Surface Modifications for Oxidation Resistance

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Accomplishments

- **Surface treatment developed at NETL based on CeO_2**
  - Applied to over 50 commercial and experimental alloys including; T430, T441, Crofer22APU.
  - For comparative purposes applied other RE surface treatment that are described in the literature.
  - RE Treatments are effective in enhancing oxidation resistance.
    - Initiated long term testing to determine effectiveness.
  - ASR measurements and single-cell test indicate surface treatment can enhance SOFC performance.
  - Modified NETL treatment to use La_2O_3
- **Investigated influence of Si levels on behavior of interconnect alloys**
  - Oxidation as a function of Si level in T430 (objective is to determine critical Si-level).

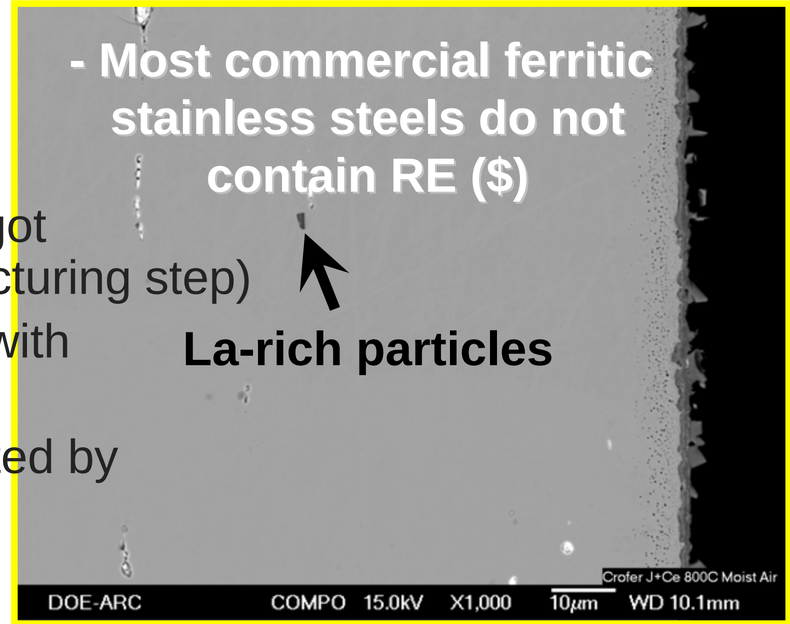
Reactive Element (RE) Effect

- **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**				

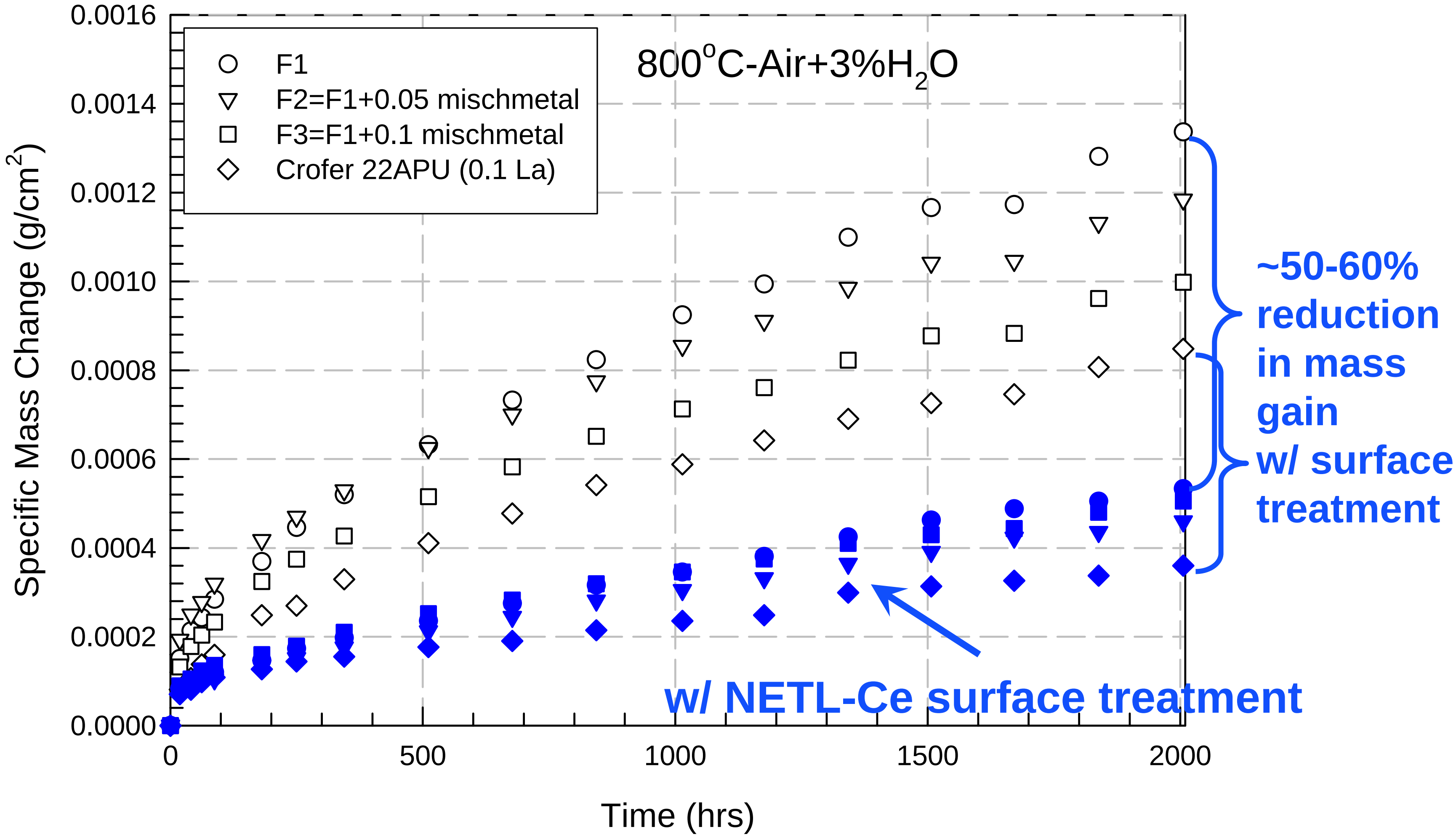
RE Surface Additions

- **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)

Effect of RE on Oxidation



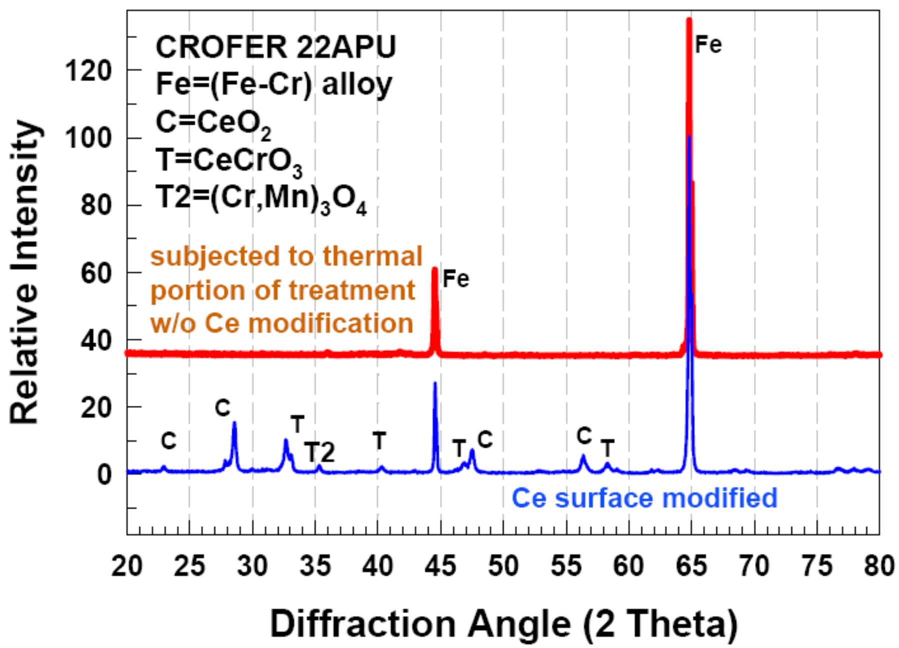
F1=Fe-22Cr-0.5Mn-0.1Ti Mischmetal is a combination of Ce, La and other RE

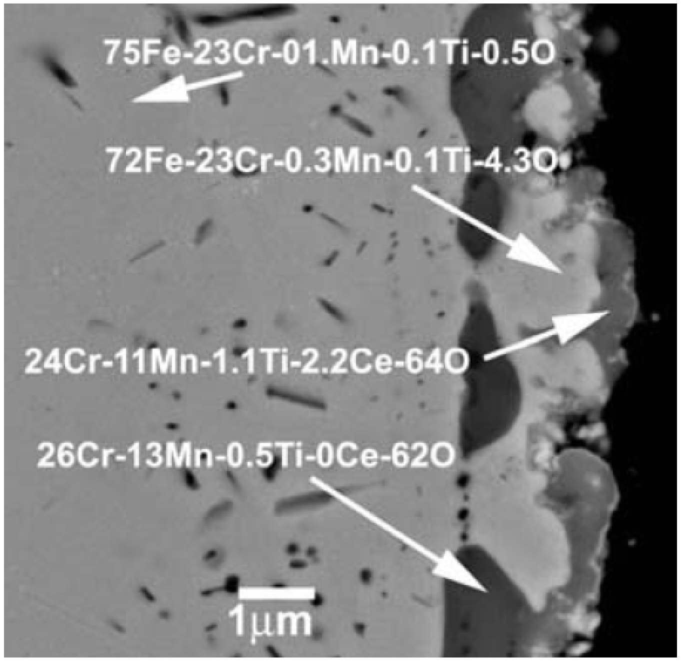
Cerium Surface Treatments

- **Developed a combination of pack cementation and superficially applied coating technique (NETL).**
  - Coat surface with a slurry mixture: **CeO_2** and halide (NaCl) activator.
  - Heat (**900ºC**) in a controlled atmosphere (x10^{-3}Torr)
  - Residual "pack" coating is washed off the surface.
- **Applied treatment described by Hou & Stringer (H/S).**
  - J. Electrochem. Soc., Vol 134, No. 7, July 1987, pp. 1836-1849.
  - Coupons heated to 200ºC were coated with a **cerium-nitrate** slurry (10w/o nitrate adjusted with HNO_3 to pH=2), followed by heating in air at **400ºC** to decompose to CeO_2.
  - Surface also cleaned in water after treatment.

Surface After Treating (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.

