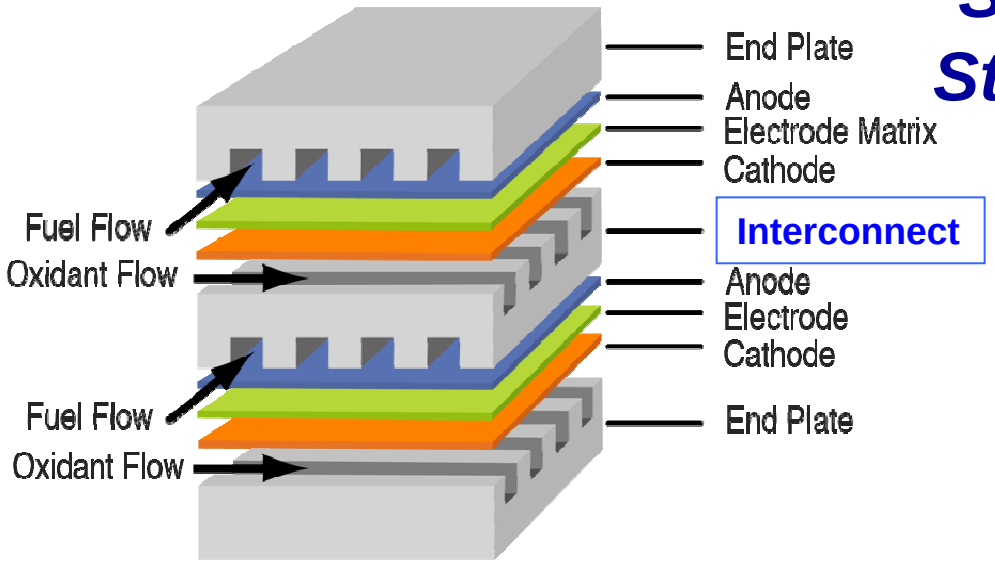
DOE/NETL-IR-2007-204

National Energy Technology Laboratory



The Performance of Ce Surface Treated Ferritic Stainless Steels for Solid Oxide Fuel Cell Interconnects

Paul Jablonski and David Alman

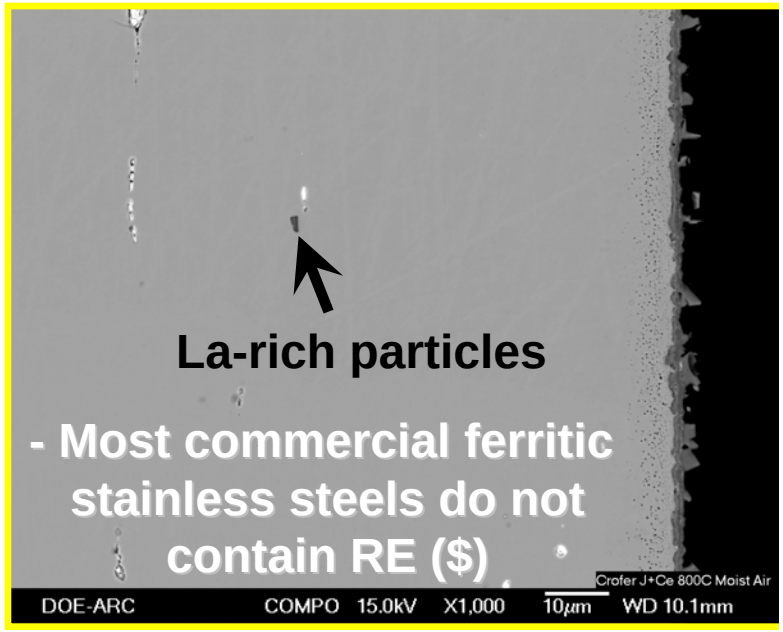
Reactive Element (RE) Effect

- **Well known that the addition of small amounts of RE (Ce, La, Y, etc) improves oxidation resistance**
- **Characteristics**
  - Reduction in the oxidation rate
    - Change in scale growth mechanisms
      - cation transport → anion transport
    - Modification of scale microstructure
      - large columnar grains → small equiaxial grains
  - Stabilize Cr_2O_3 scales at lower Cr levels
  - Improvement in scale adhesion

Alloy	*Fe*	*Cr*	*Mn*	*Si*	*Ti*	*Al*	*La*
Crofer 22APU	Bal	22.0	0.5	--	0.08	--	0.06 La
ZMG232	Bal	22.0	minor: Mn, Ni, Zr, La				

RE Additions

- **Melt addition**
  - + Elements added during ingot production (single manufacturing step)
  - – Difficulty in melting (react with crucibles)
  - – Surface concentration limited by solubility and diffusivity

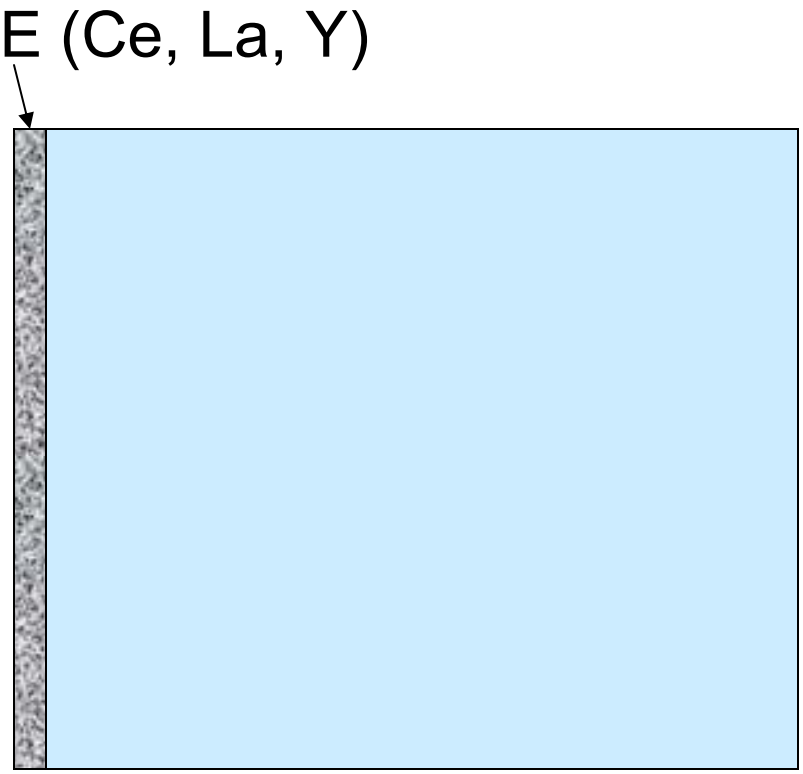


- **Surface treatments**
  - + Rare Earth concentrated where needed (at surface)
  - + Applied to any alloy
  - – ($) “Extra” manufacturing step.
  - ? Long term effectiveness (as with any coating or surface treatment)

RE Treatment

RE Added to the Metal Surface Prior to Testing

Modified Pack Cementation (NETL-RE[1])

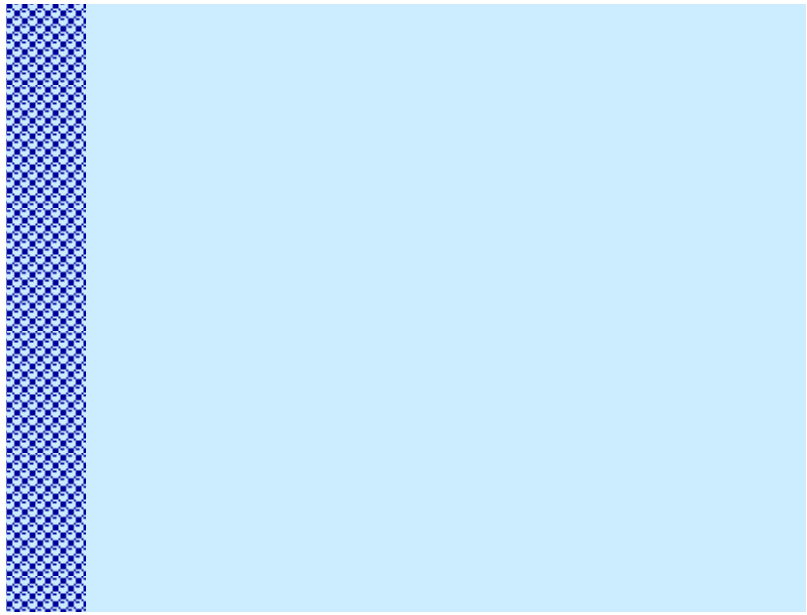


[1] Patent Applied for.

