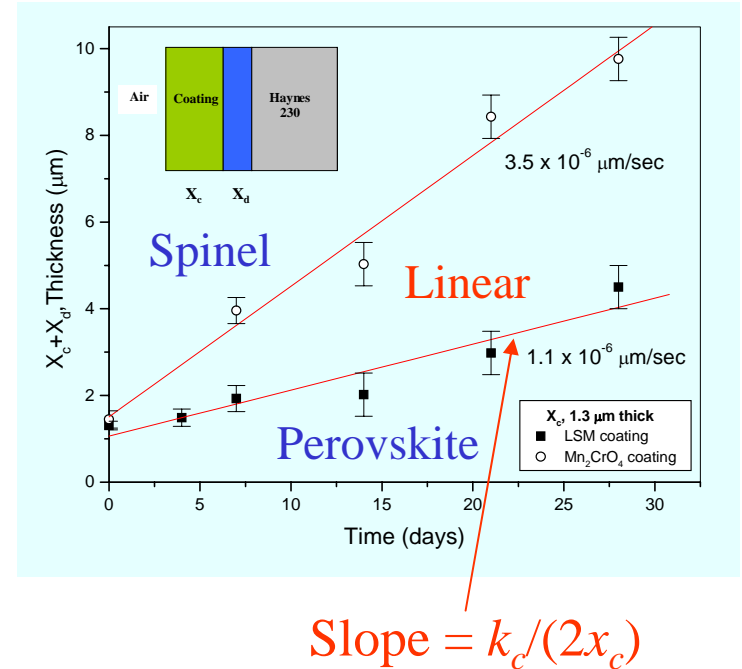
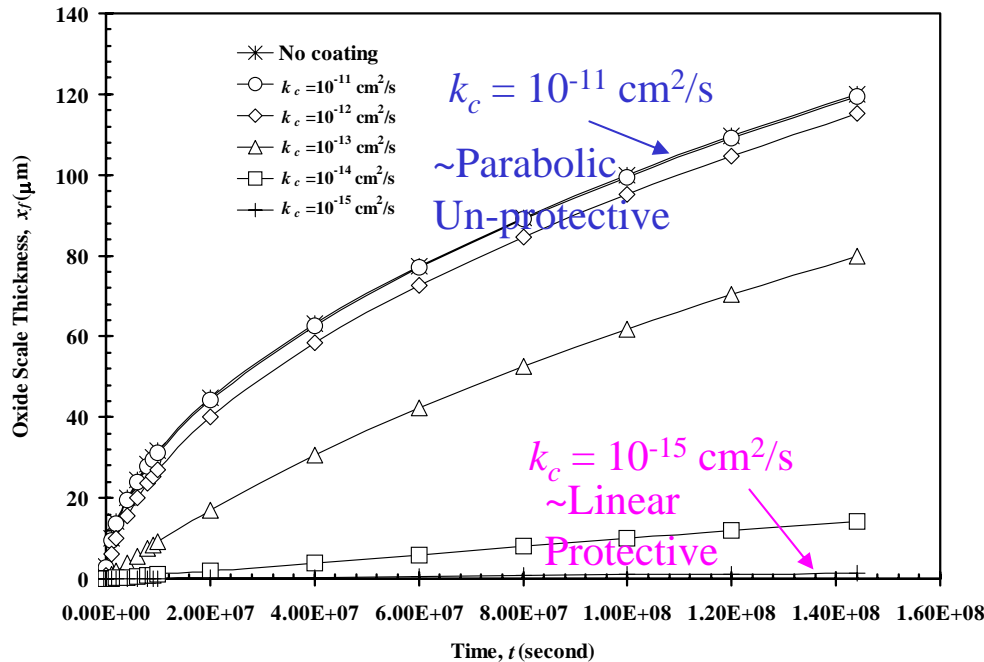
(b) Protective coating

$$k_c x_f \ll 2k_f x_c$$

$$x_f \approx \frac{k_c}{2x_c} t$$

Preferred Case: Oxidation
Kinetics independent of
Base alloy: **LINEAR**

Calculations Based on Model Comparison with Experimental Results



Parabolic rate constant of the alloy, $k_f = 10^{-12} \text{ cm}^2/\text{s}$

k_c for LSM at 800°C is estimated to be $\sim 2.86 \times 10^{-14} \text{ cm}^2/\text{s}$

Calculation of Oxide Scale Thickness

Alloy rate constant: $k_f = 10^{-12} \text{ cm}^2/\text{s}$

Coating thickness: $x_c = 5 \text{ } \mu\text{m}$

Time (Sec)	Time (hrs)	x_f in μm No Coating	x_f in μm $k_c=10^{-11}$ cm^2/s	x_f in μm $k_c=10^{-12}$ cm^2/s	x_f in μm $k_c=10^{-13}$ cm^2/s	x_f in μm $k_c=10^{-14}$ cm^2/s	x_f in μm $k_c=10^{-15}$ cm^2/s
1×10^6	278	10.0	9.51	6.18	1.0	0.1	0.01
1×10^7	2,778	31.62	31.13	27.01	9.16	1.0	0.1
1×10^8	27,778	100	99.5	95.12	61.8	9.9	1.0
1.44×10^8	40,000	120.0	119.5	115.1	80.0	14.2	1.44

Site-Specific Doping

- Doping on **specific sites** to alter point defects.
- Strategy used in the past in BaTiO_3 (perovskites), LiAl_5O_8 (spinel).
- Objective is to **suppress oxygen ion transport** – without drastically lowering the electronic conductivity.

What is the minimum electronic conductivity that the coating must have?

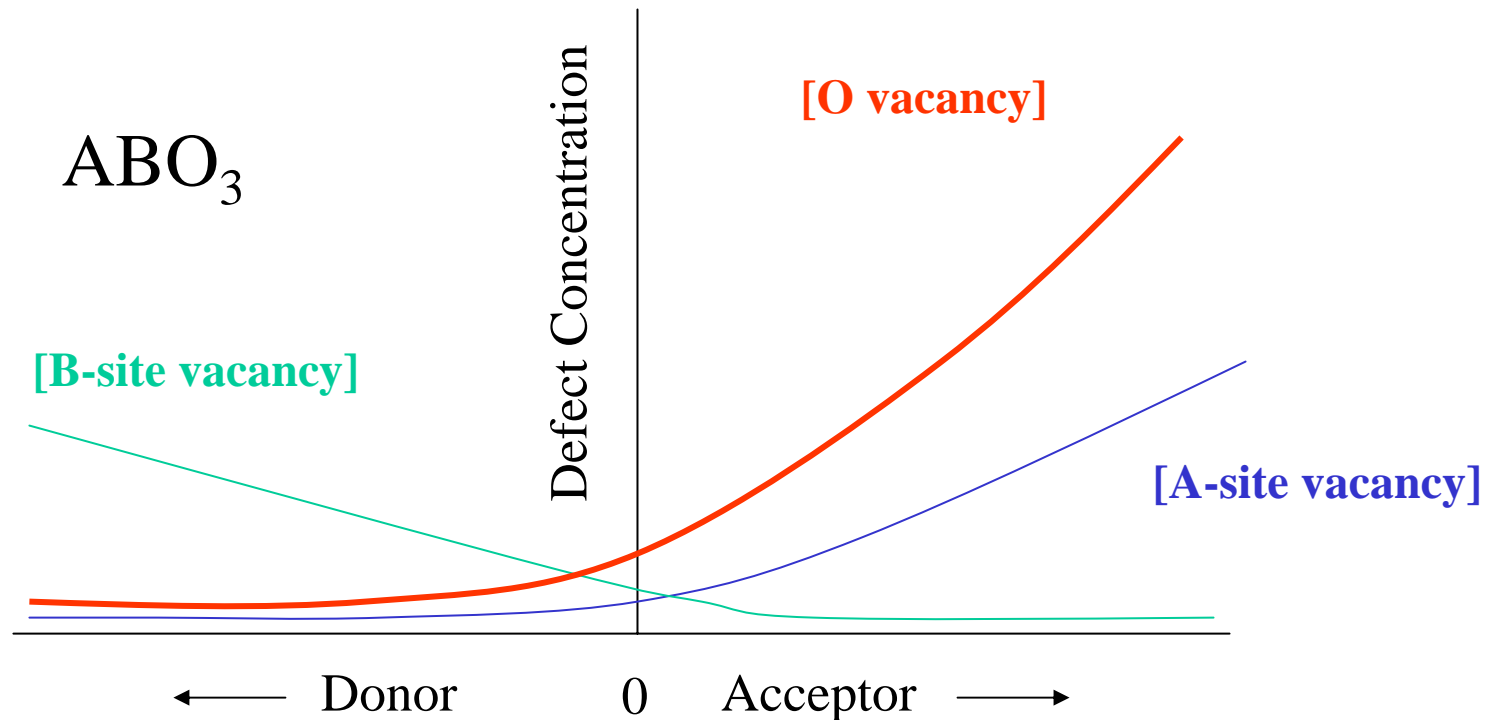
Suppose the coating 5 microns in thickness.