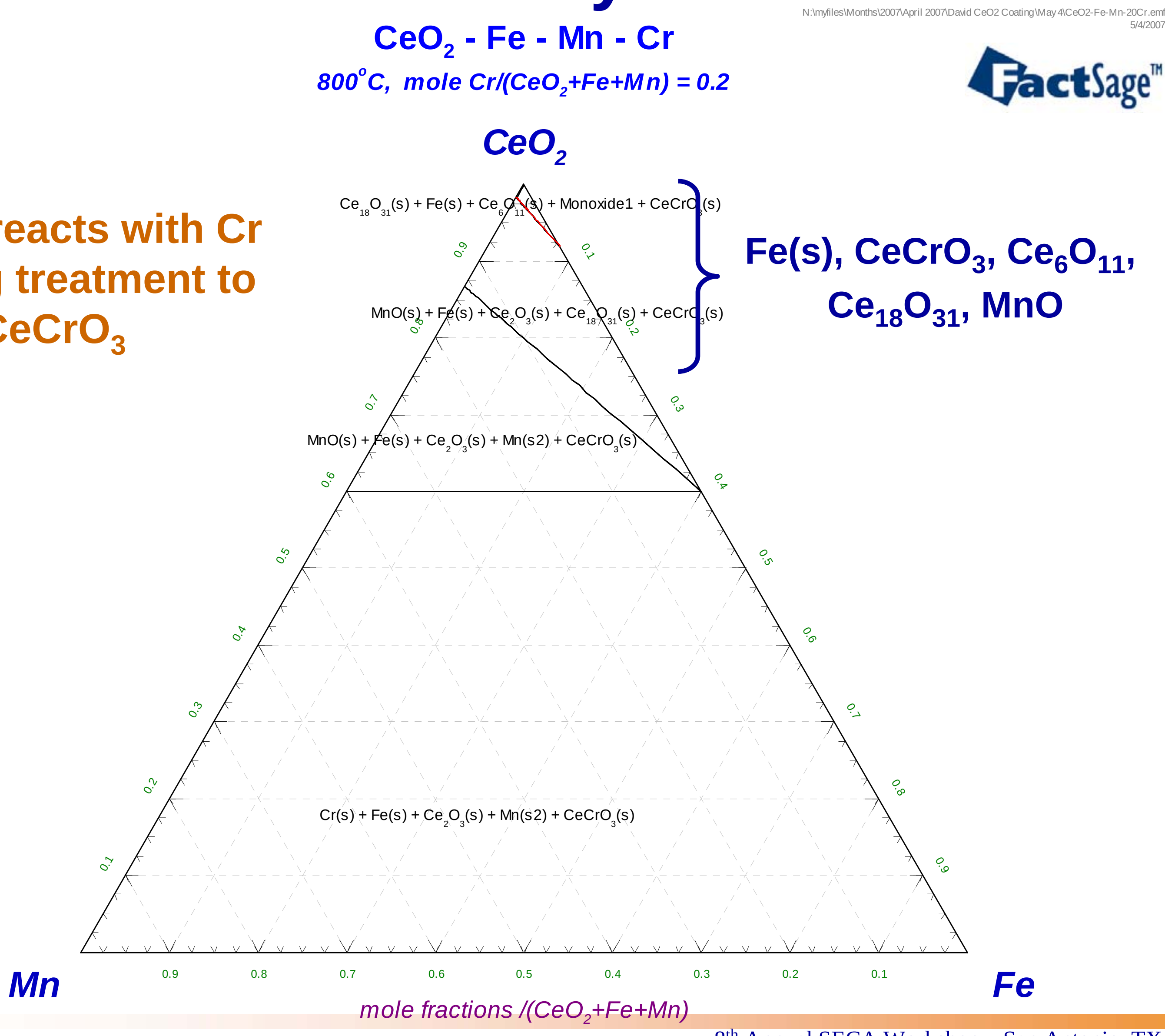




Crofer+Ce (NETL)

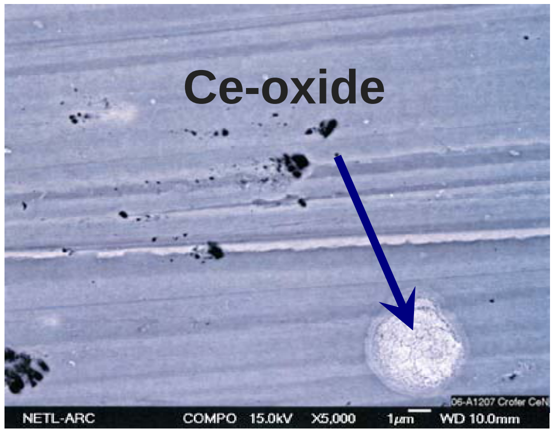
Thermodynamics

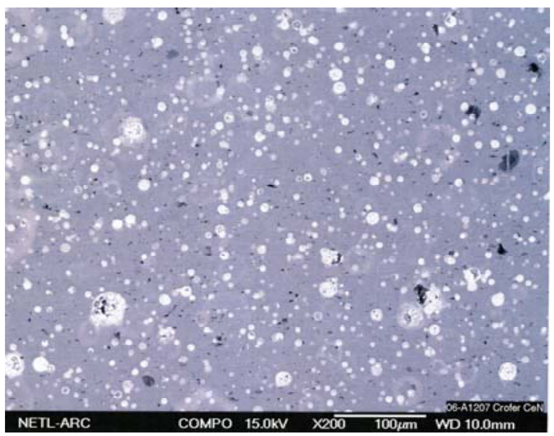
CeO_2 reacts with Cr during treatment to form $CeCrO_3$



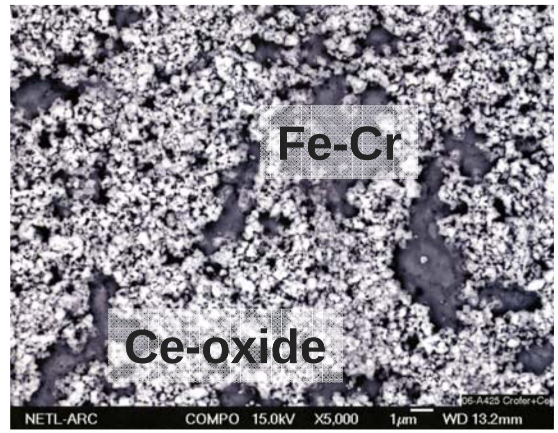
Surfaces After Treating

CeN-based (H/S: 400^oC)



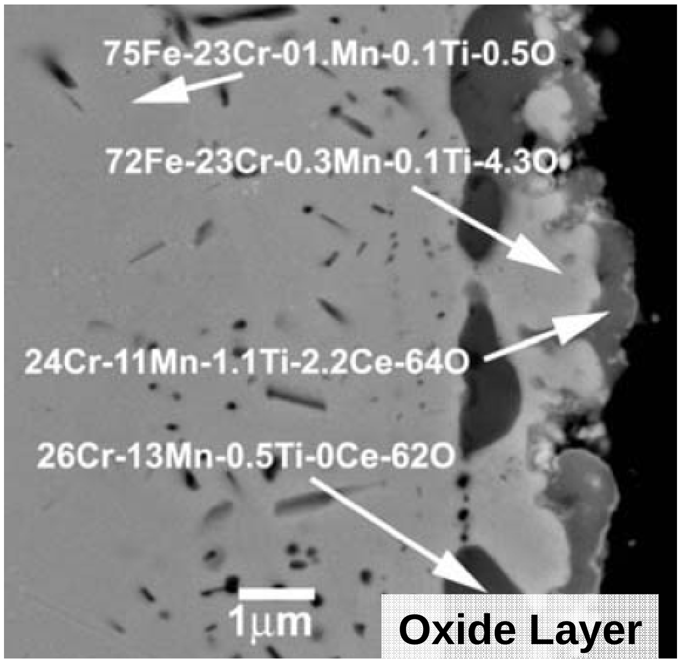


CeO_2-based (NETL:900^oC)



Surfaces After Treating (Prior to Oxidation)

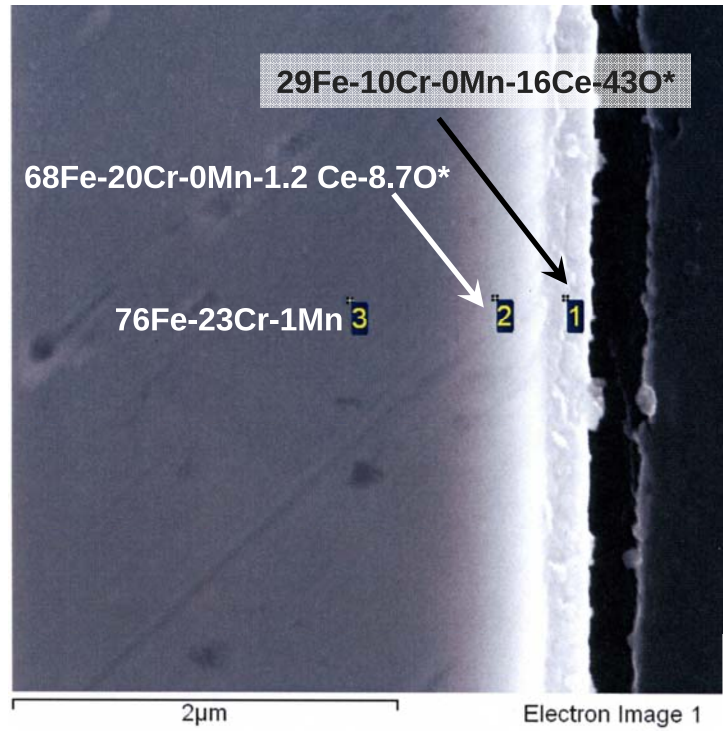
Crofer+Ce (NETL)



CeO_2-Based

Max Temp 900°C

Crofer+Ce (H/S)