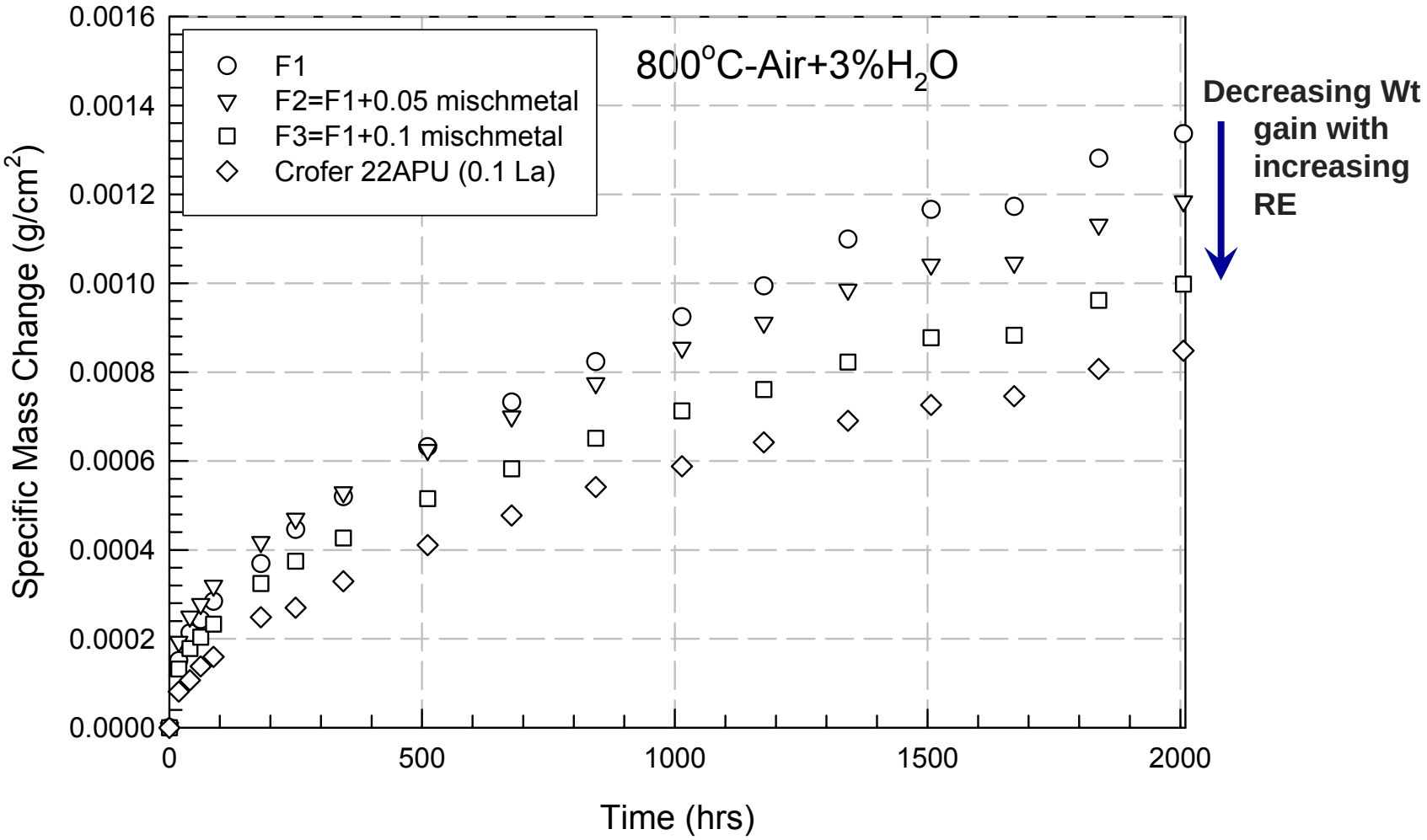
RE is Incorporated into the Outer Surface Creating a Slow Growing Oxide Scale

Oxide scale incorporating RE surface addition

(not a coating but a “treatment”)