If $\sigma_{el} \sim 1 \text{ S/cm}$, ASR due to coating will be $0.0005 \text{ } \Omega\text{cm}^2$

If $\sigma_{el} \sim 0.1 \text{ S/cm}$, ASR due to coating will be $\sim 0.005 \text{ } \Omega\text{cm}^2$

Site Specific Doping in Perovskites & Spinel

- 1) "Phase Transformation Kinetics in Doped LiAl_5O_8 - LiFe_5O_8 System", S. J. Kim, Z. C. Chen and A. V. Virkar, *J. Am. Ceram. Soc.*, **71** [10] C428-C432 (1988).
- 2) "The Effect of Aliovalent Dopants on Cation Diffusion in TiO_2 - SnO_2 ", D. Drobeck, A. V. Virkar and R. M. Cohen, *J. Phys. Chem. of Solids*, **51** [8] 977-88 (1990).
- 3) "Interdiffusion and Kirkendall Effect in Doped BaTiO_3 - BaZrO_3 Perovskites: Effect of Vacancy Supersaturation", S. Gopalan and A. V. Virkar, *J. Am. Ceram. Soc.*, **82** [10] 2887-2899 (1999).



Approach to Materials Selection

- Perovskites, Spinel, TiO_2 .
- Perovskites – LaMnO_3 with donor doping on the B-site.
- TiO_2 – donor doping.

LaMnO_3 (LM)

$\text{La}_{0.95}\text{Sr}_{0.05}\text{MnO}_3$ (LSM) Higher ionic and electronic conductivities than LM

$\text{LaMn}_{0.95}\text{Ti}_{0.05}\text{O}_3$ ($\text{LT}_{0.05}\text{M}$) Lower ionic and electronic conductivities than LM

$\text{LaMn}_{0.95}\text{Ti}_{0.05}\text{O}_3$ ($\text{LT}_{0.1}\text{M}$) Lower ionic and electronic conductivities than $\text{LT}_{0.05}\text{M}$

$\text{Ti}_{0.98}\text{Ta}_{0.02}\text{O}_2$

$\text{Ti}_{0.98}\text{Nb}_{0.02}\text{O}_2$

In all of the above materials, electronic conductivity \gg ionic conductivity

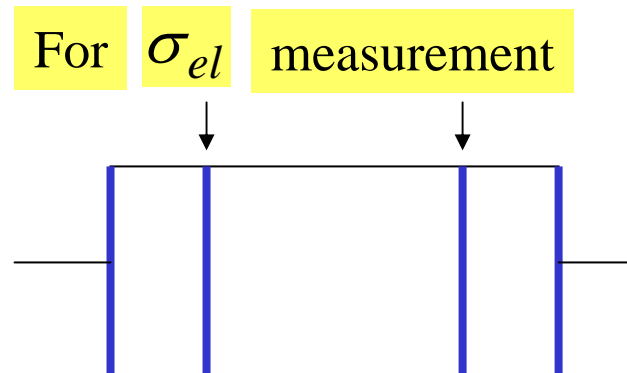
Fabrication of Prospective Coating Materials in Bulk Form

- Ball milling- For 24 hrs with zirconia media and ethanol.
- Calcination- At 1100°C for 2 hrs.
- Binder - Polyethylene glycol
- Pressing - 10000 lb.
- Isostatic - 2000psi pressing
- Sintering - At 1400°C for 2 hr
– TiO₂ at 1500°C
- Density - Archimedes Measurement

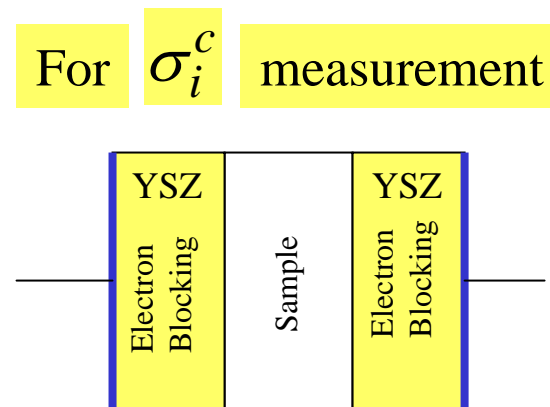
Weighing powder
Ball milling
Drying
Calcination
Ball milling
Drying
Binder addition
Pressing
Isostatic pressing
Sintering
Density measurement
Electrical characterization
Microscopy

Electrical Characterization of Prospective Coating Materials

- Four Probe DC conductivity measurement (0.04 A): Total conductivity, which is mainly σ_{el} .
- Two probe, Hebb-Wagner DC polarization measurement (50 μ A): Ionic conductivity, σ_i .