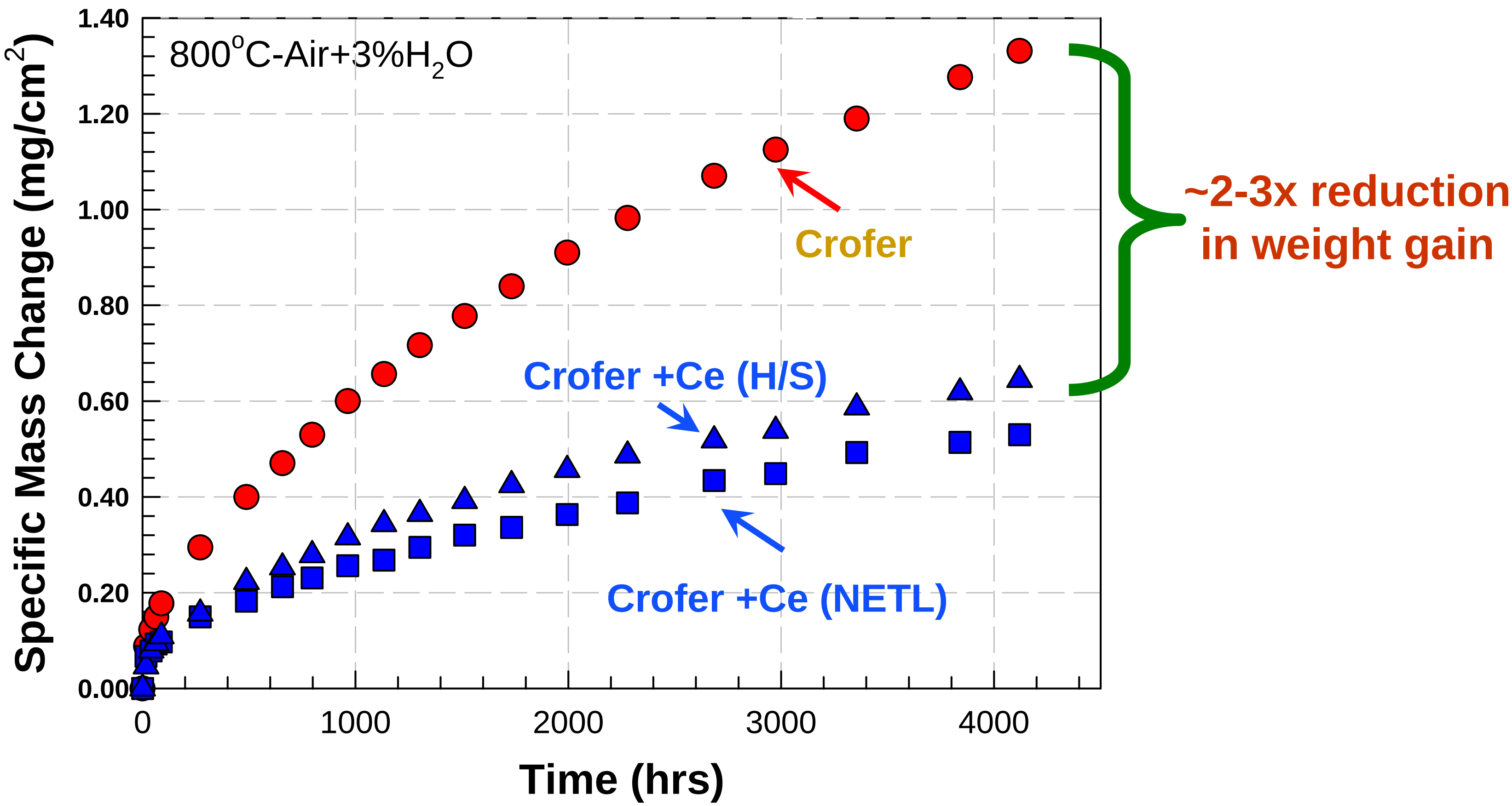


CeN -Based

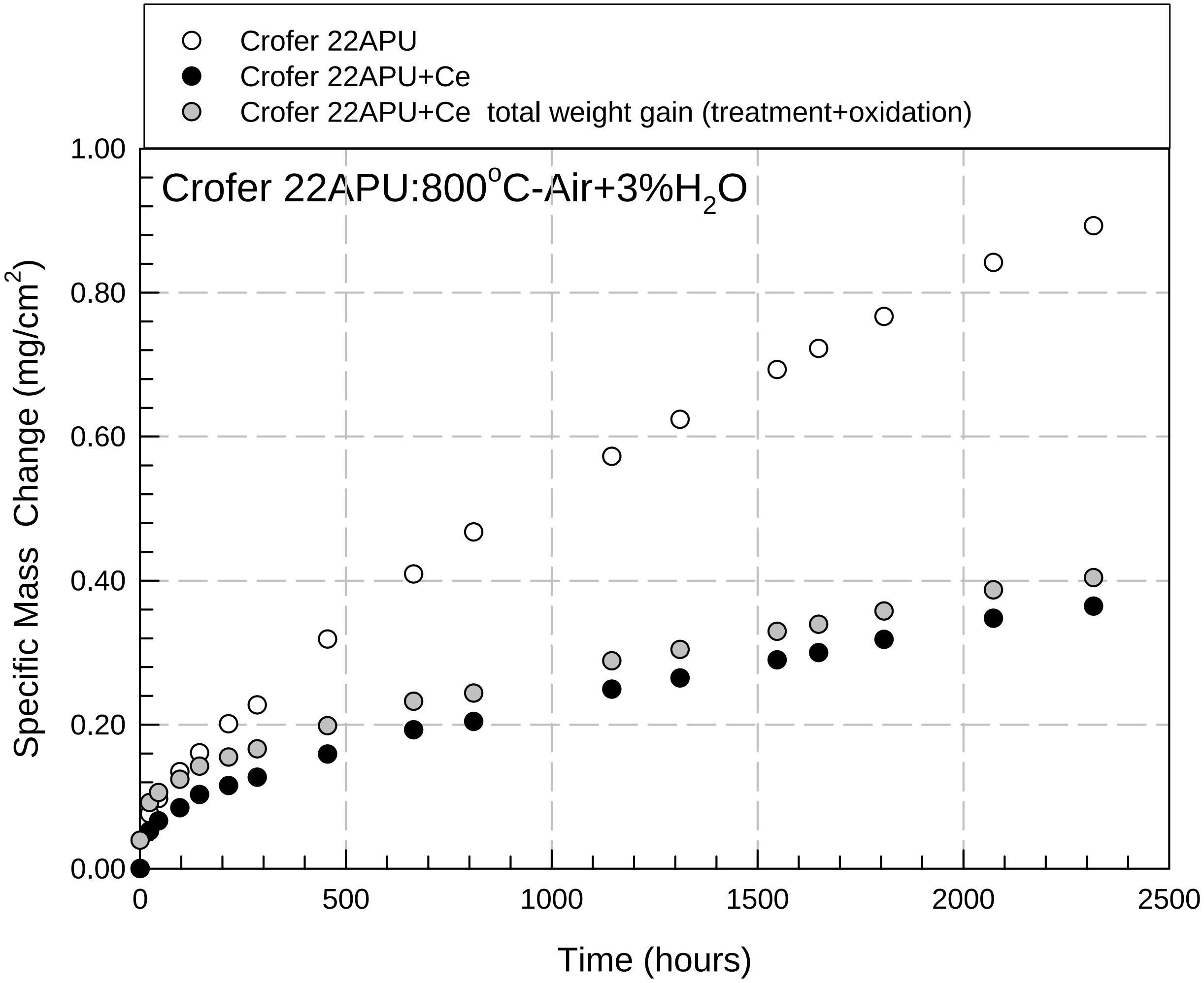
Max Temp 400°C

*not accurate due to edge effect (rounding of edge during sample preparation), however, indicates Ce is present at the surface.

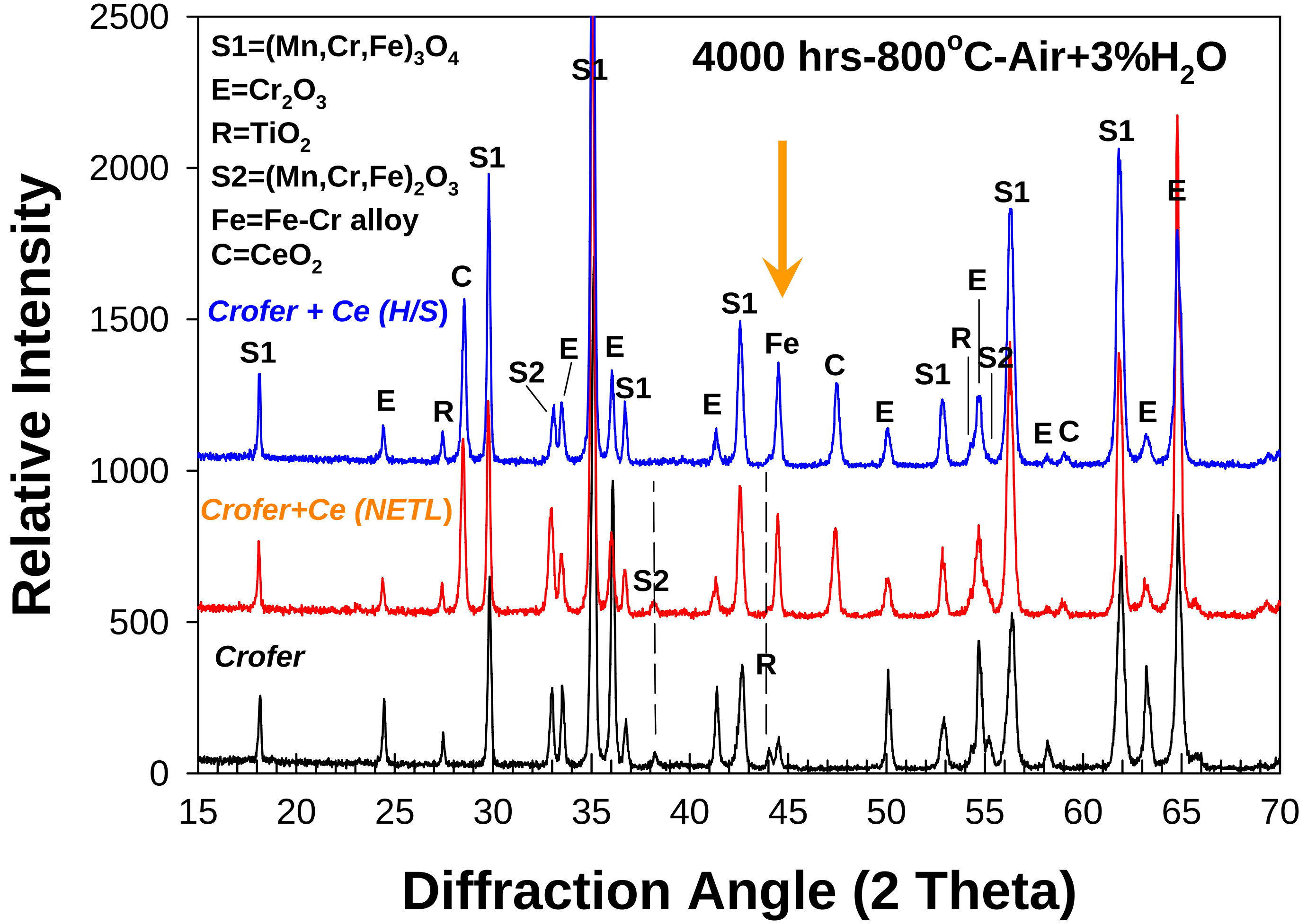
Influence of Surface Treatment on Oxidation



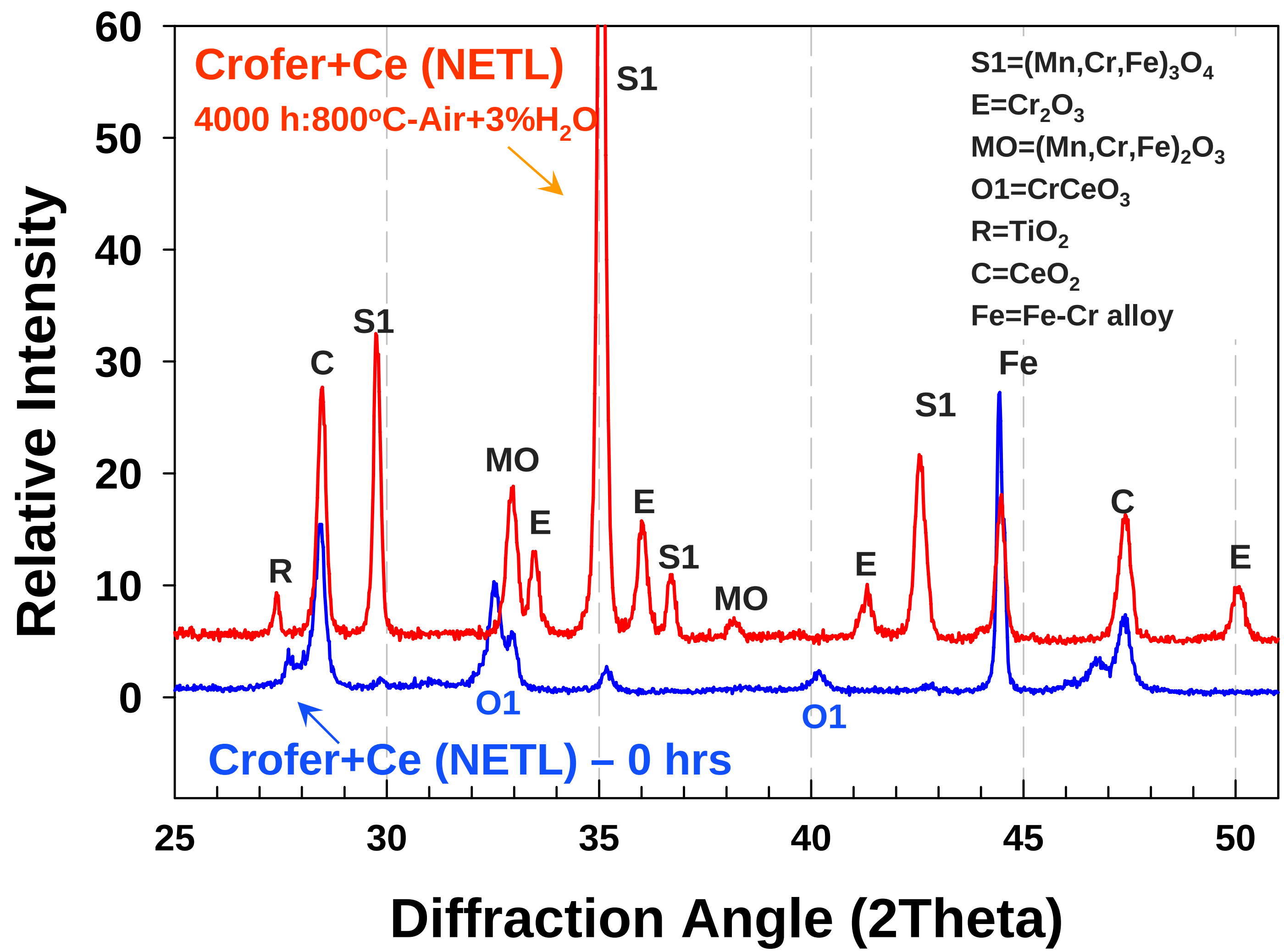
Total Oxidation NETL Ce-Surface Treatment