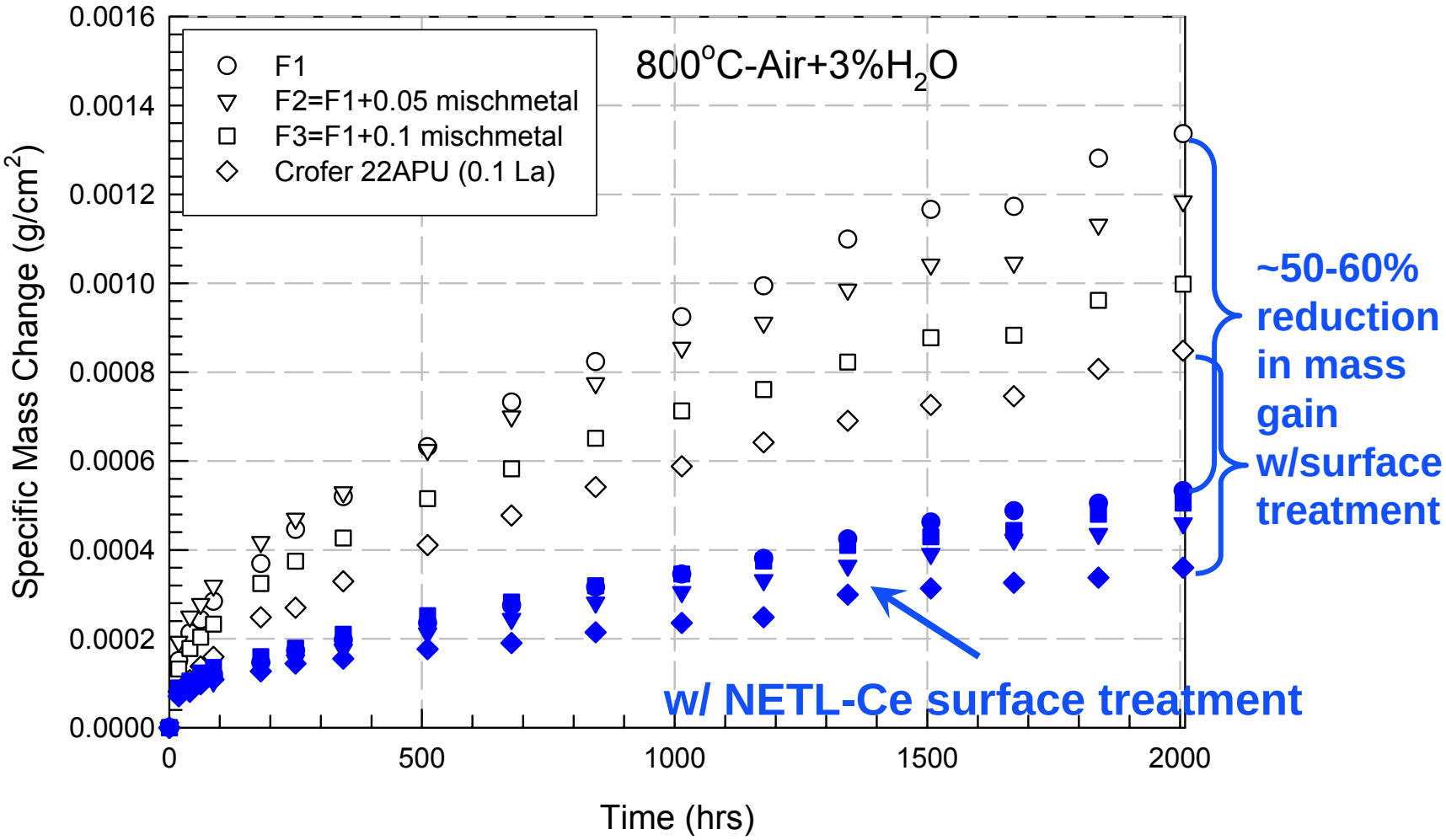


Effect of RE on Oxidation



F1=Fe-22Cr-0.5Mn-0.1Ti Mischmetal is a combination of Ce, La and other RE

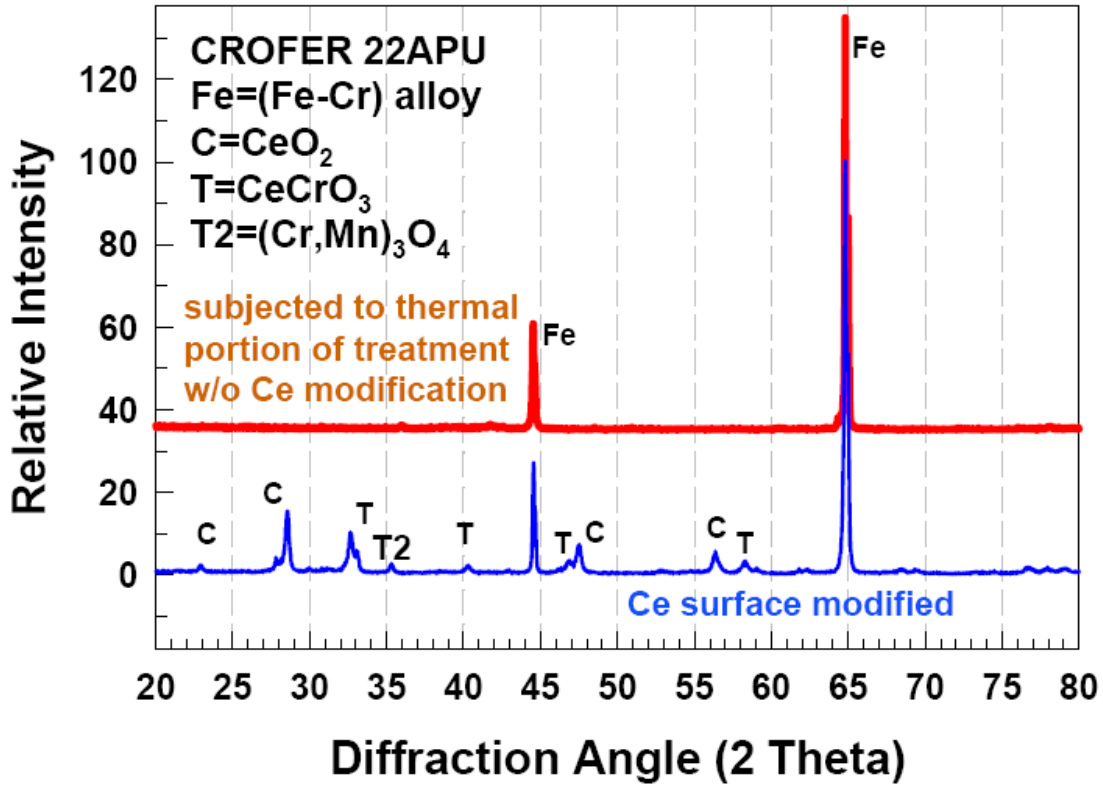
Effect of RE on Oxidation



F1=Fe-22Cr-0.5Mn-0.1Ti Mischmetal is a combination of Ce, La and other RE

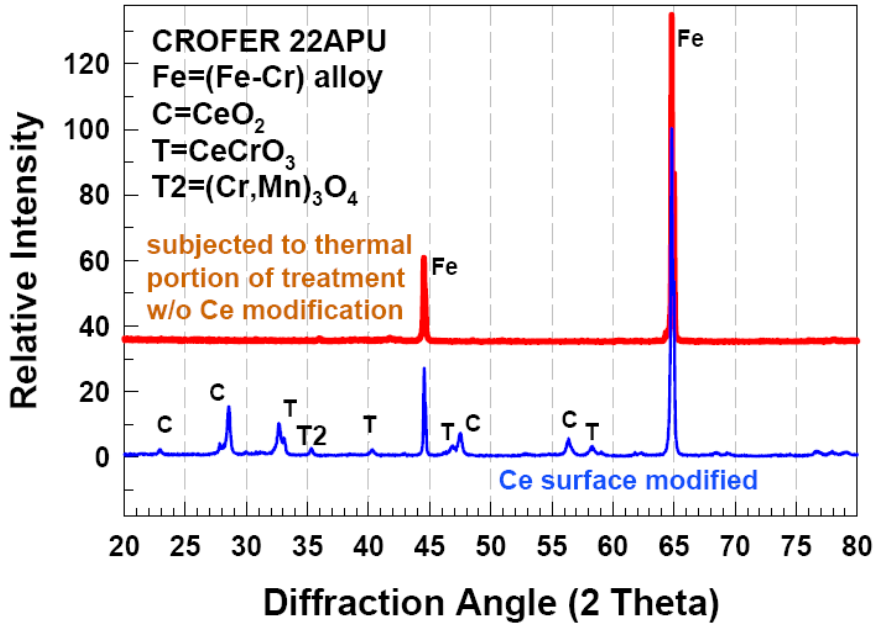
Post Surface Treatment/Prior to Testing (CeO_2-NETL)

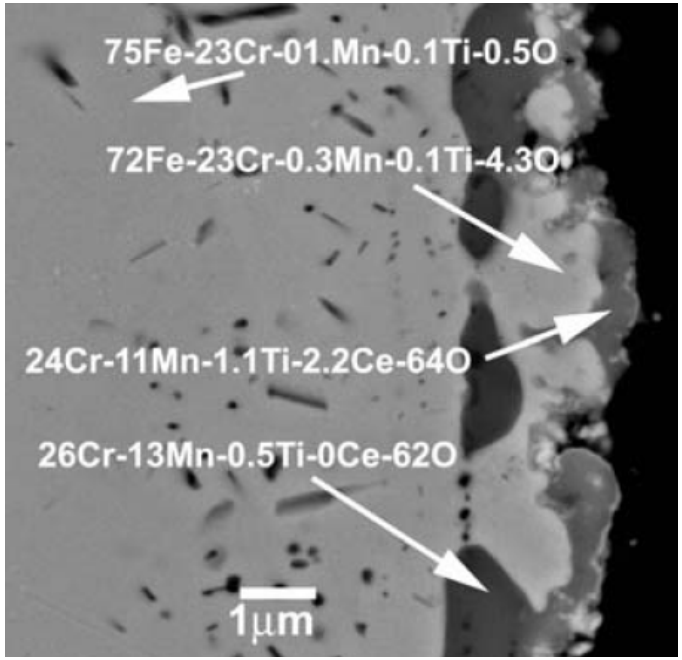
- The surface treatment pre-oxides the surface.