Four probe DC

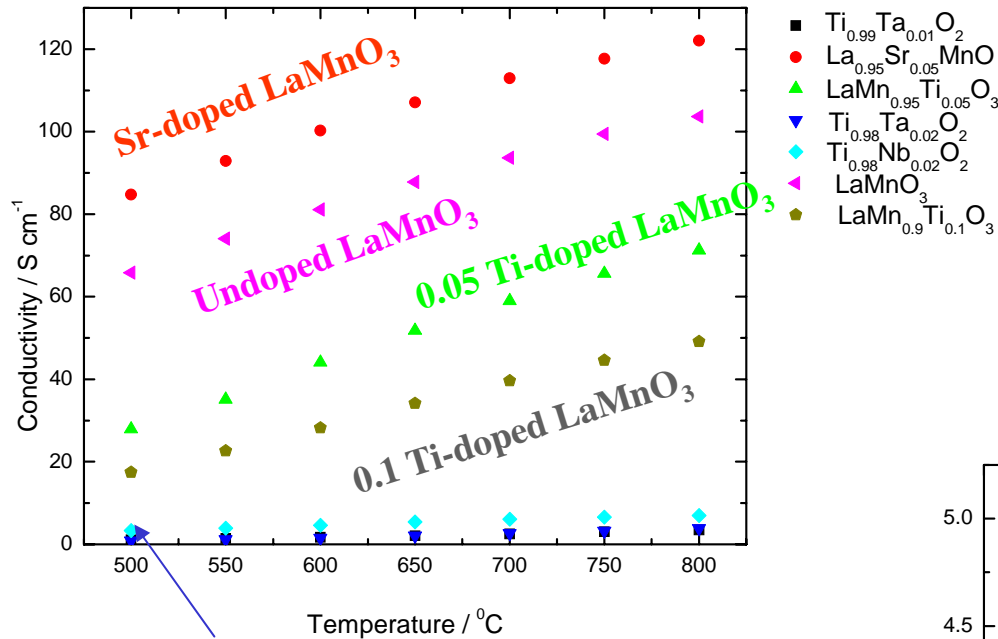


Good Bond

Two probe DC –Hebb-Wagner

Four Probe DC Conductivity

4 probe DC Conductivity vs Temperature graph

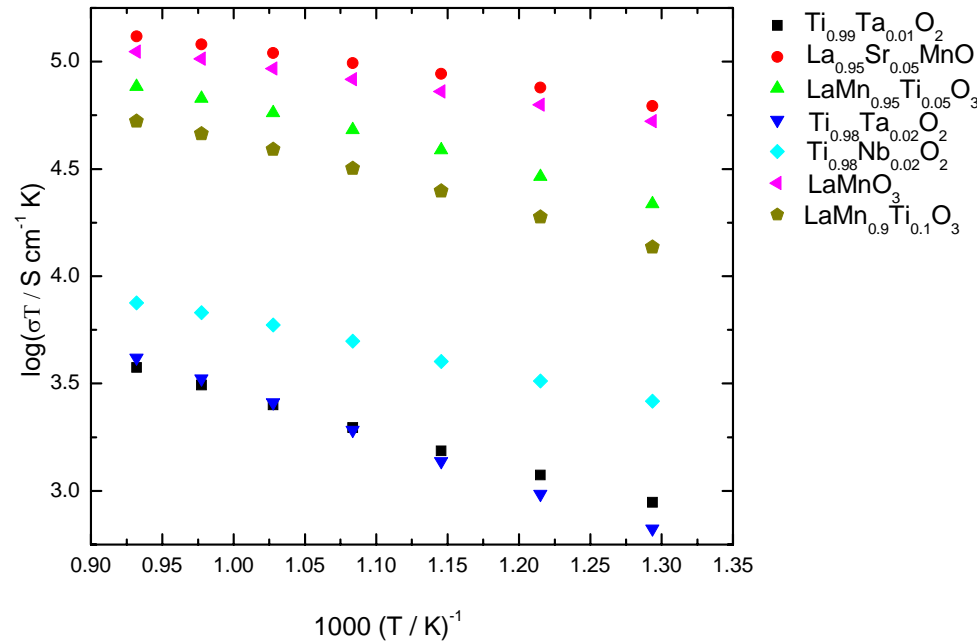


Sr increases σ_{el} and σ_i^c

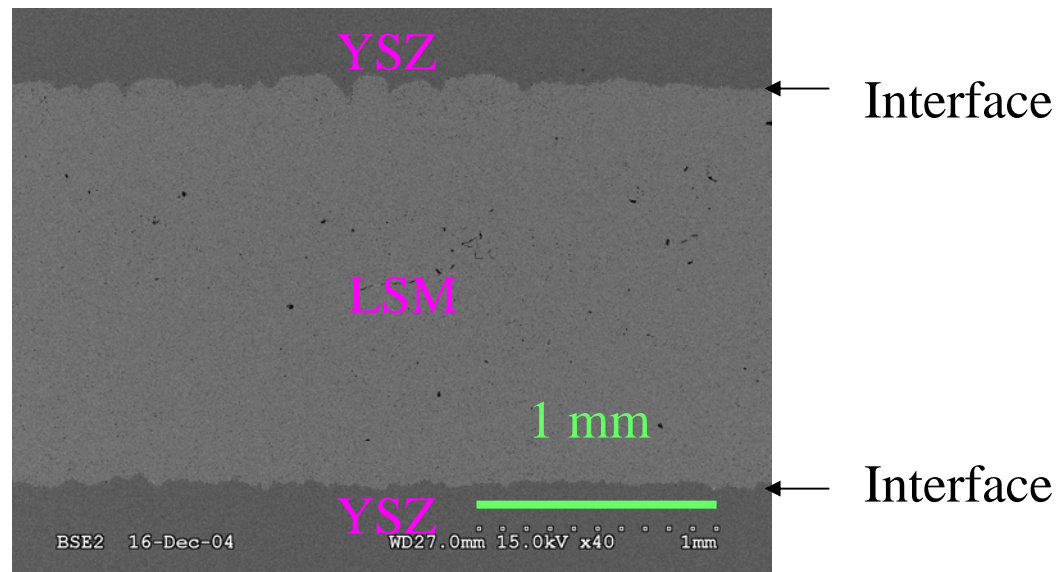
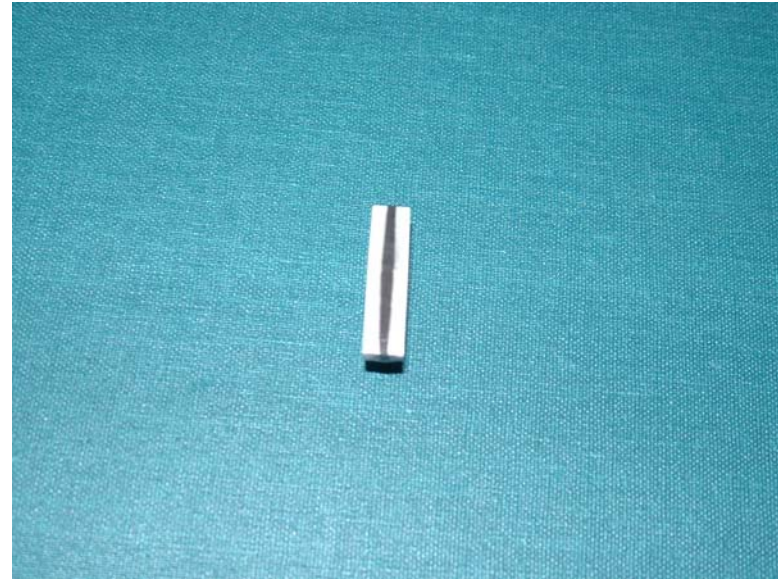
Ti decreases σ_{el} and σ_i^c