Influence of Surface Treatment on Oxidation



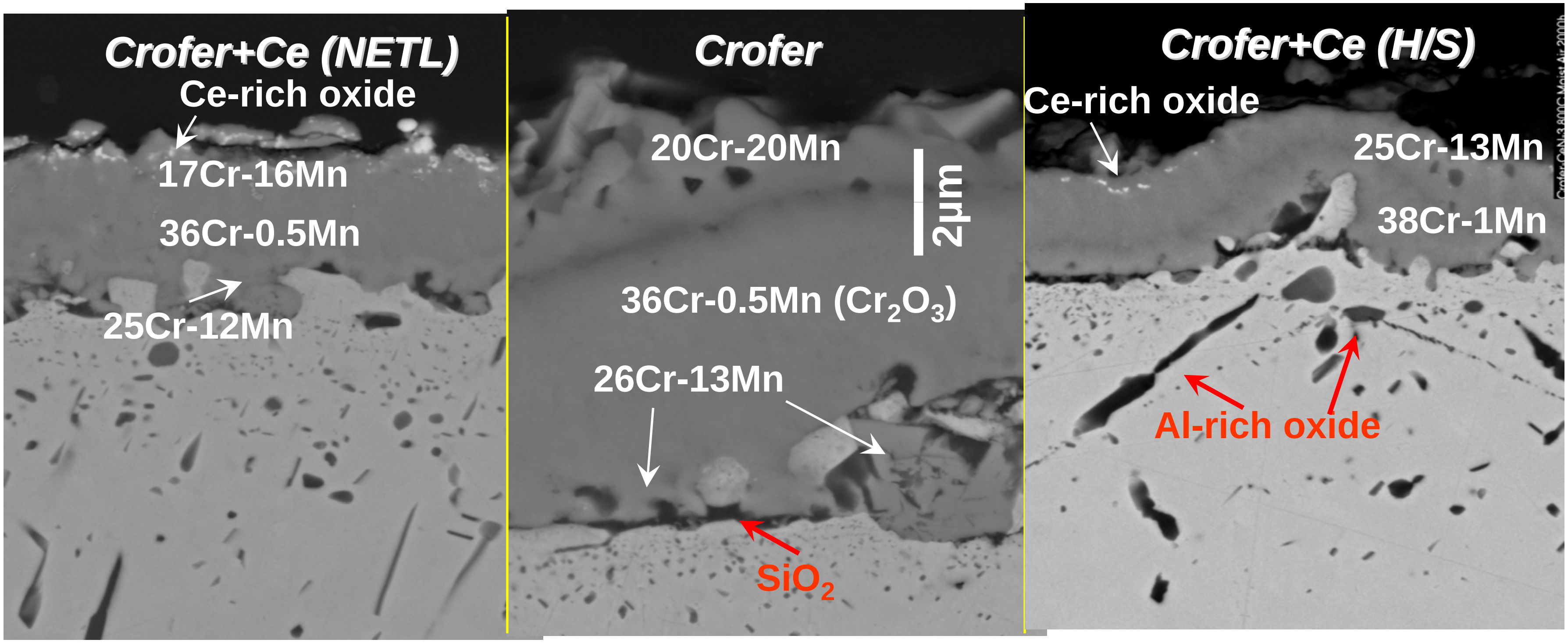
Oxide Scale Formation



Influence of Surface Treatment on Oxidation

800^{o}C-2000h-Air+3%H_2O

thinner oxide scales with surface treatments

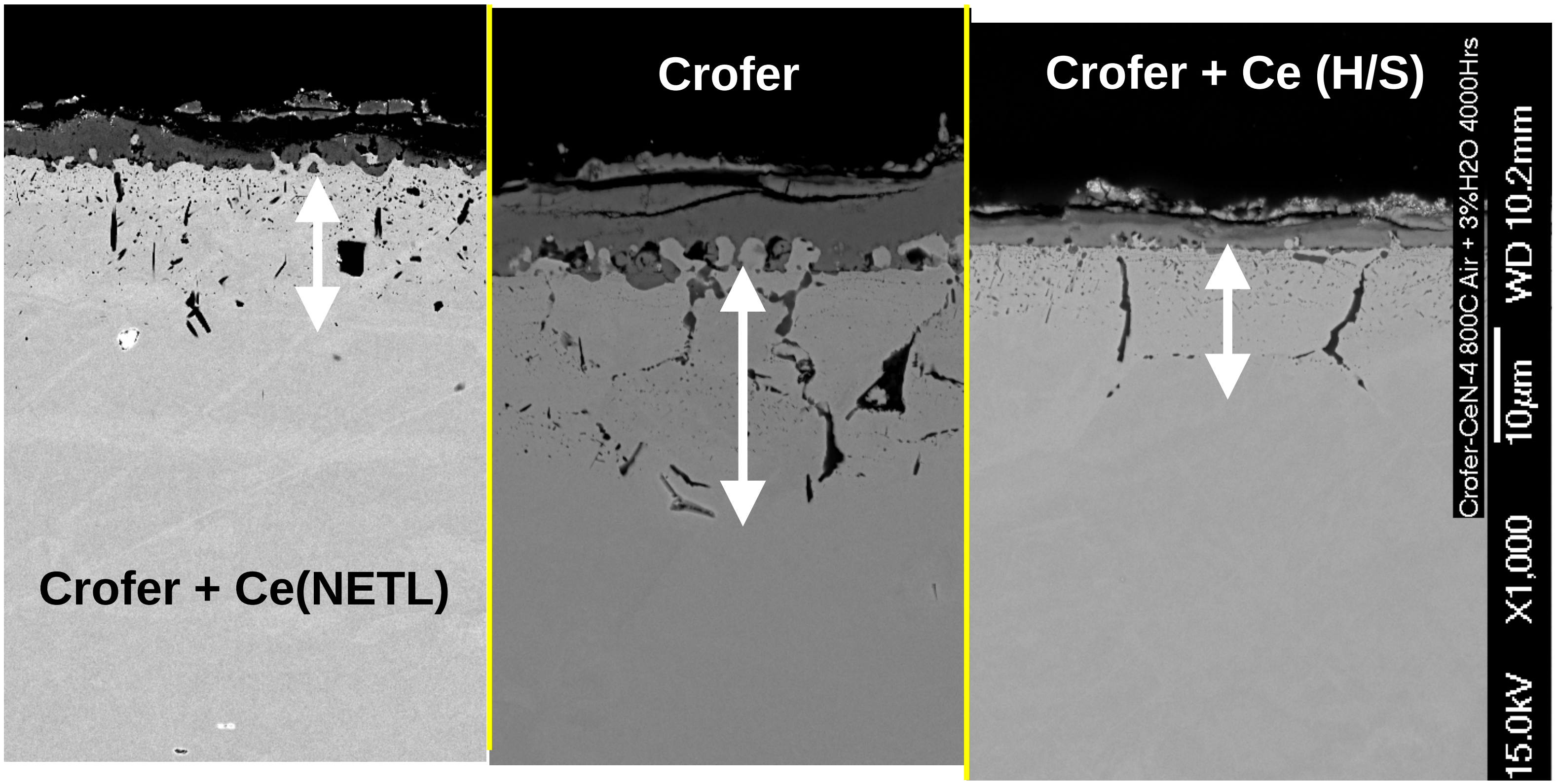


Detailed scale microstructures can be found in D.E. Alman and P.D. Jablonski, "Effect of Minor Elements and a Cerium Surface Treatment on the Oxidation Behavior of an Fe-22Cr-0.5Mn (Crofer 22APU) Ferritic Stainless Steel, *International Journal of Hydrogen Energy*, accepted for publication (2006), currently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

NETL

Influence of Surface Treatment on Oxidation

800°C-4000hrs-Air+3%H_2O

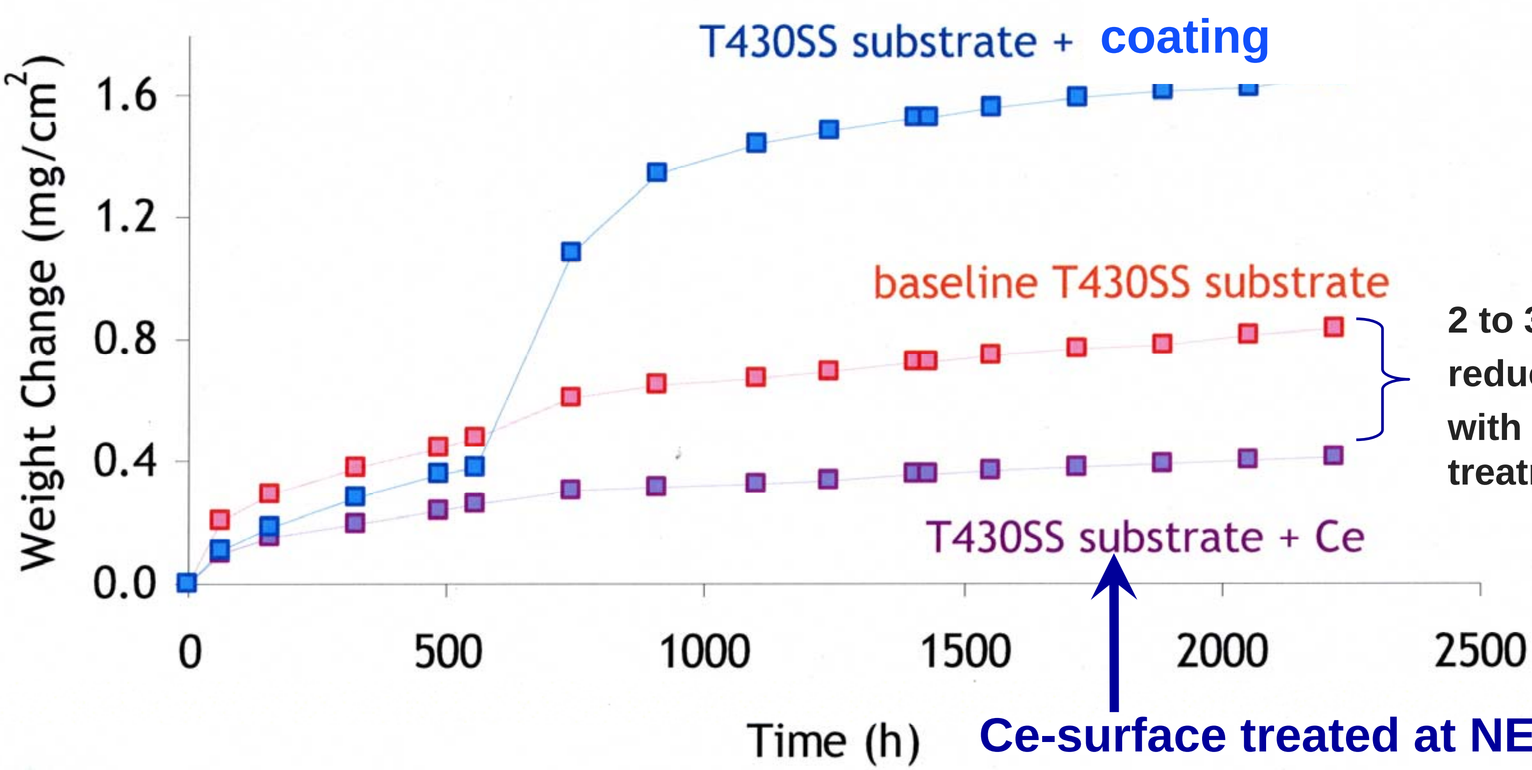


Minimize internal oxidation

Surface Treatments

- **Slows scale growth**
  - Scale microstructures were similar with NETL and H/S treatment methods.
- **Minimizes internal oxidation.**
  - Indicates slower 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.
  - Pre-oxidation during NETL treatment
    - (initial oxidation of H/S?)
- **Why?**
  - Scale microstructure is changed
    - (high diffusivity columnar to low diffusivity equiaxed)
  - Ce in oxide changes diffusion through oxide.
  - NETL-ORD IAES project at CMU to investigate influence of RE on transient oxidation.