Post Surface Treatment/Prior to Testing (CeO_2-NETL)

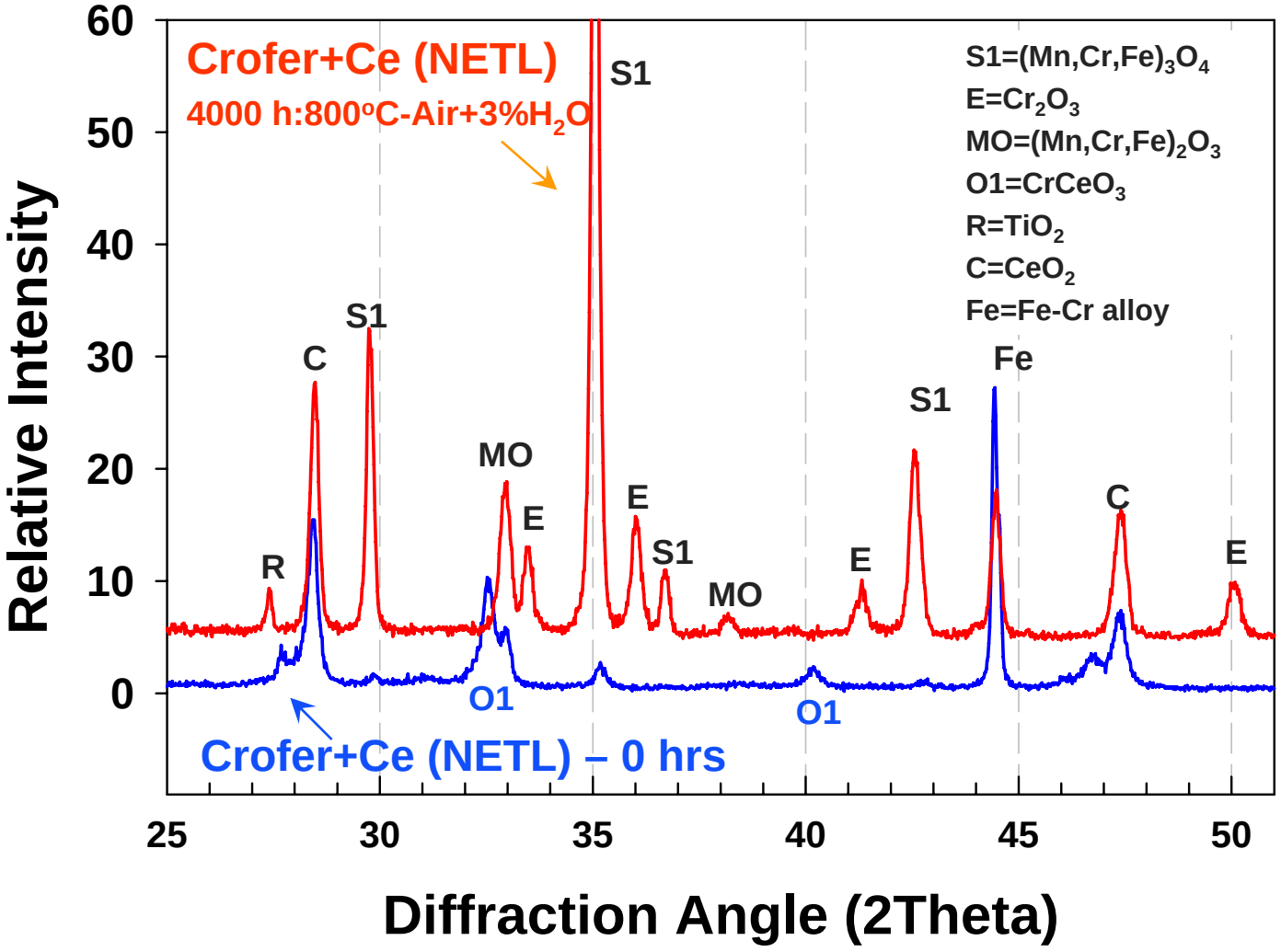
- The surface treatment pre-oxides the surface. Ce-rich oxide forms at the gas-substrate surface. A Cr-Mn oxide forms underneath the Ce-rich oxide.



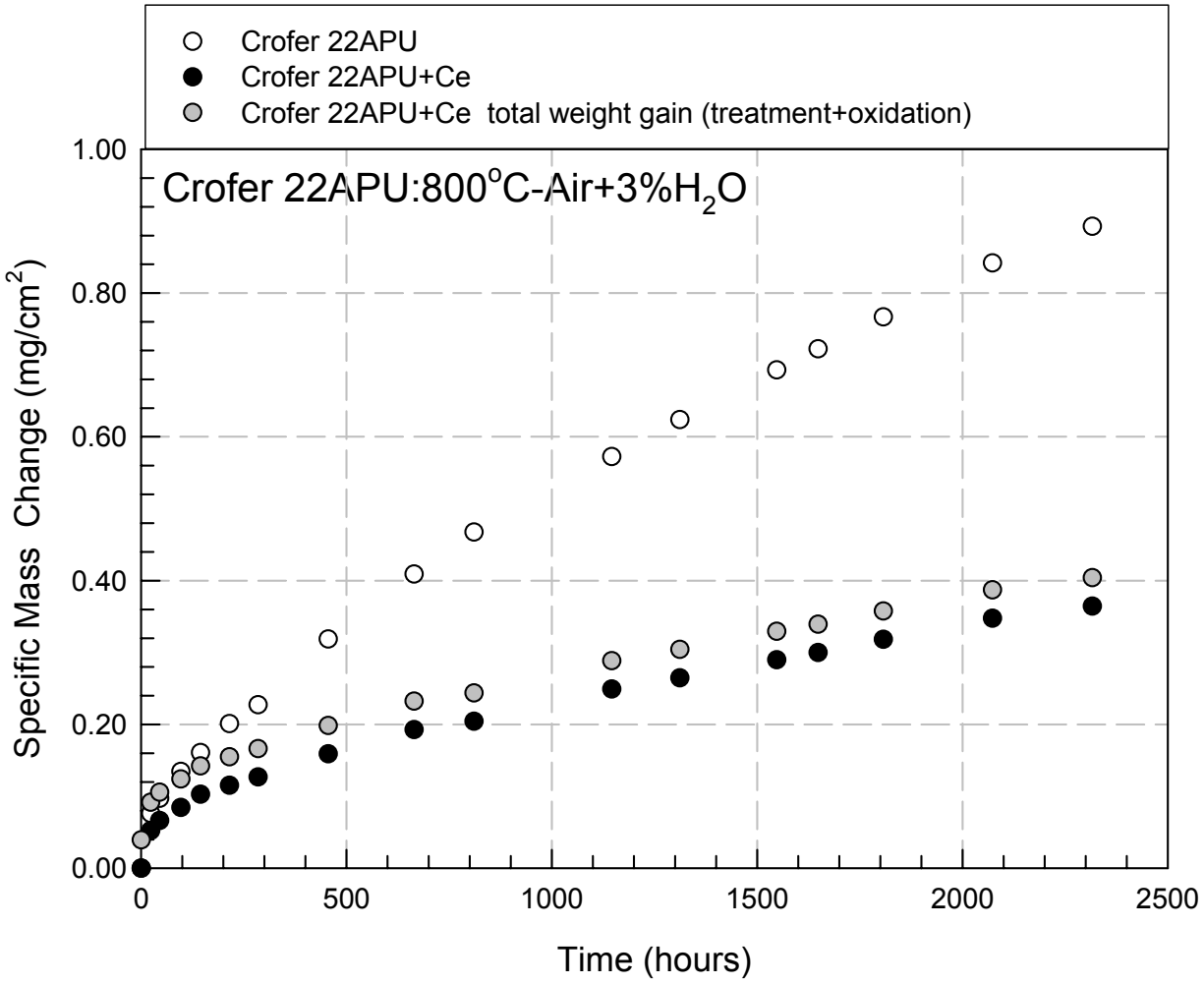


Crofer+Ce (NETL)