Even at 500°C, the σ_{el} of doped TiO₂ is greater than 1 S/cm

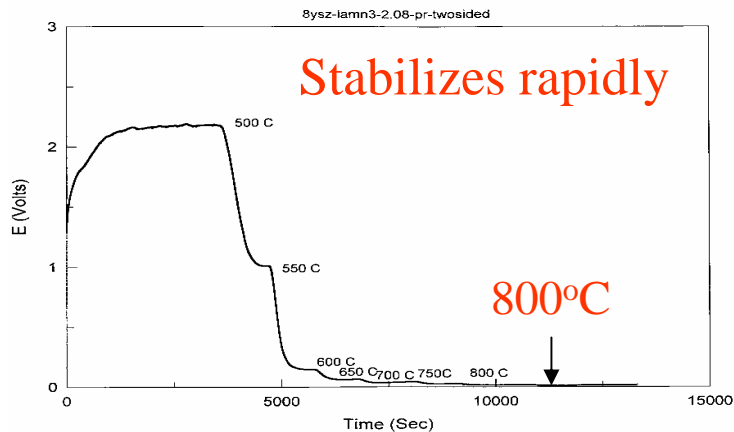
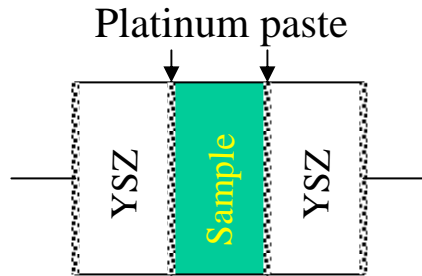
4 probe DC log(σT) vs 1000/T



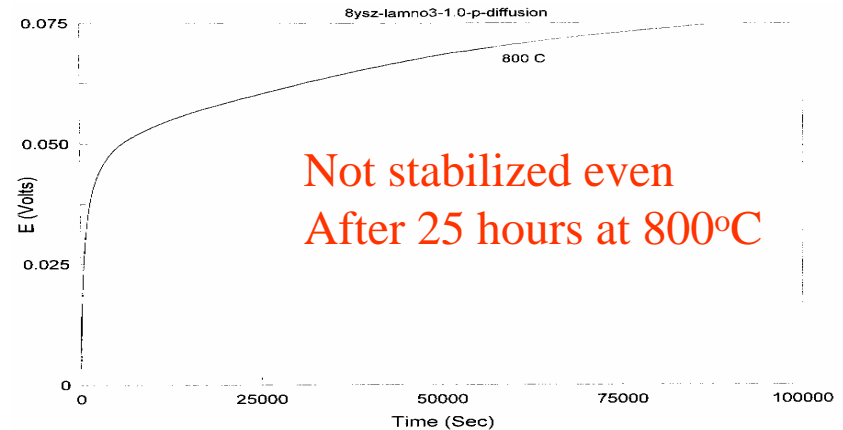
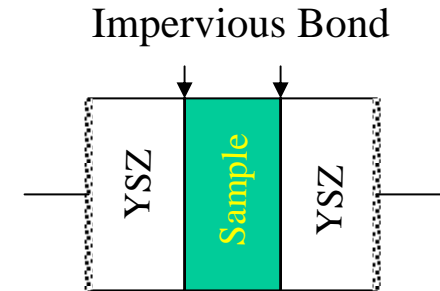
Sandwich Samples for Hebb-Wagner Measurements: LSM-YSZ Interface



Blocking Electrode Measurements

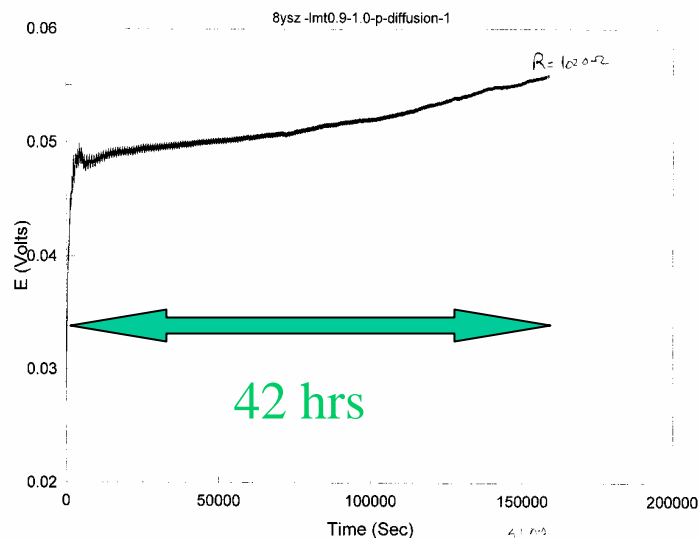


YSZ/LaMnO₃/YSZ
 Without a bond (platinum paste)
 Stabilizes rapidly
 Incorrect measurement

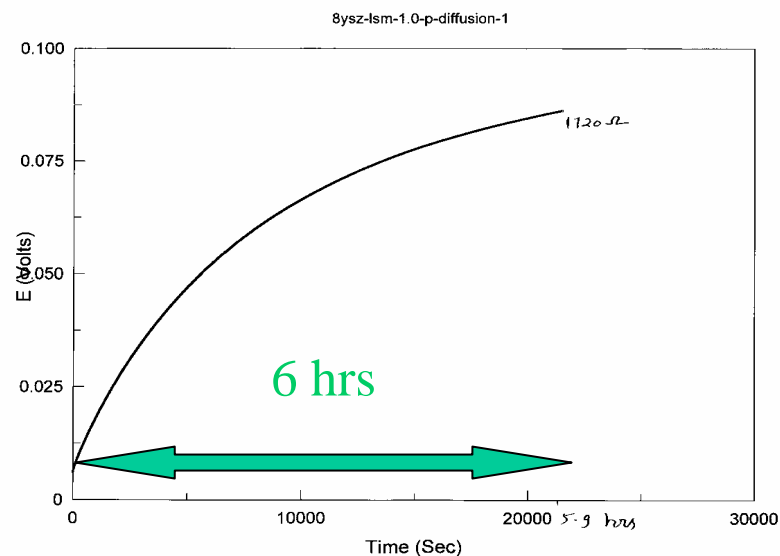


YSZ/LaMnO₃/YSZ
 Co-sintered – Good bond
 Does not readily stabilize
 Reliable measurement – only when stabilized
 Stabilization time could be days or longer

Additional Examples of Blocking Electrode Measurements



YSZ/Ti-doped LaMnO₃/YSZ
At 800°C: Slower kinetics of
Equilibration, because of lower
Ionic conductivity.



YSZ/Sr-doped LaMnO₃/YSZ
At 800°C: Faster kinetics of
Equilibration, because of higher
Ionic conductivity.