Coatings on T430 Stainless Steel



2 to 3 times reduction with Ce-surface treatment

Ce-surface treated at NETL

Tested at Allegheny

800°C in air+7%H_2O

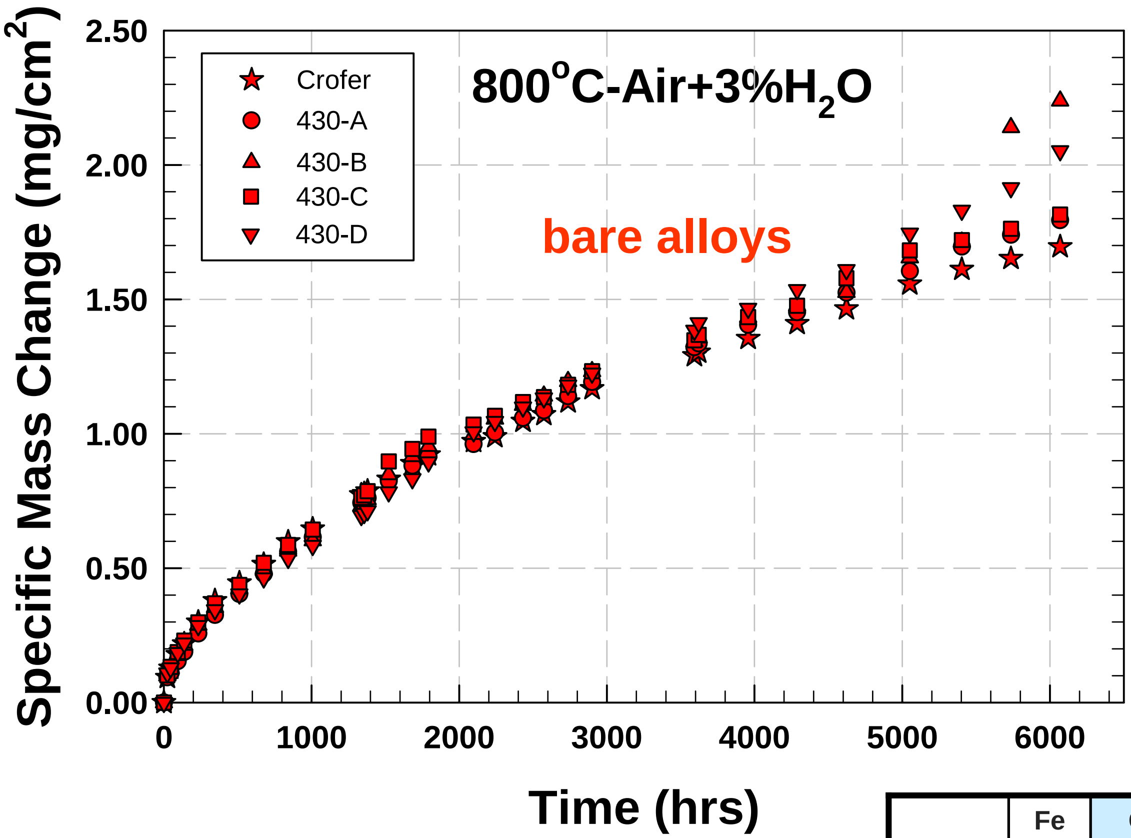
T430=Fe-17Cr-0.5Mn

ATI Allegheny Ludlum
Allegheny Technologies

J. Rakowski, 2006

NETL

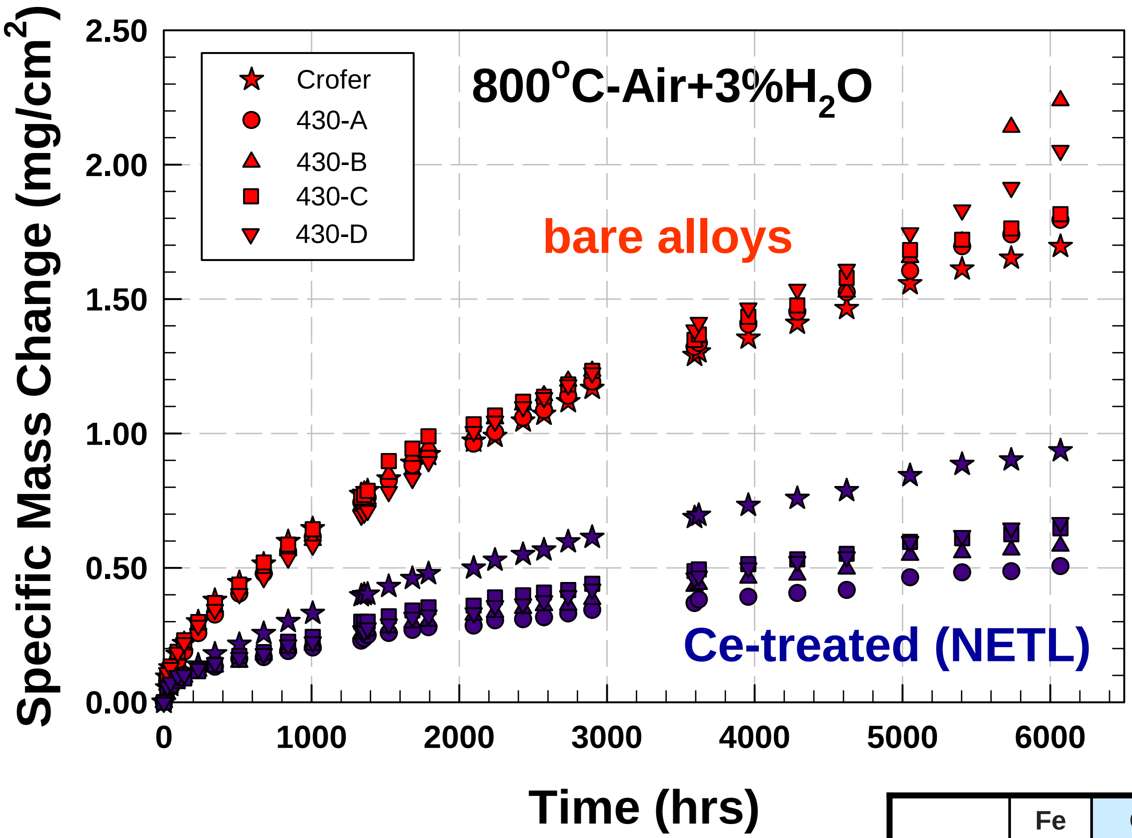
Long Term Exposure



	Fe	Cr	Mn	Ti	Si	Al
430-A	Bal	16.85	0.44	<0.01	<0.01	<0.01
430-B	Bal	17.03	0.47	<0.01	<0.01	<0.01
430-C	Bal	17.13	0.49	<0.01	<0.01	<0.01
430-D	Bal	17.11	0.52	0.080	<0.01	<0.01
Crofer	Bal	22.42	0.45	0.092	0.12	0.13

430 alloys produced at NETL
Oxidation test in progress

Long Term Exposure



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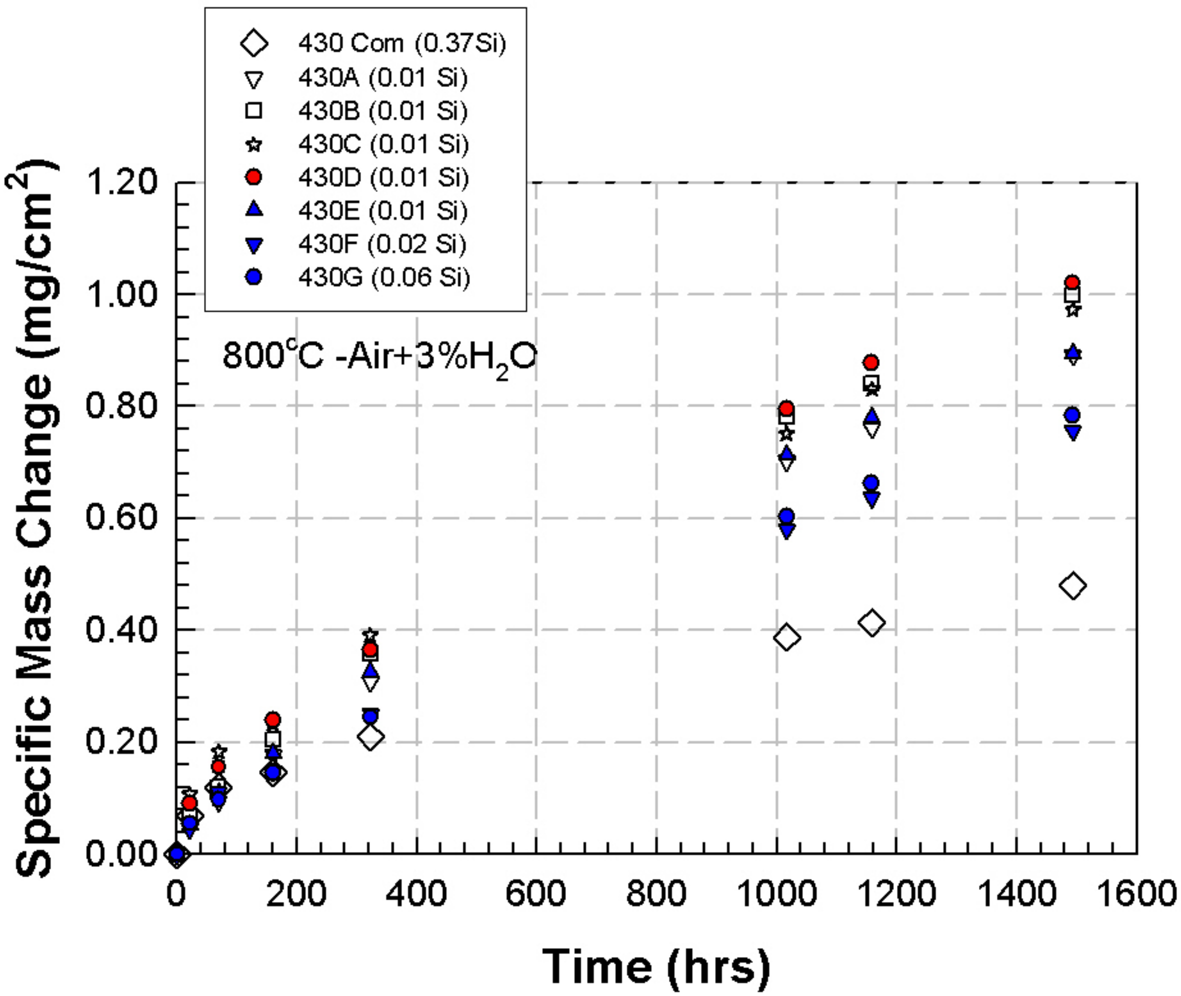
NETL