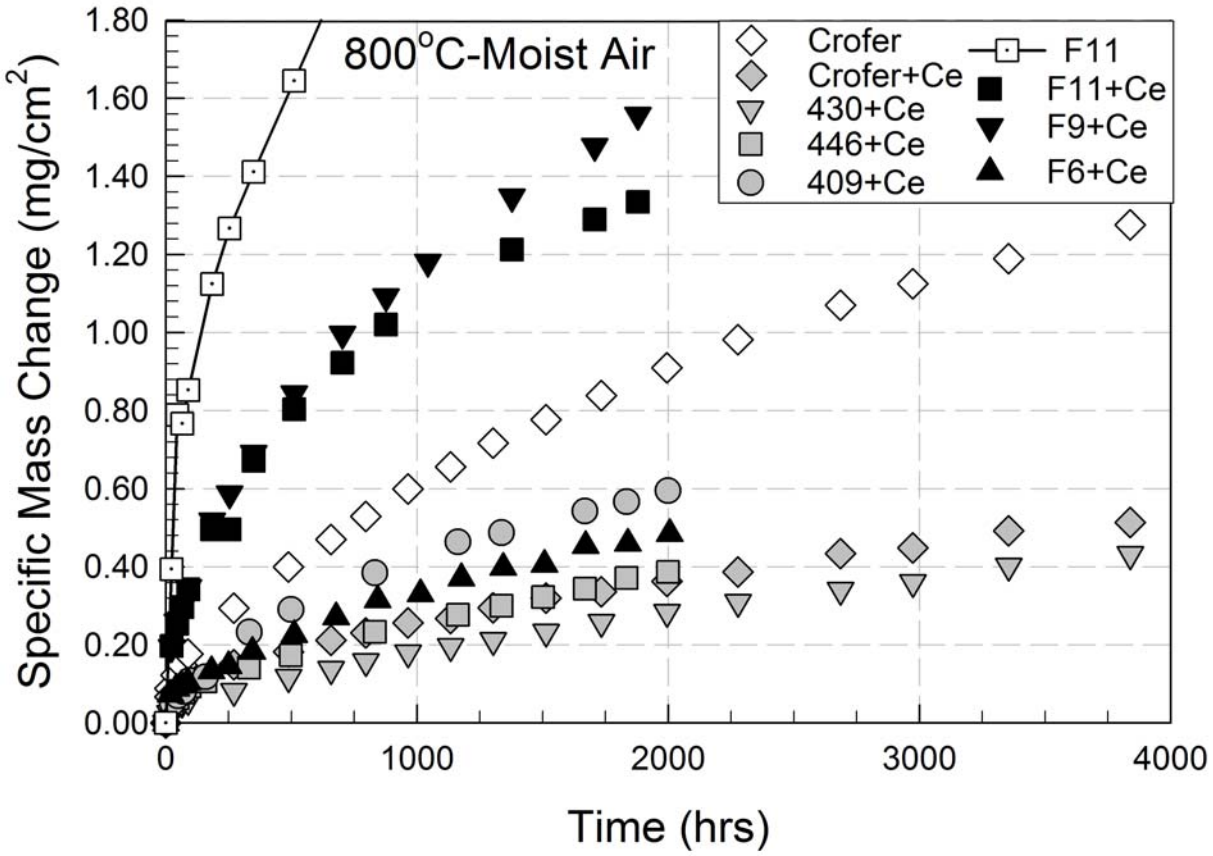
Oxide Scale Formation



Total Oxidation NETL Ce-Surface Treatment



NETL Ce Surface Treatment Applied to Commercial and Experimental Ferritic Alloys

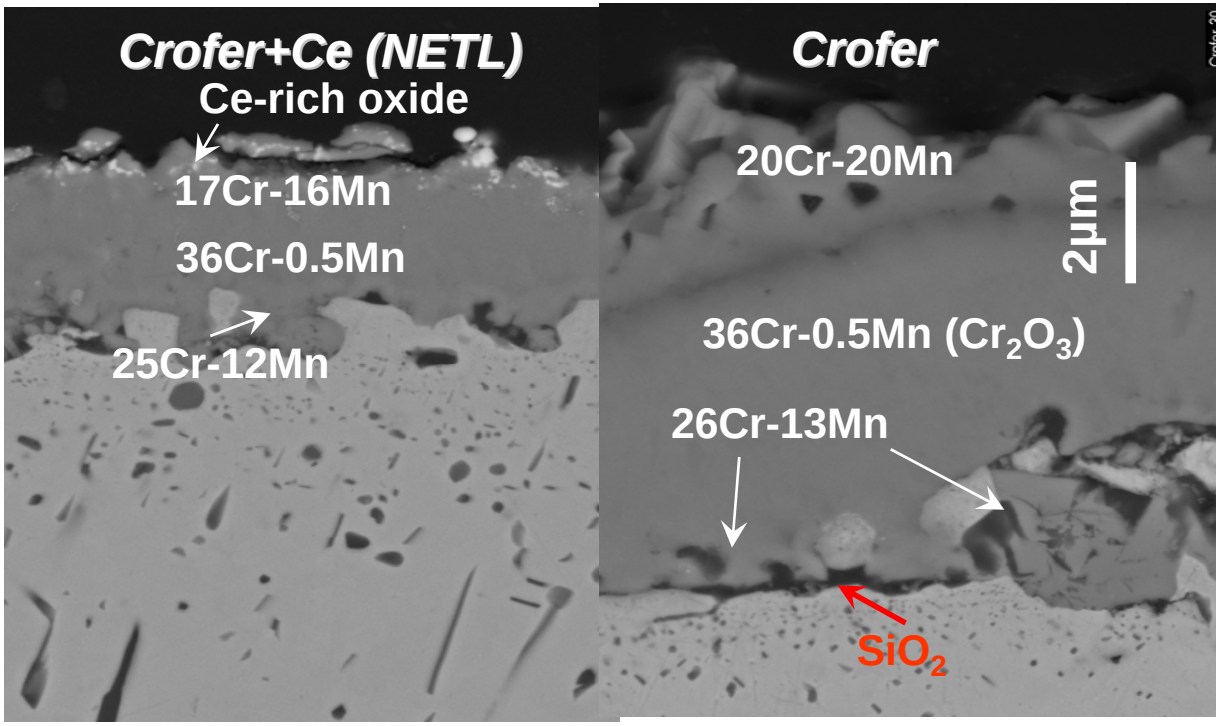


	Crofer	409	430	446	F6	F9	F11
Cr	22	12	17	26	22	12	22
Si (Ti)	(0.1)	0.5	0.5	0.5	(0.3)	(1)	(1)

Influence of Surface Treatment on Oxidation

800°C-2000h-Air+3%H_2O

thinner oxide scales with surface treatment



Detailed scale microstructures can be found in D.E. Alman and P.D. Jablonski, "Effect of Minor Elements and a Cerium Surface Treatment on the Oxidation Behavior of an Fe-22Cr-0.5Mn (Crofer 22APU) Ferritic Stainless Steel, *International Journal of Hydrogen Energy*, accepted for publication (2006), currently available on line at www.sciencedirect.com.

NETL Ce Surface Treatment

- **Slows scale growth**
- **Minimizes internal oxidation.**
  - Indicates slow oxygen diffusion through the scale.
- **Ce at surface modifies initial stages of transient oxidation → alters the subsequent growth of the scale→ enhanced oxidation resistance.**
  - formation of $CeCrO_3$ – type oxide during transient oxidation.
  - Nucleates M_3O_4 phase during NETL Ce treatment
- **Why slower scale growth?**
  - Scale microstructure is changed
    - (high diffusivity columnar to low diffusivity equiaxed)
  - Ce in oxide changes diffusion through oxide.