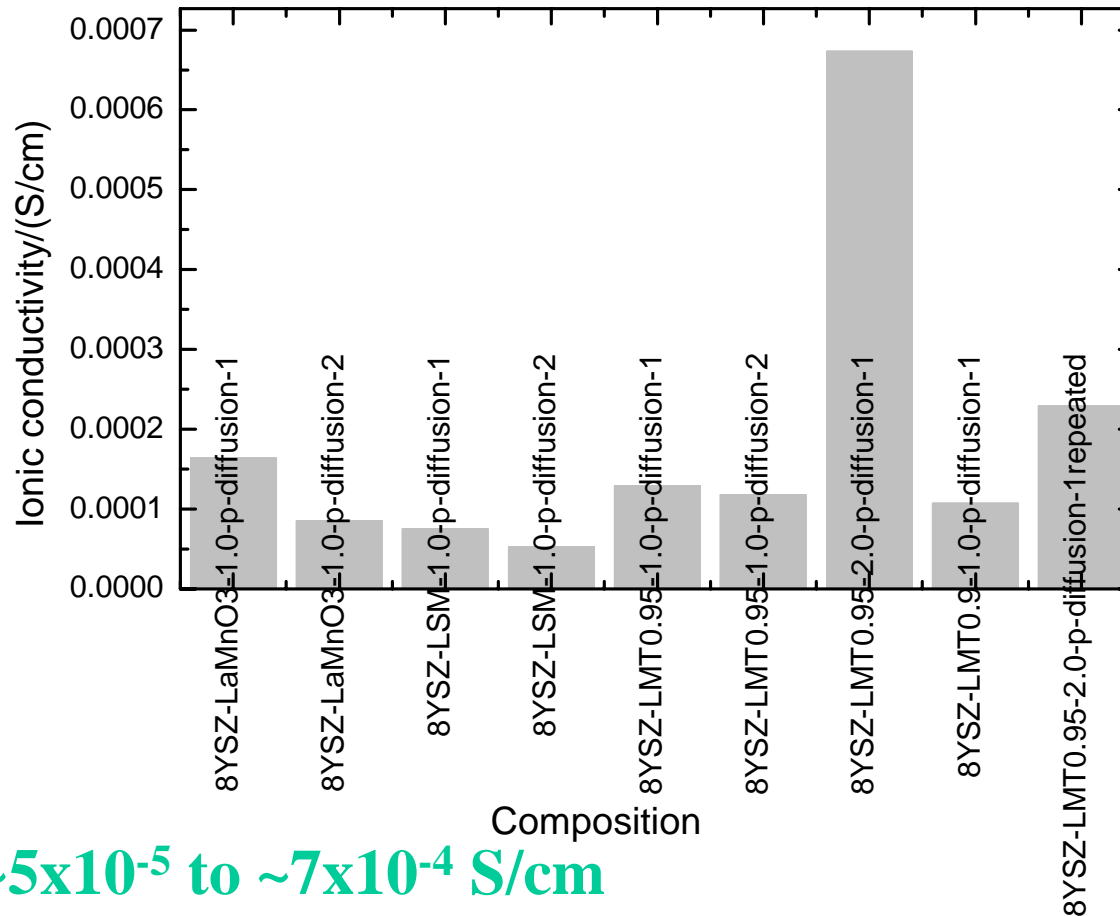
Kinetics of Stabilization: Hebb-Wagner Polarization Method

- 1) Kinetics of stabilization (voltage or current, depending upon constant current or constant voltage experiment) depends on:
 - (a) Ionic and electronic conductivities of the three layers; namely the two YSZ layers, and the sample.
 - (b) Lengths of the three individual layers. The larger the lengths (thicknesses) the longer the time required – dependence is exponential ^{a,b}.
- 2) Four probe measurement is more difficult due to the longer sample lengths.
- 3) Kinetics is not describable by first order kinetics (not one time constant).
- 4) For typical transport parameters and sample dimensions,
the time required for stabilization can be hours, days, months?

a) "Internal Pressurization in Cationic Solid Electrolytes", A. V. Virkar, *J. Mater. Sci.*, **20**, 552-562, (1985).

b) "Internal Precipitation of Molecular Oxygen and Electromechanical Failure of Zirconia Solid Electrolytes", A. V. Virkar, J. Nachlas, A. V. Joshi and J. Diamond, *J. Am. Ceram. Soc.*, **73** [11] 3382-3390 (1990).

Preliminary Results on Ionic Conductivity Measurements (Hebb-Wagner) at 800°C



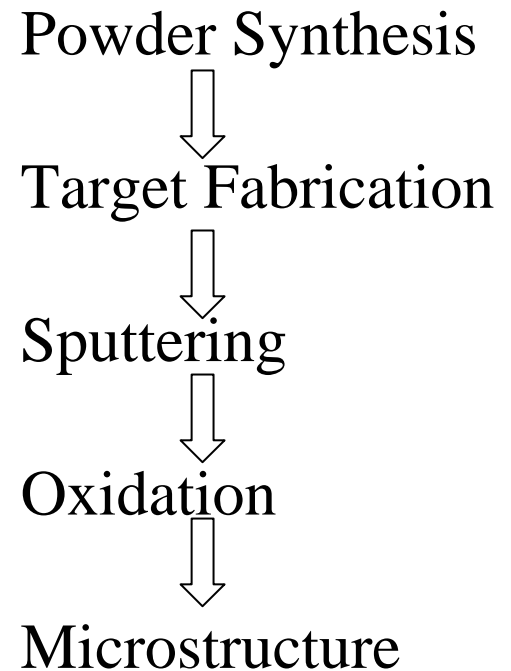
Range: $\sim 5 \times 10^{-5}$ to $\sim 7 \times 10^{-4}$ S/cm

All are overestimates (may be by orders
Of magnitude): Not equilibrated

Hebb-Wagner measurements will need to be done on thin sandwich structures.

Preliminary Oxidation Studies

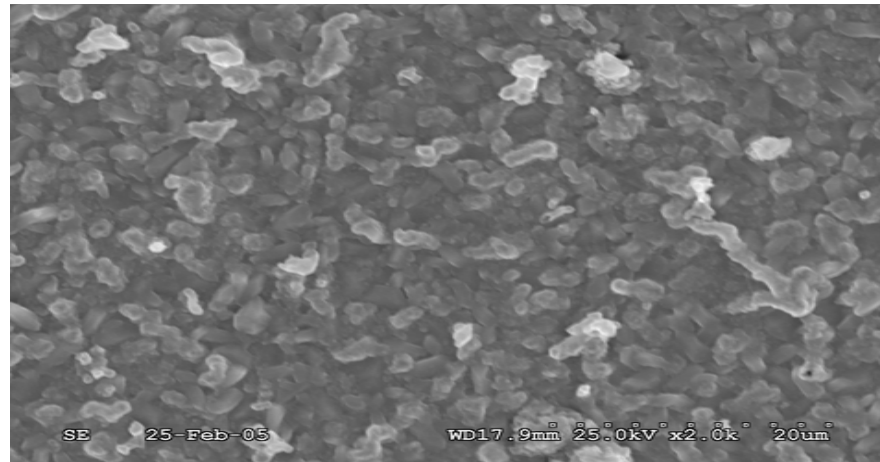
- Oxidation studies initiated on uncoated and coated samples.
- Alloy foils selected include **SS430, Inconel 718, Haynes 230**.
- Ceramic coatings of thicknesses **1, 2, 3, and 5** μm deposited by PVD



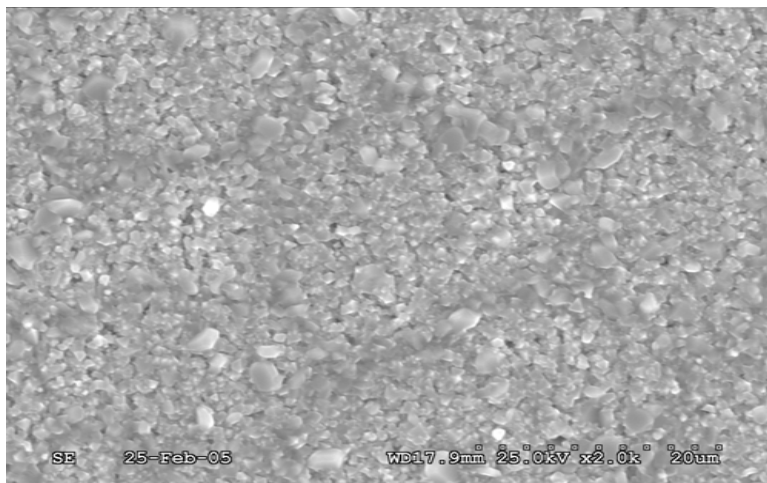
Oxidation Studies on Uncoated Foils:

Air, 800°C, 4days

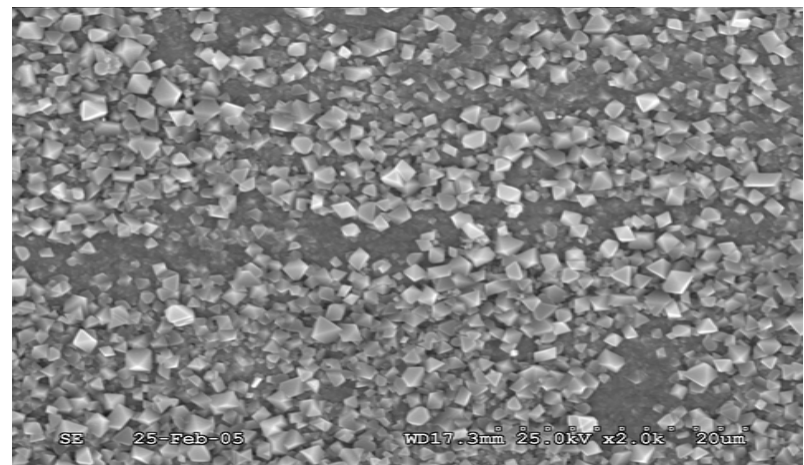
INC718_HT800_4days_2kx



H230_HT800_4days_2kx

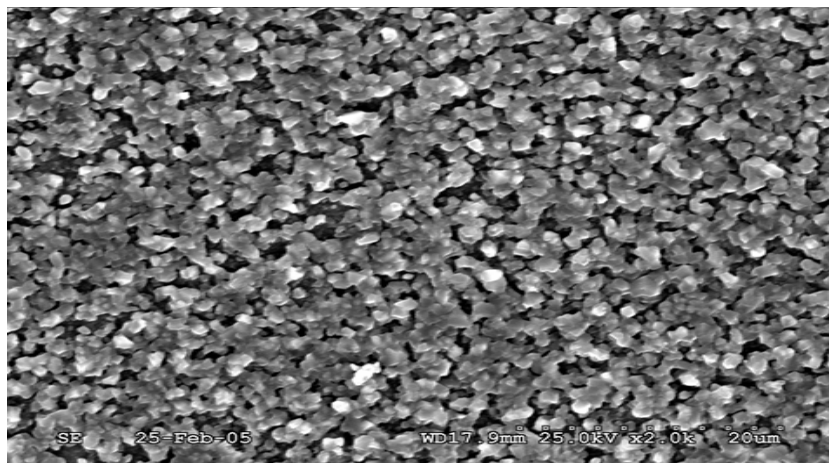


SS430_HT800_4days_2kx

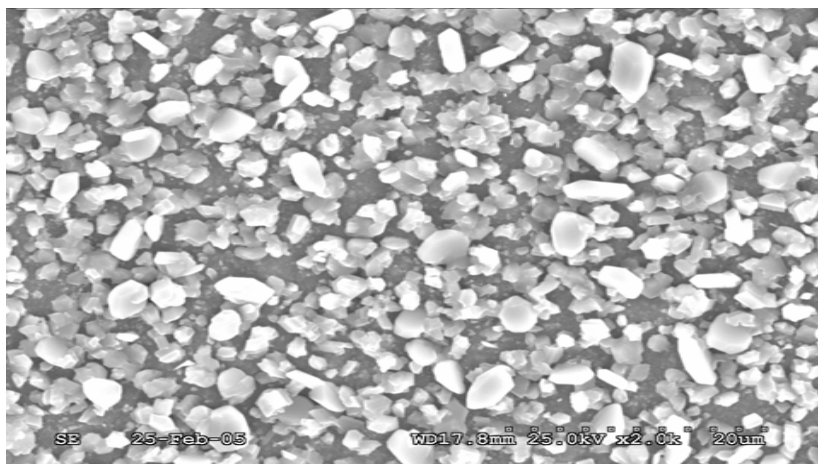


Oxidation Studies on $\text{Ti}_{0.98}\text{Ta}_{0.02}\text{O}_2$ -coated ($1\text{ }\mu\text{m}$) Foils