Influnence of Si Content: T430

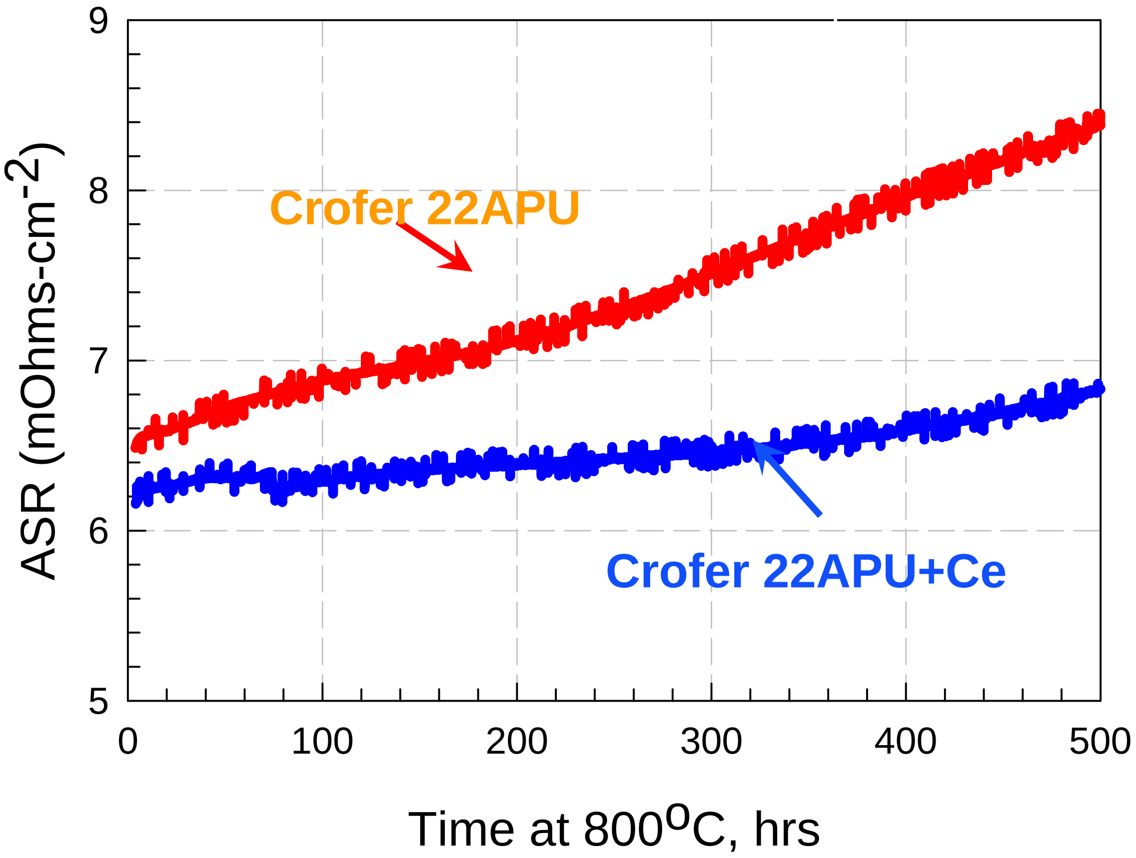


Testing is in progress

Electrical Performance

Lower ASR ✓ for SOFC interconnect

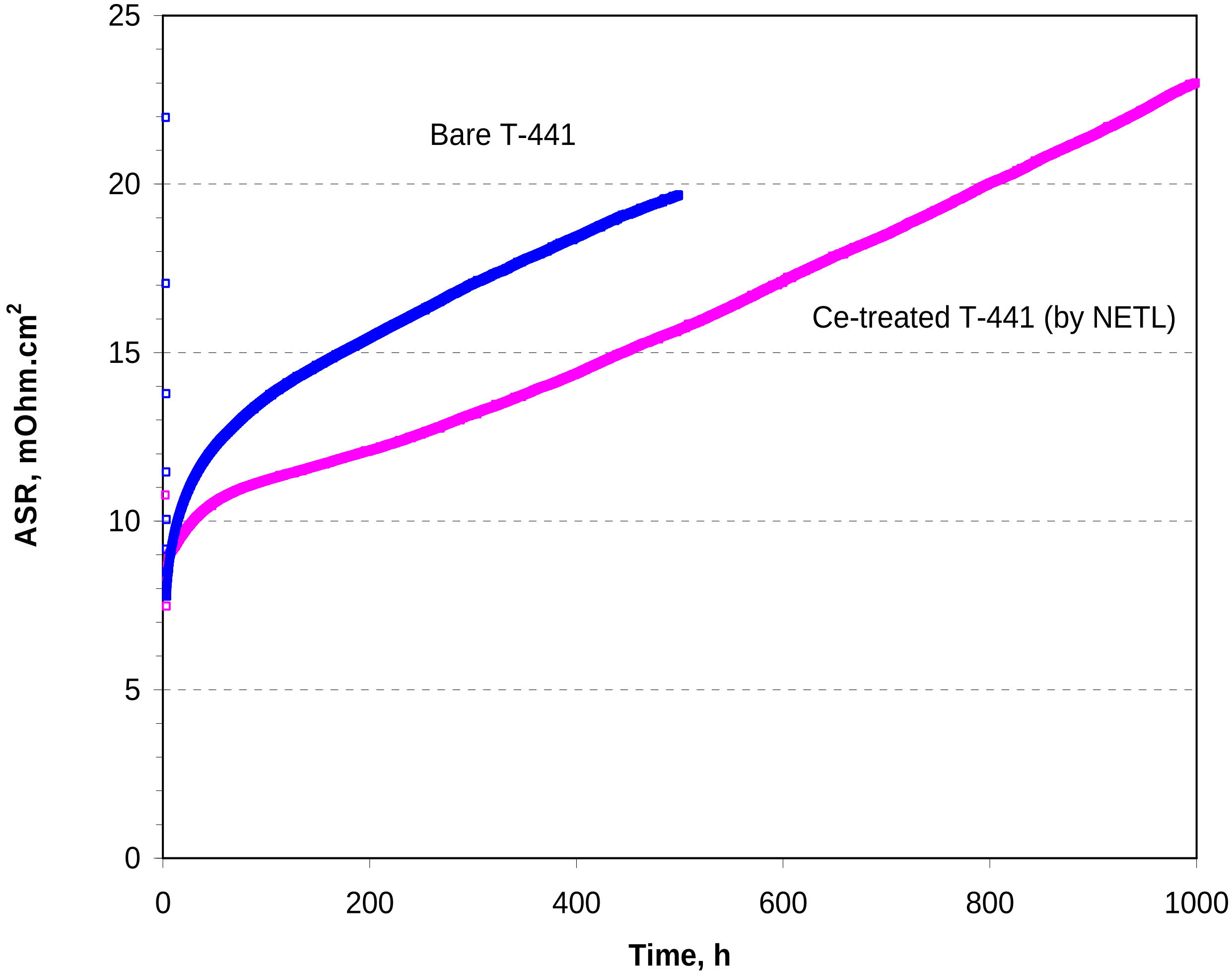
Measurements made by G. Xia & Z.G.Yang, PNNL