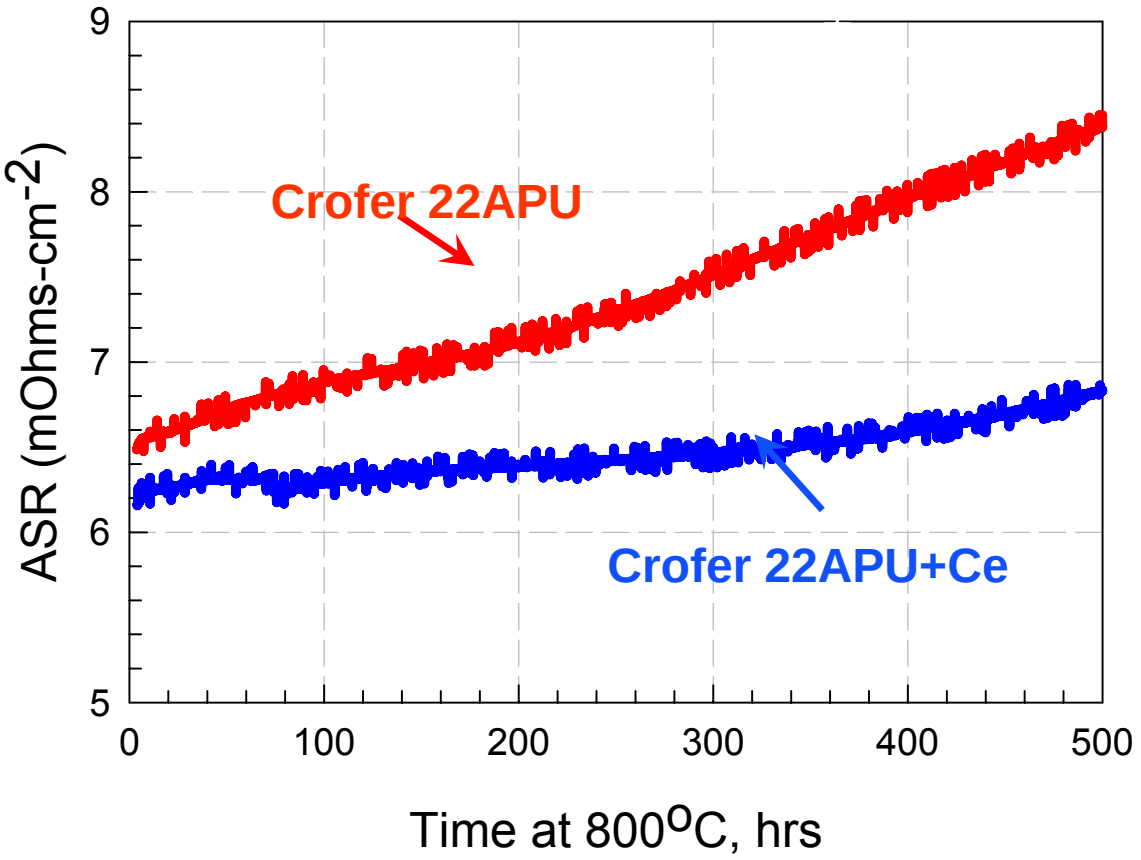
Application of NETL Ce Surface Treatment to SOFC Interconnect

- ASR Test Results
- Button Cell Test Results

Electrical Performance

Lower ASR ✓for SOFC interconnect

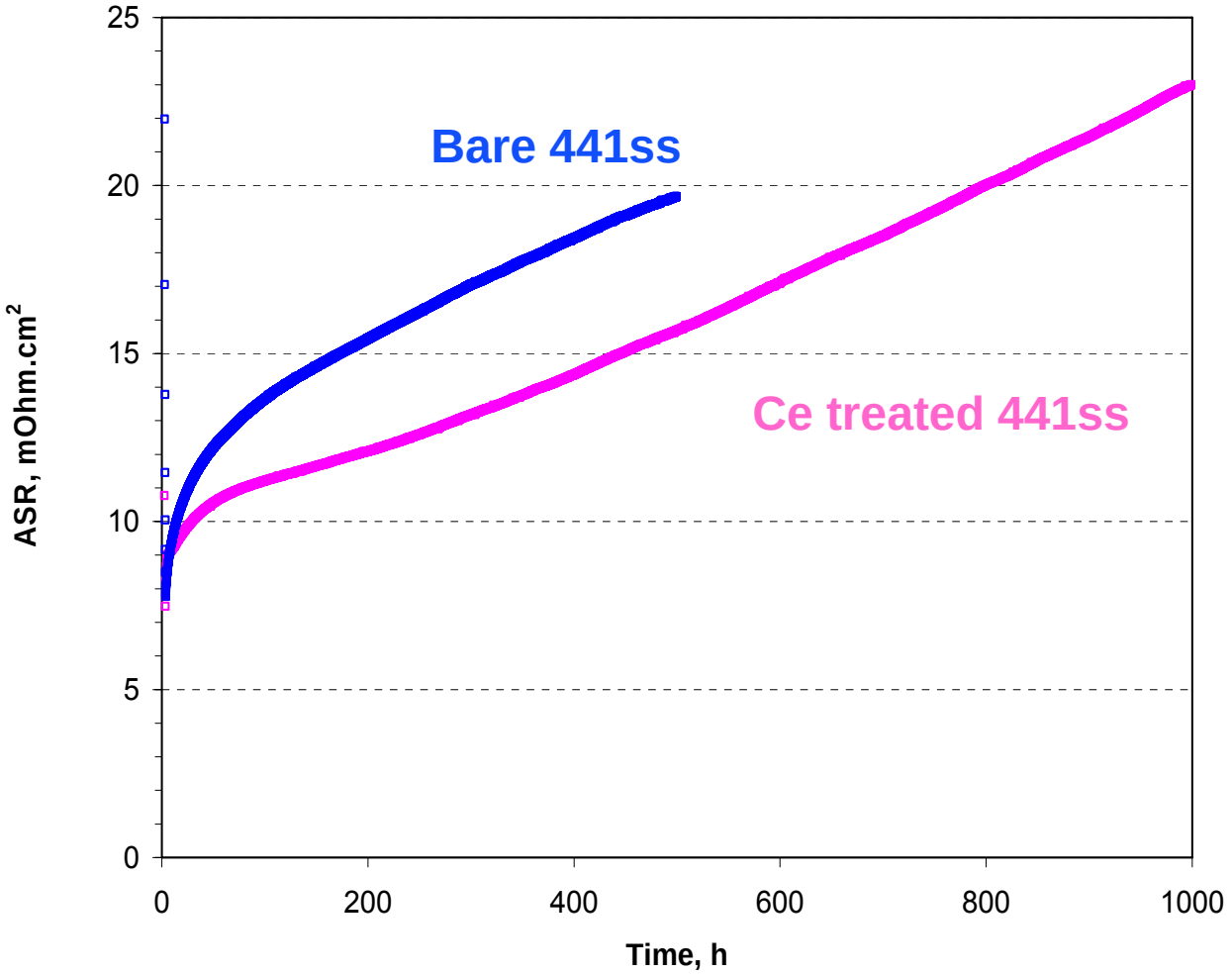
Measurements made by G. Xia & Z.G.Yang, PNNL



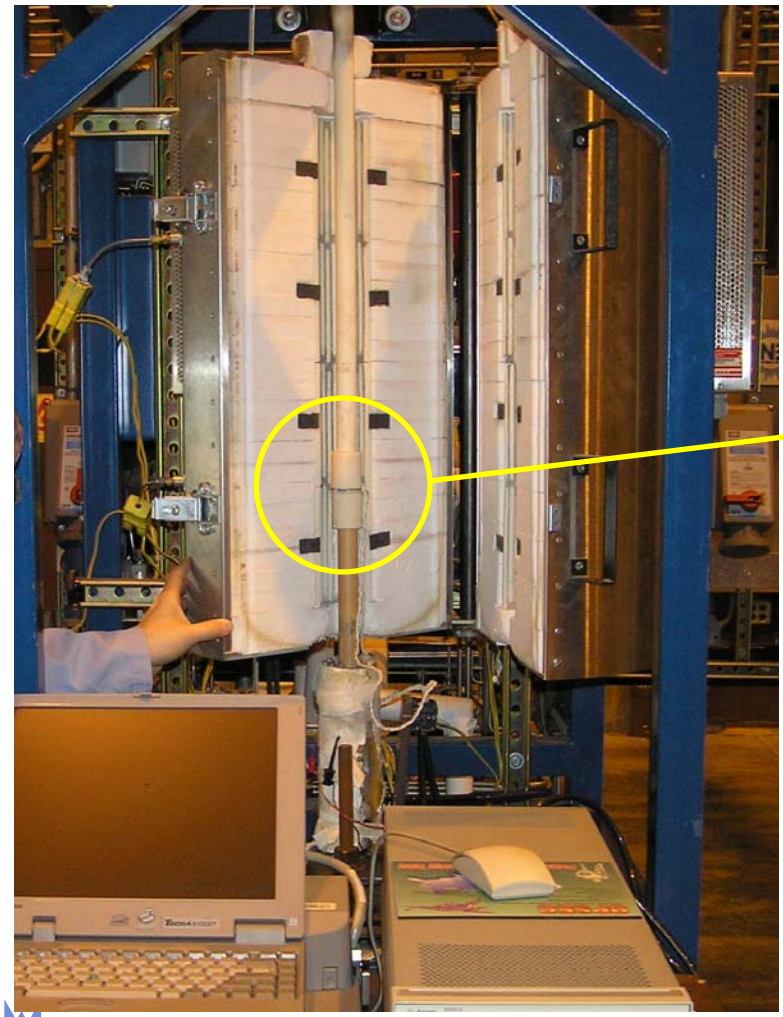
Samples pre-oxidized at 800ºC for 100 hours prior to testing