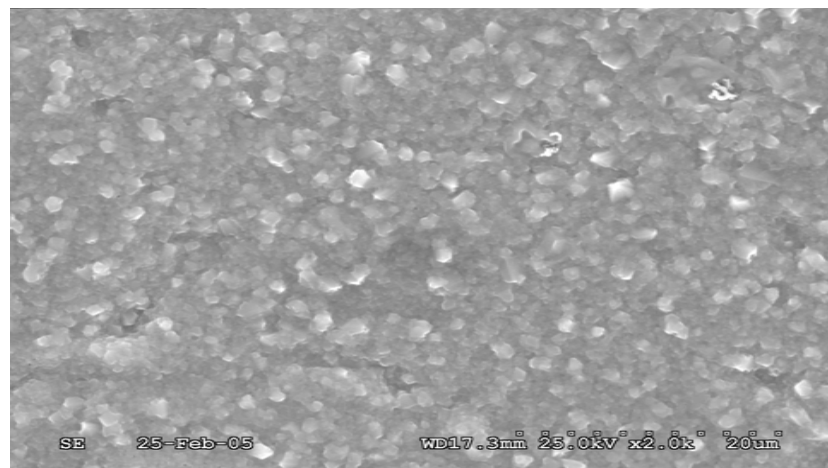
INC718_TiO2Ta_HT800_4days_2kx



H230_TiO2Ta_HT800_4days_2kx

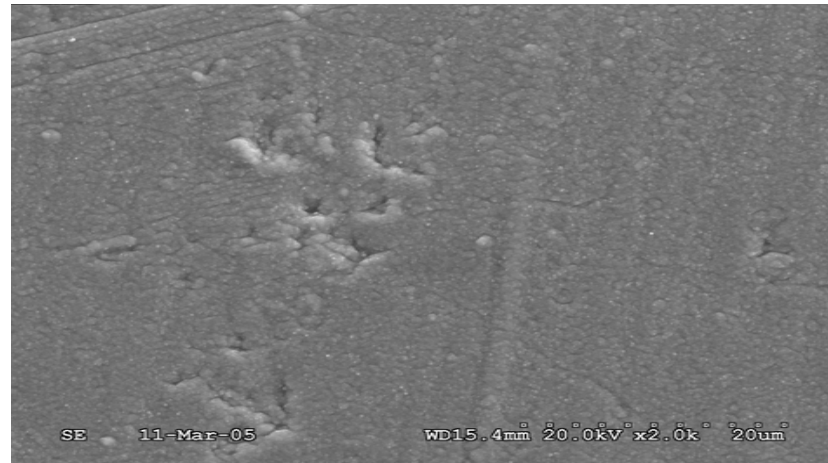


SS430_TiO2Ta_HT800_4days_2kx

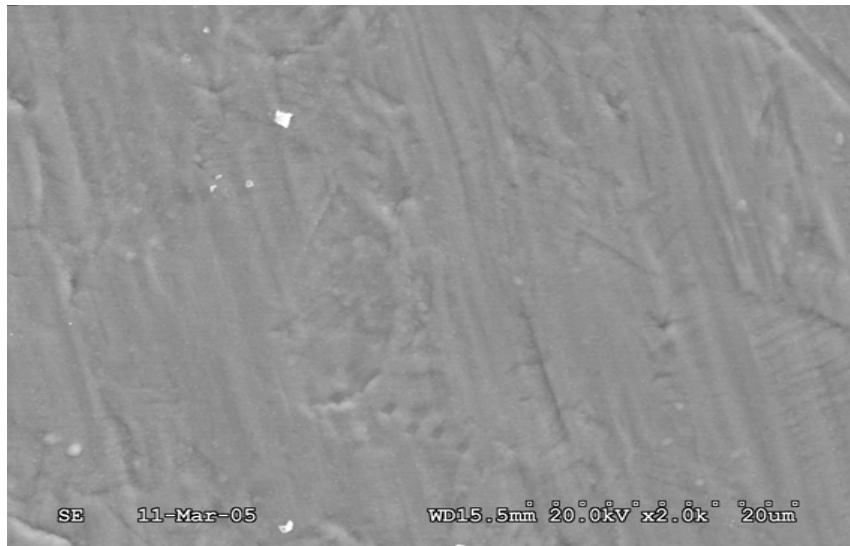


Oxidation Studies on $\text{LaMn}_{0.9}\text{Ti}_{0.1}\text{O}_3$ -coated ($2\text{ }\mu\text{m}$) Foils

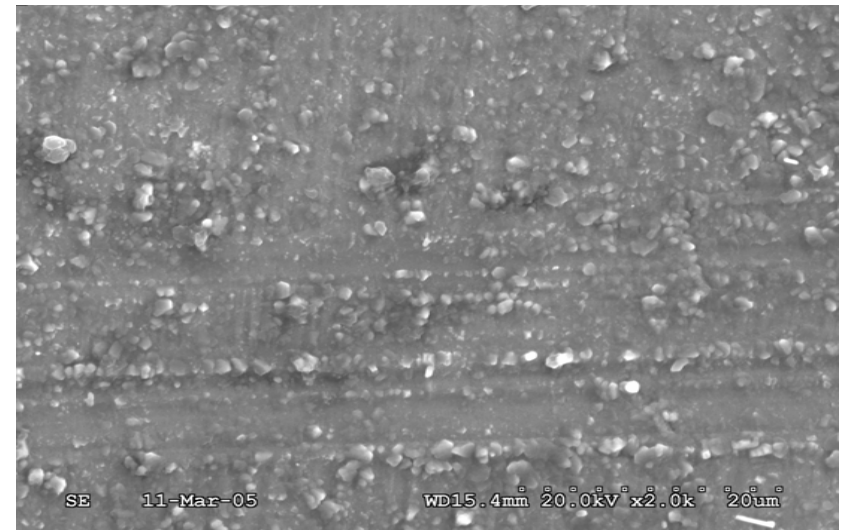
INC718_LMT0.9_2um_HT800_4DAYS_2kx.



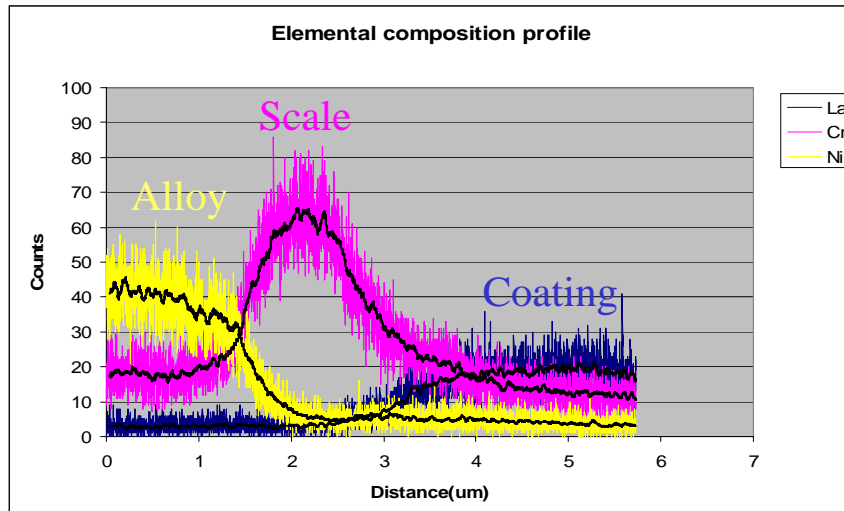
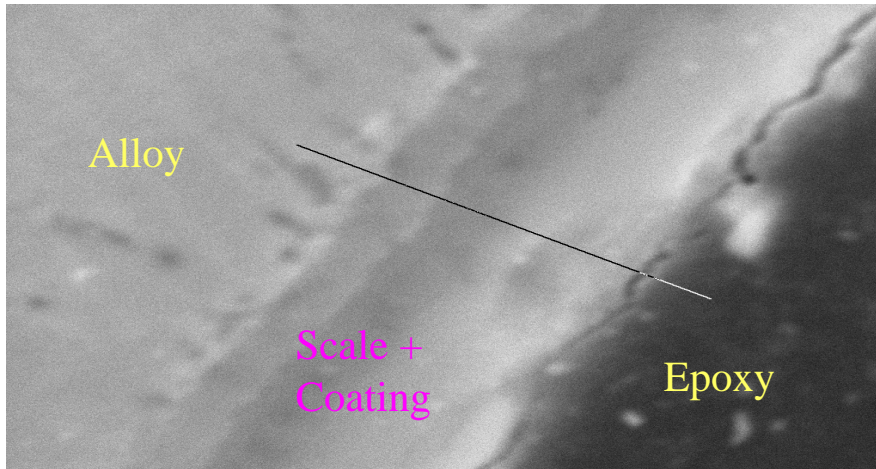
H230_LMT0.9_2um_HT800_4DAYS_2kx