Samples pre-oxidized at 800°C for100 hours prior to testing

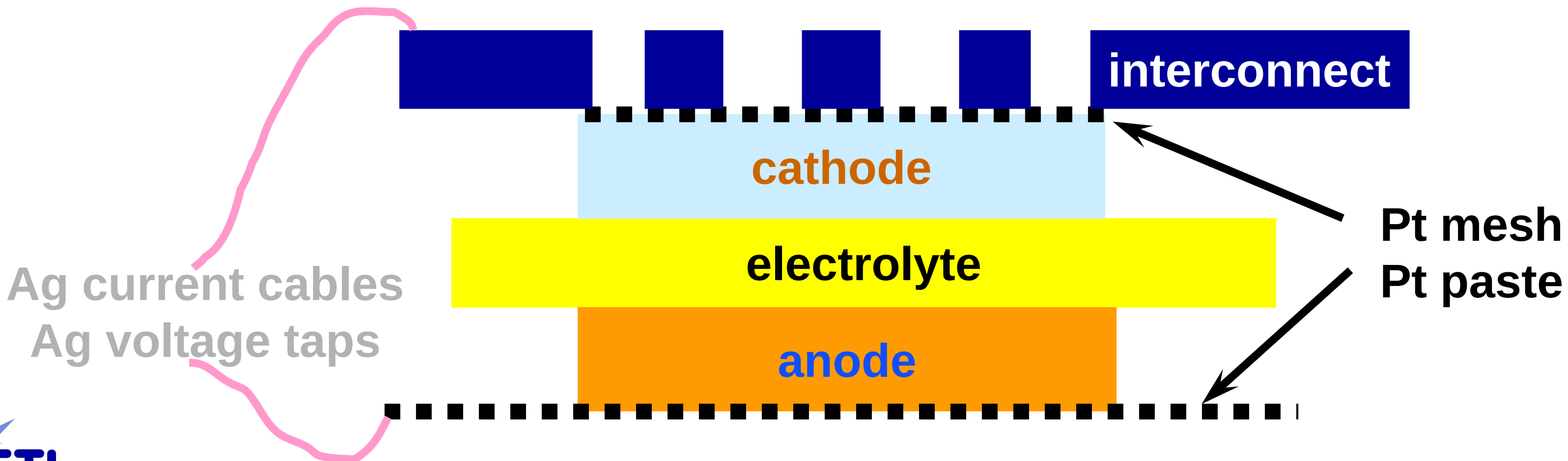
Electrical Performance

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

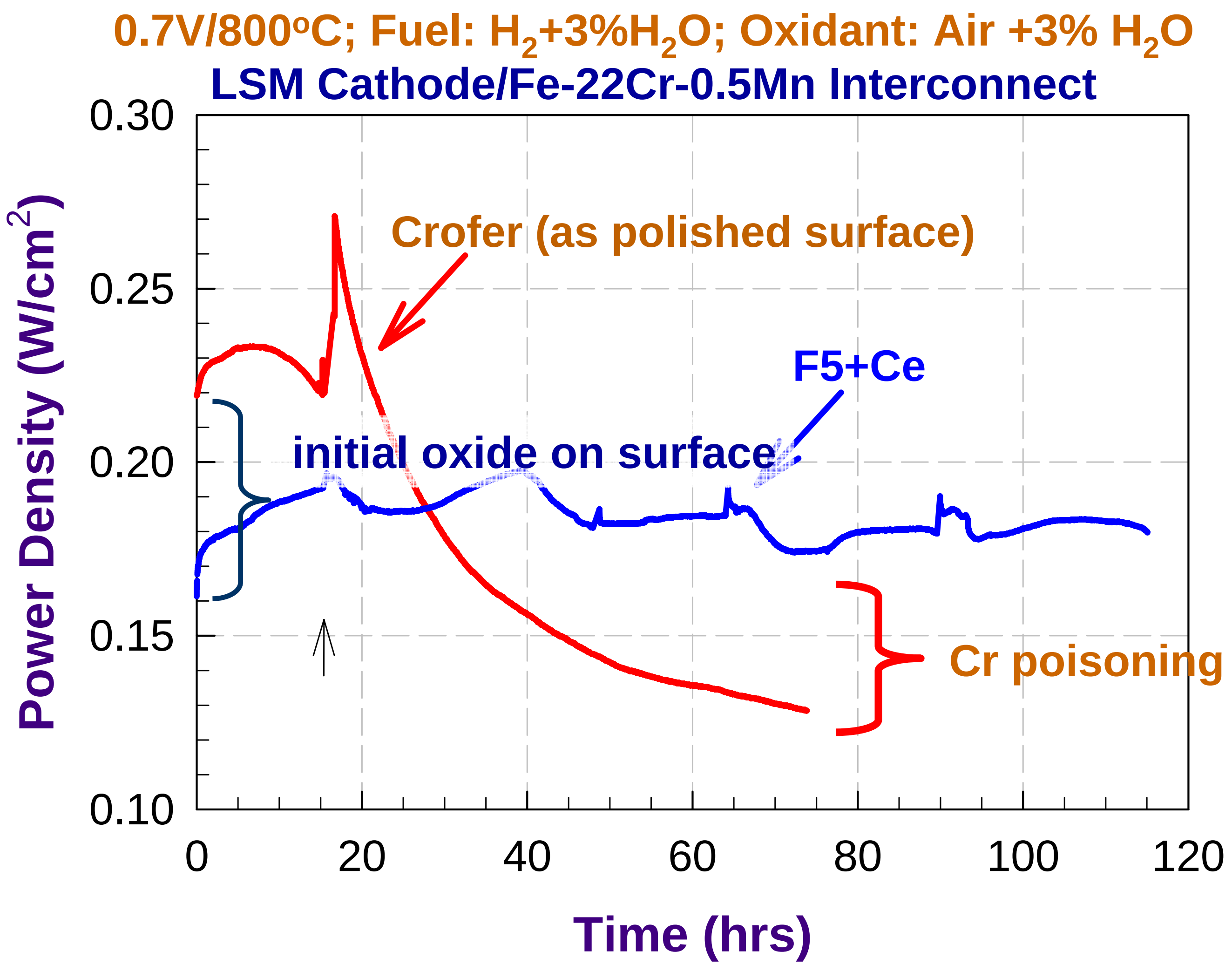


Laboratory Scale Testing

- "Button" cell test frames in Morgantown
- Fe-22Cr-0.5Mn steel current collector was attached to the cathode with Pt paste (a Pt mesh placed between interconnect and cathode).
- Pt mesh attached to anode.
- Ag current cables and voltage taps spot welded to current collectors



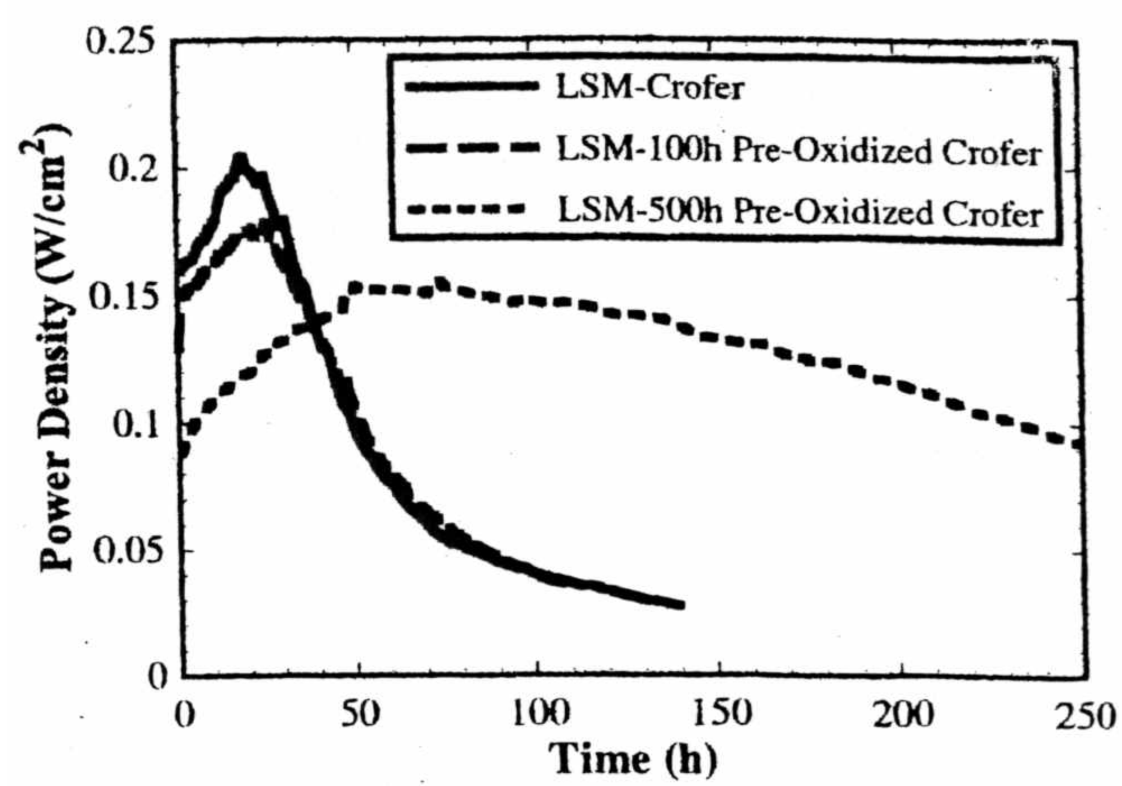
Laboratory Scale Cell Performance



Results published: D.E. Alman, C.D. Johnson, W.K. Collins, and P.D.Jablonski, "The Effect of Cerium Surface Treated Ferritic Stainless Steel Current Collectors on the Performance of Solid Oxide Fuel Cells (SOFC)," *Journal of Power Sources,* Vol 168, 2007, pp. 351-355.

Pre-Oxidized Current Collectors

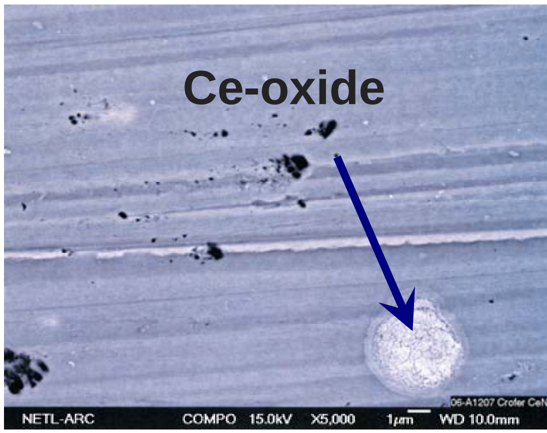
- ***S.P. Simner, Anderson, Xia, Yang, Pederson, Stevenson, J. Electrochemical Soc., vol 154 (4), pp. A740-A745, 2005***

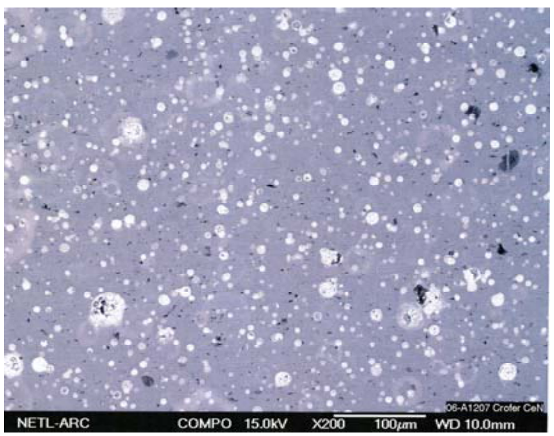


Behavior of cell with Ce-treated interconnect (previous slide) similar to behavior of cells with pre-oxidized interconnects.

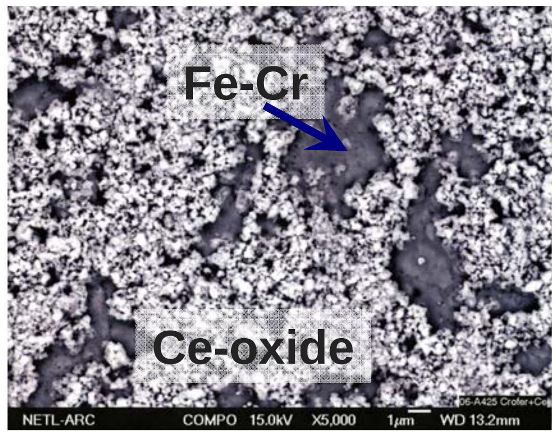
NETL Treatment with La_2O_3

CeN-based (H/S: 400^{o}C)

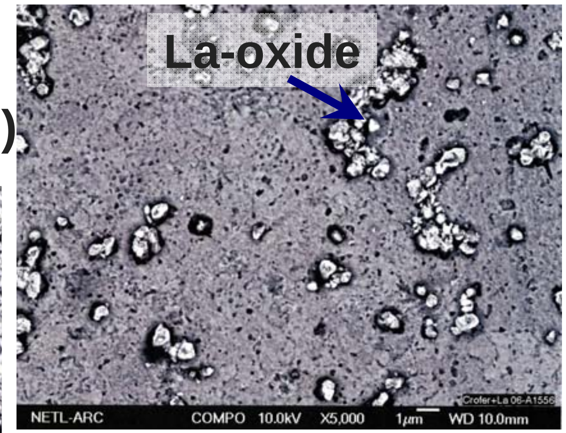


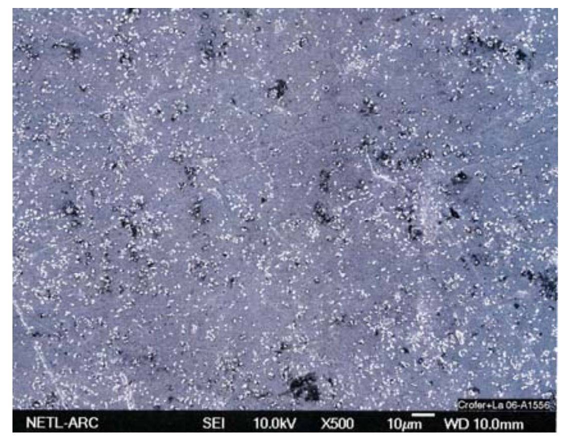


CeO_2-based (NETL:900^{o}C)