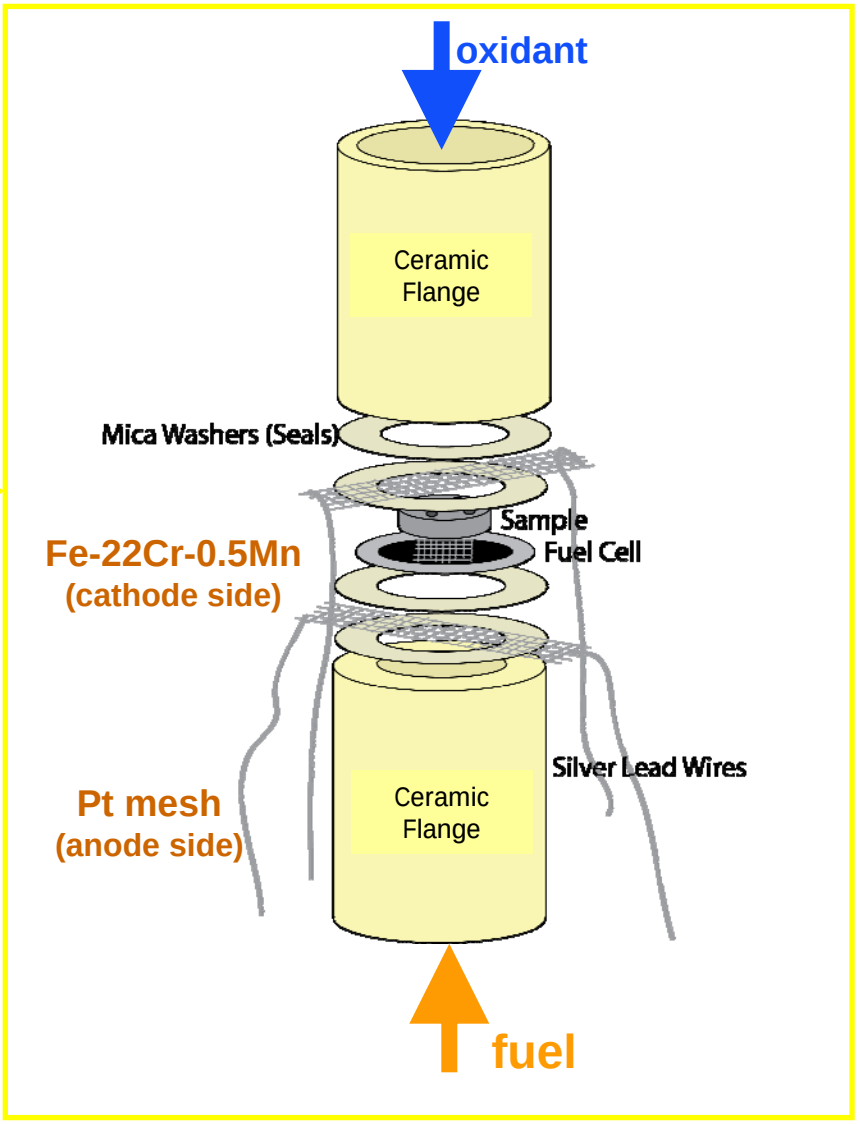
Electrical Performance

ASR Measurements performed by PNNL (Z.G. Yang)
800°C, air; LSM cathode//LSM contact//interconnect



SOFC TEST APPARATUS





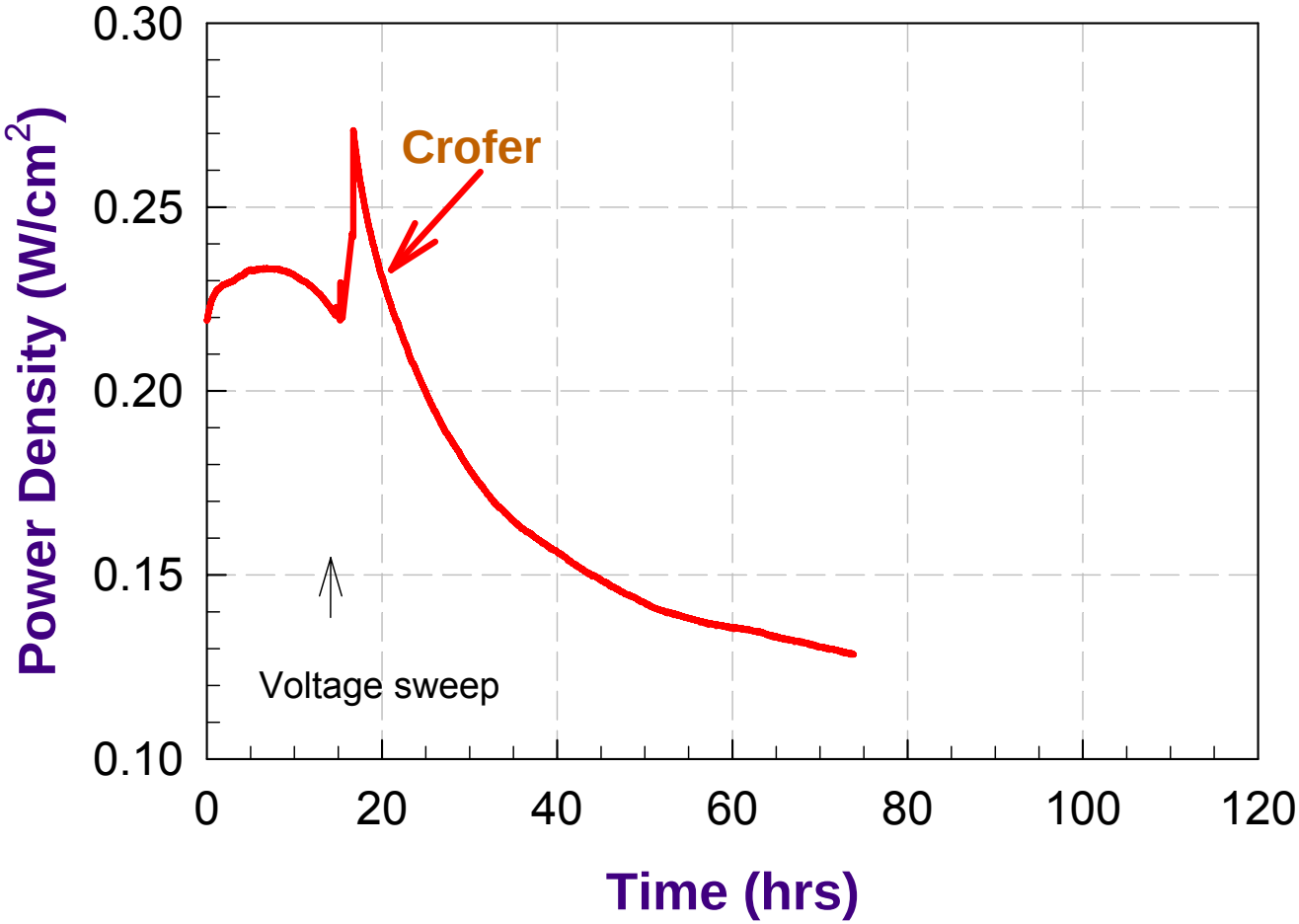
LABORATORY SCALE SOFC TESTING: OPERATING CONDITIONS

- **Heated to 800°C (2hrs)**
  - N_2 on anode side: air+3%H_2O on cathode side
- **800°C (2hrs)**
  - 10%H_2/90%N_2 mixture on anode side
- **Cell Operation**
  - Fuel: 97% H_2/3%H_2O at 400 cm^3/min
  - Oxidant: air+3%H_2O at 1000 cm^3/min
  - Constant voltage: 0.7V
  - Periodic voltage sweeps: 1.1V to 0.V
- **Cathode Current Collector Surface Condition**
  - Untreated condition: polished (1 μm diamond)
  - Ce-treated condition: cleaned with scotch-brite® pad in water