SS430_LMTpt9_2um_HT800_4DAYS_2kx



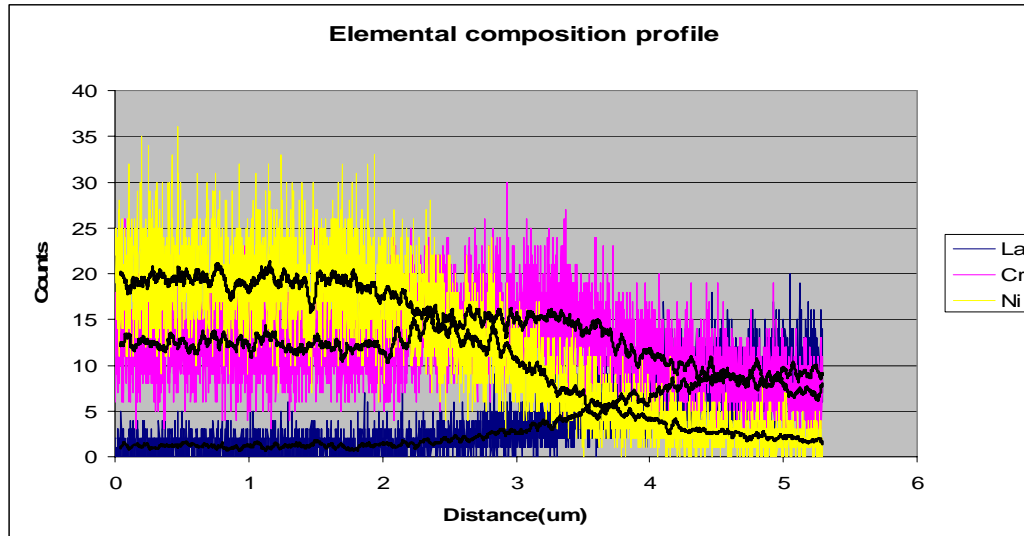
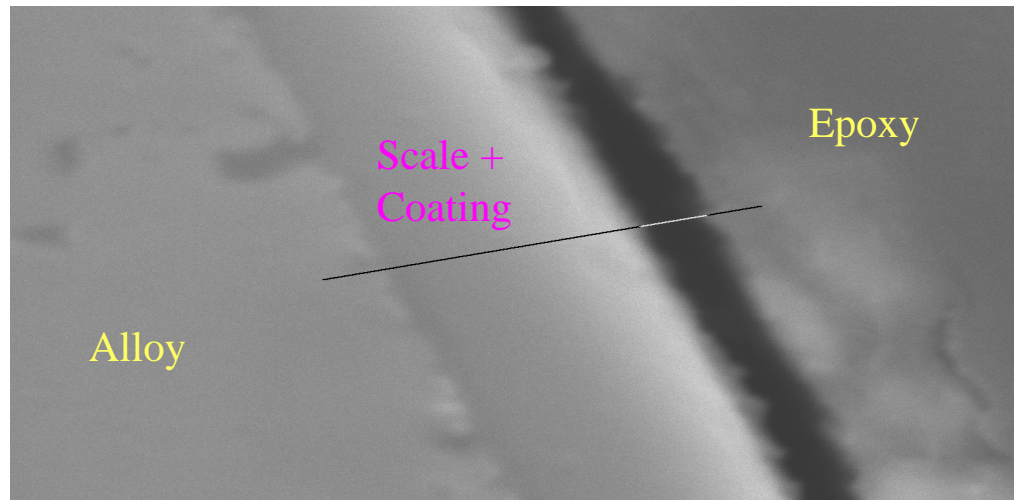
Composition profile across Inc718-oxide layer- $\text{LaMn}_{0.9}\text{Ti}_{0.1}\text{O}_3$ coating: 800°C, 8 days



- Composition profiles of elements La, Cr, Ni across metal-oxide layer-coating interface. Metal on left side, coating on right side and oxide layer in the center.
- **Sample:** 8 days oxidized Inc718 with 2 μm $\text{LaMn}_{0.9}\text{Ti}_{0.1}\text{O}_3$ coating, at 800°C

Estimated $k_c \sim 4 \times 10^{-14} \text{ cm}^2/\text{s}$

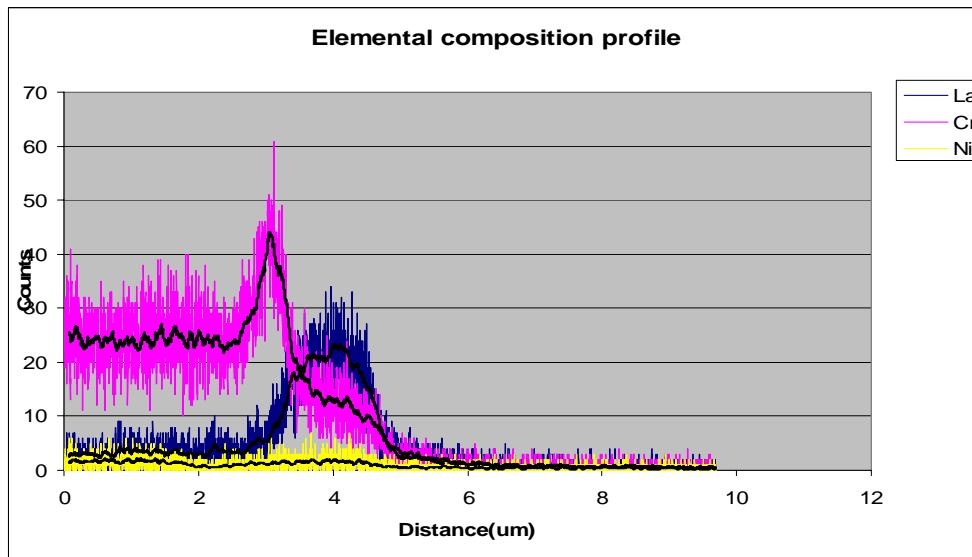
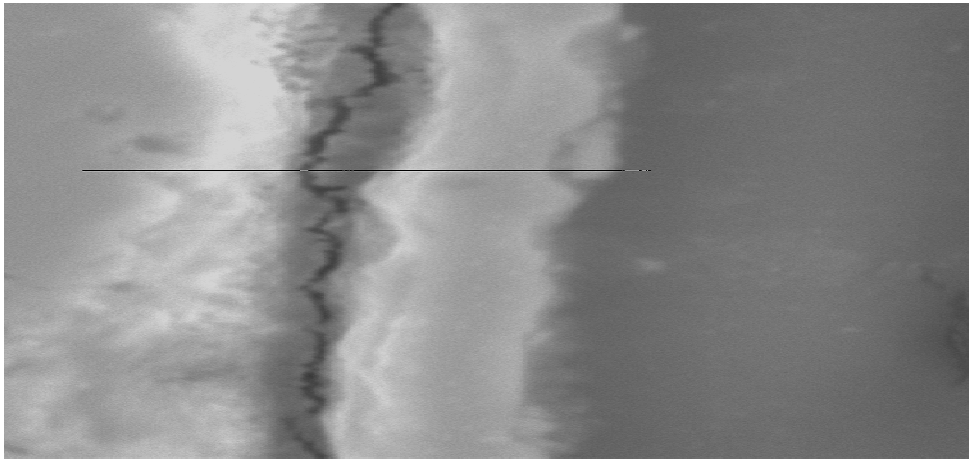
Composition profile across Haynes 230-oxide layer - $\text{LaMn}_{0.9}\text{Ti}_{0.1}\text{O}_3$ coating



- Composition profiles of elements La, Cr, Ni across metal-oxide layer-coating interface. Metal on left side, coating on right side and oxide layer in the center.
- Sample: 8 days oxidized Haynes 230 with $2\mu\text{m}$ $\text{LaMn}_{0.9}\text{Ti}_{0.1}\text{O}_3$ coating, at 800°C

Estimated $k_c \sim 3 \times 10^{-14} \text{ cm}^2/\text{s}$

Composition profile across SS430-oxide layer- $\text{LaMn}_{0.9}\text{Ti}_{0.1}\text{O}_3$ coating



- Composition profiles of elements La, Cr, Ni across metal-oxide layer-coating interface. Metal on left side, coating on right side and oxide layer in the center.
- Sample: 8 days oxidized SS430 with $2\mu\text{m}$ $\text{LaMn}_{0.9}\text{Ti}_{0.1}\text{O}_3$ coating, at 800°C

Estimated $k_c \sim 3 \times 10^{-14} \text{ cm}^2/\text{s}$

Summary

- 1) A few prospective coating materials were identified.
- 2) Some doped coating materials were made.
- 3) Electrical characterization (electronic and ionic conductivities) was initiated.
- 4) Oxidation studies on coated foils of stainless steels and nickel-based alloys was initiated.
- 5) Ex-situ measurements and oxidation studies are used to estimate oxidation kinetics – to design superior coating materials through defect chemistry.
- 6) ASR measurements will be initiated shortly.
- 7) For accurate measurements of ionic conductivity, thinner sandwich structures are planned.