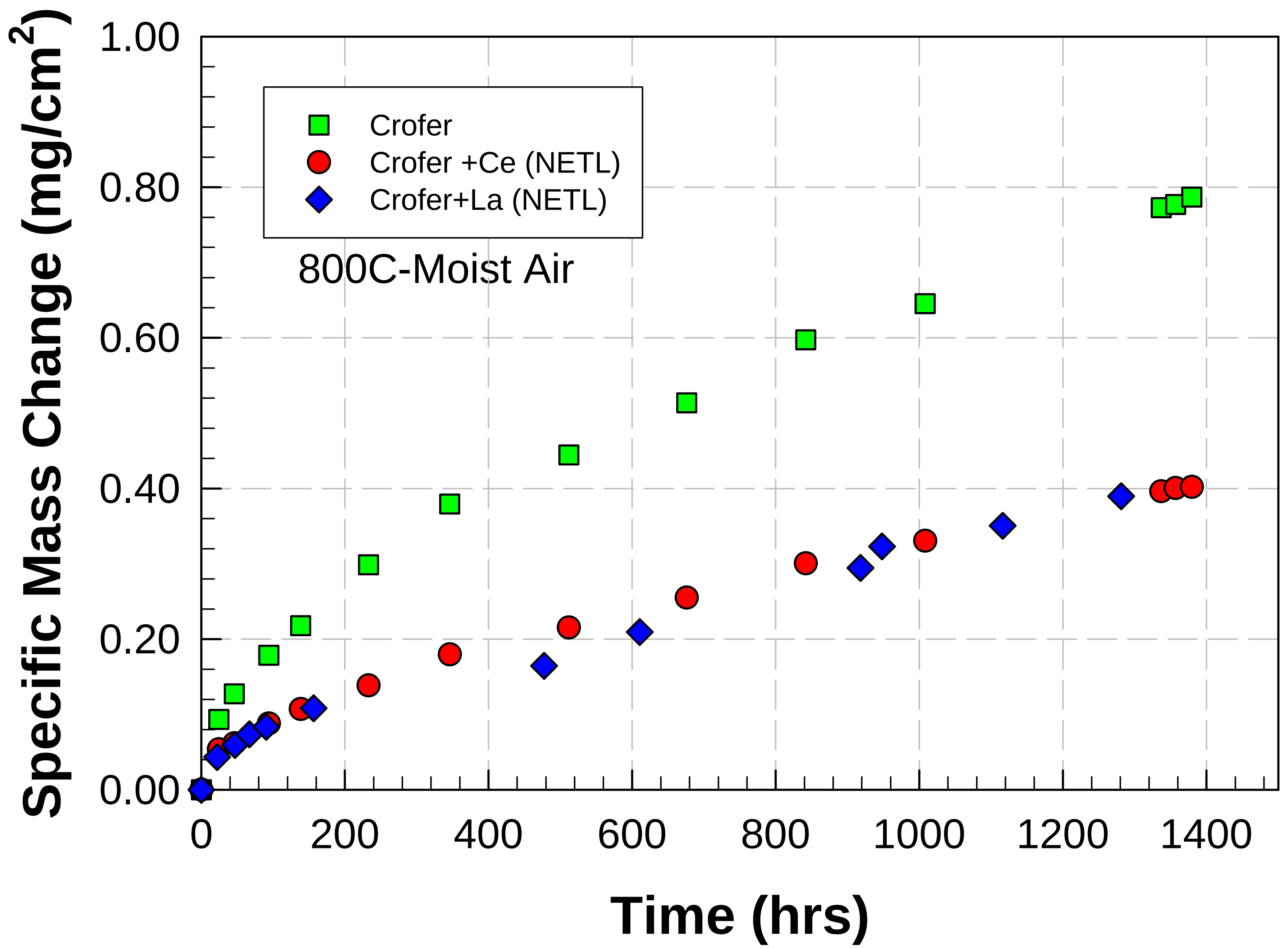
La_2O_3-based (NETL:900^{o}C)



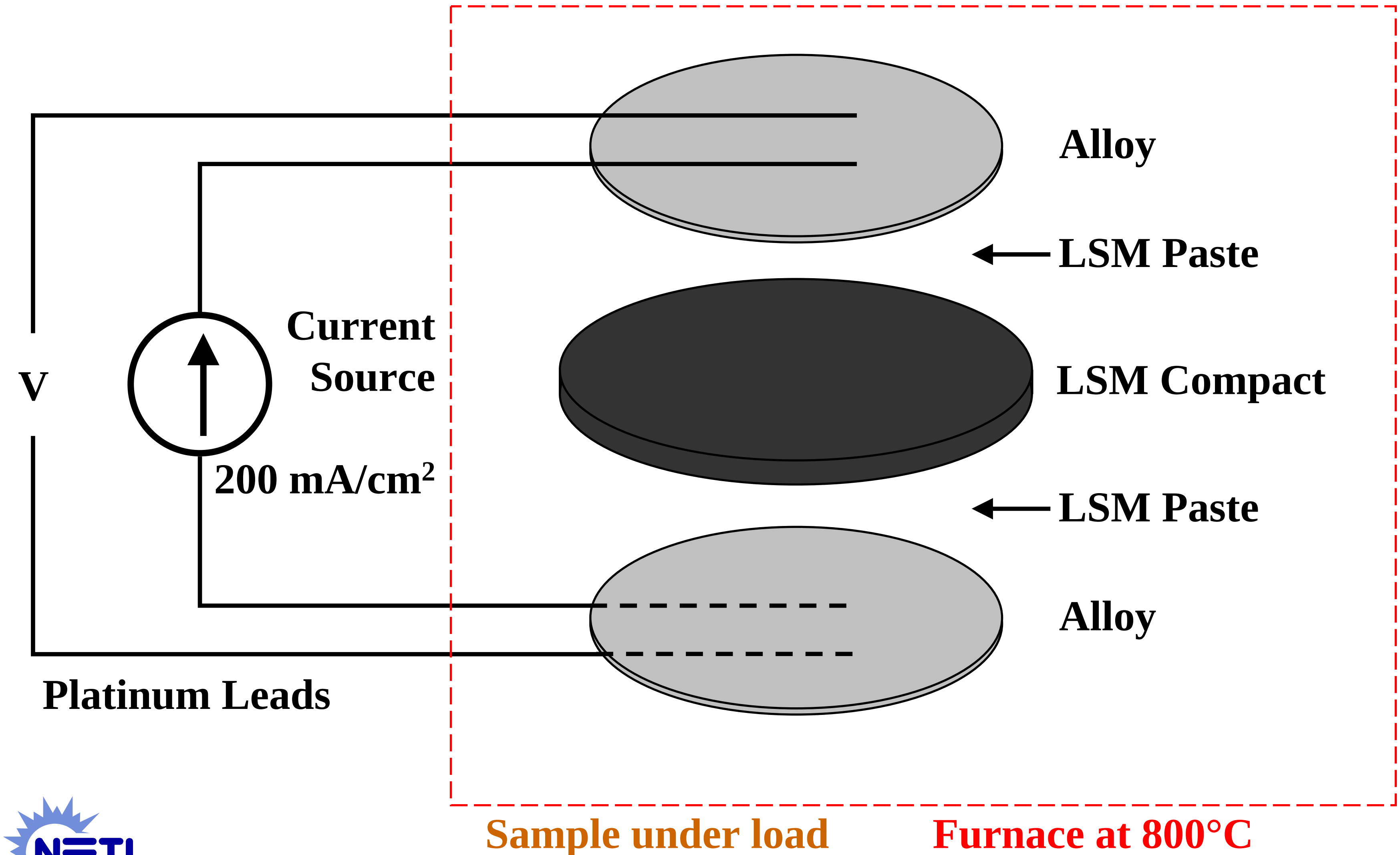


composition is at%

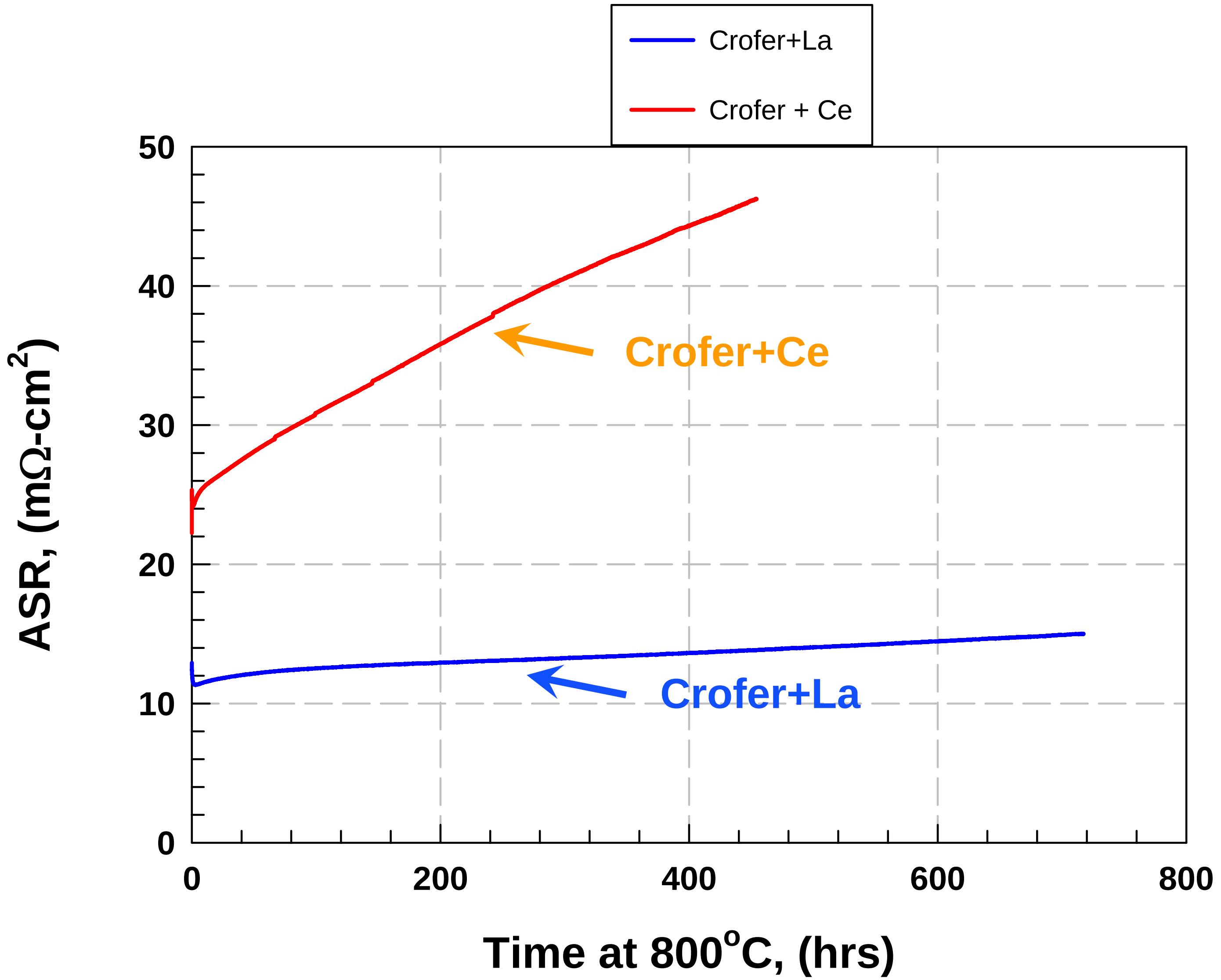
Effect of Rare Earth



Initial Conductivity: ASR Experimental Setup



Electrical Performance



Summary

- **RE surface treatments effective in improving oxidation resistance.**
  - Applied to ferritic stainless steels for interconnect application (Crofer and Type 430).
  - Both Ce-based methods (NETL and H/S) were effective.
  - Thinner oxide scales with treatment.
  - Thinner internal oxidation zone.
  - La modification to the NETL method was effective.
  - ASR measurements indicate that slower scale growth will enhance SOFC performance.

On-Going and *Future Work*

- **Continue long term exposures on Ce- and La-treated samples**
  - to determine if and when breaks-down occurs
  - accelerated tests
  - *Longer term ASR (or cell tests)*
- **Continue investigation influence of Si content**
  - Determine critical Si level (oxidation *and ASR*)
  - *Low cost production of low Si steels using recycled scrap (develop innovative slag additives to getter Si during metling).*

Experimental Alloys and RE Surface Treated Materials Available For Evaluation by SECA Participants

Contact:
Paul D. Jablonski: 541.967.5982 or
David E. Alman: 541.967.5885

Thermal Treatment (TC) Only is *Ineffective*