CELL PERFORMANCE

0.7V/800°C; Fuel: H_2+3%H_2O; Oxidant: Air +3% H_2O

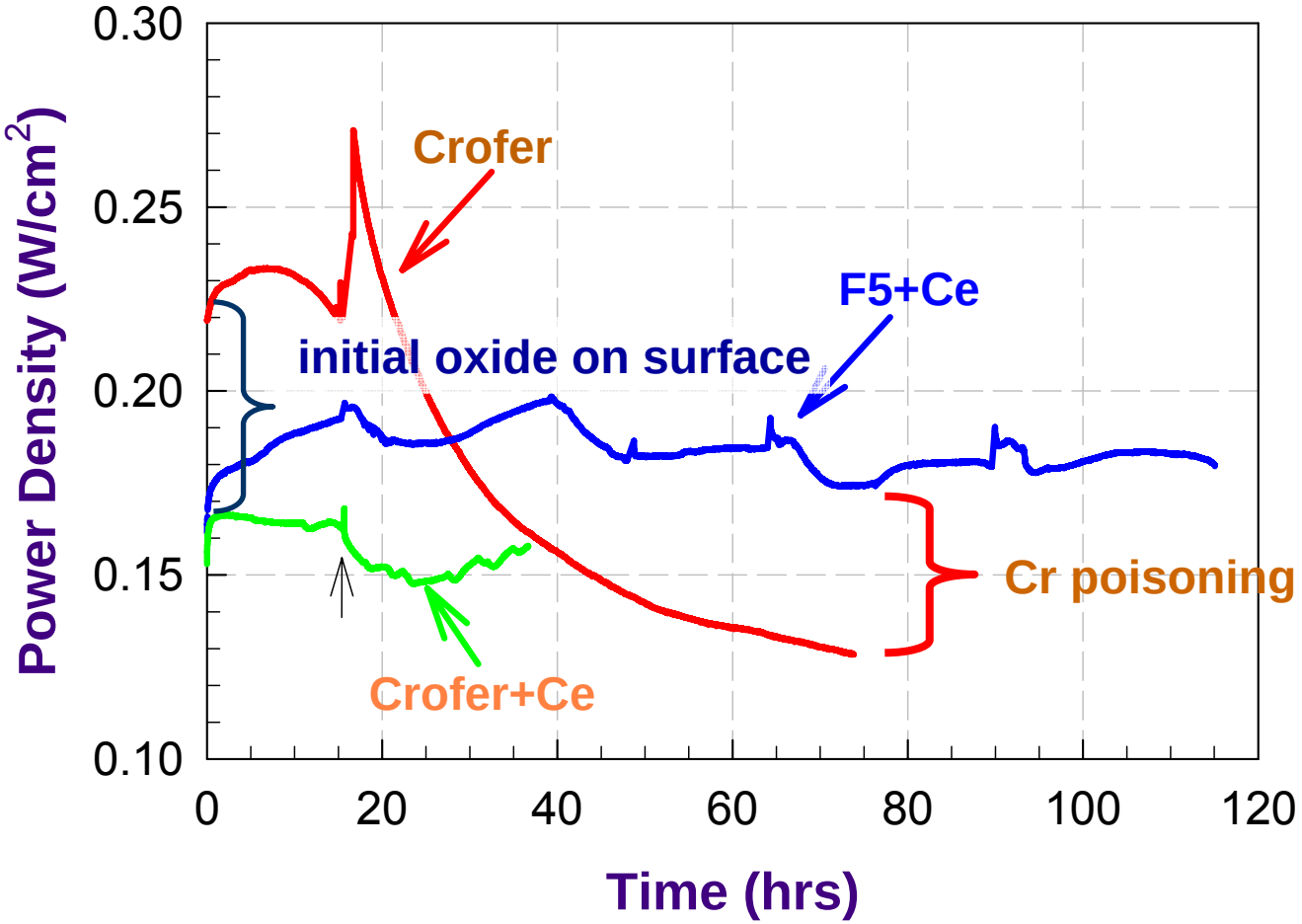
LSM Cathode/Fe-22Cr-0.5Mn Interconnect



CELL PERFORMANCE

0.7V/800°C; Fuel: H_2+3%H_2O; Oxidant: Air +3% H_2O

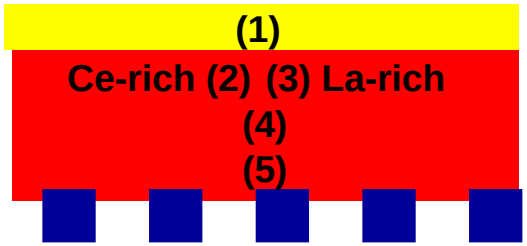
LSM Cathode/Fe-22Cr-0.5Mn Interconnect



ANALYSIS OF Cr IN CATHODE

Cr composition by WDX (weight percent)

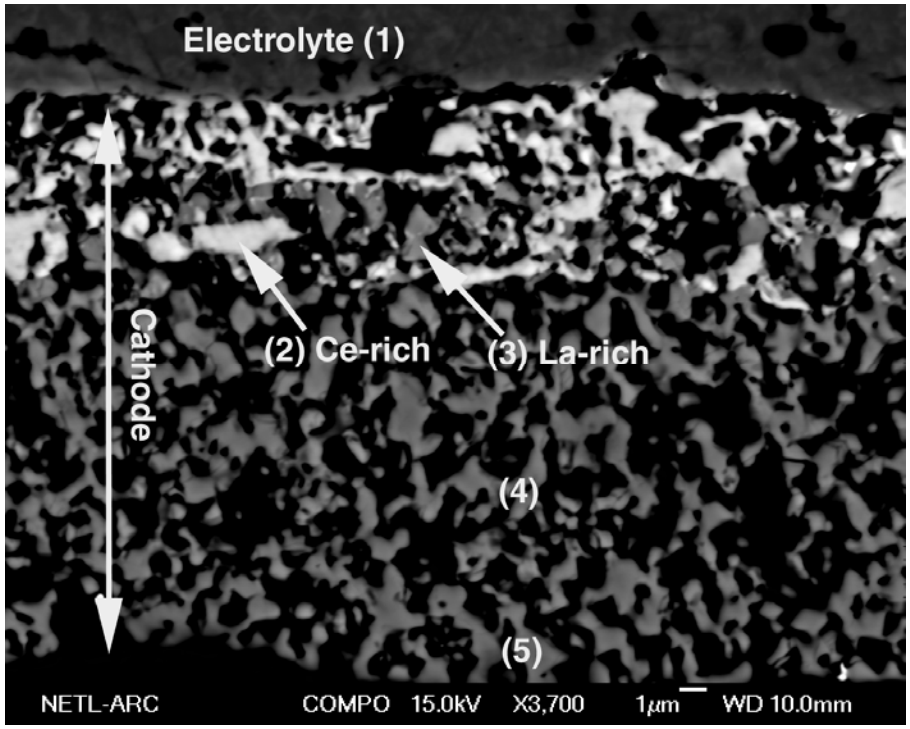
	Crofer (78 h)	F5+Ce (117 h)	Crofer+Ce (38 h)
(1)	0.00	0.00	0.00
(2)	*0.02*	*0.02*	*0.00*
(3)	*0.48*	*0.15*	*0.08*
(4)	0.08	0.08	0.11
(5)	0.09	0.09	0.08



Electrolyte

Cathode

Interconnect



Summary

- **RE surface treatment is more effective than alloy additions alone.**
- **RE surface treatments are effective in reducing oxidation rate.**
  - Applied to ferritic stainless steels for interconnect application (12-26 Cr alloys).
- **ASR measurements indicate that slower scale growth will enhance SOFC performance.**
- **Improved button cell performance with NETL Ce surface treatment.**

Acknowledgements

- Gordon Xia and Z. Gary Yang from PNNL for performing the ASR measurements.
- Chris Johnson from NETL-Morgantown for assistance with initial SOFC button cell testing.