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National Energy Technology Laboratory

Influence of a Cerium Surface Treatment on the Oxidation Behavior of Commercial Fe- and Ni- Base Alloys

David E. Almian and Paul D. Jablonski

1450 Queen Ave., S.W.
Albany, OR 97321
www.netl.doe.gov

High Temperature Degradation of Fe-, Ni- and Co- Based Alloys: Alloying Element and Corrosive Environments
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NETL

Office of Fossil Energy

Acknowledgements

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- Paul Danielson (metallography)
- Keith Collins and Steve Matthes (SEM)
- Marisa Arnold (ESCA, XRF, oxidation experiments)
- Richard Chinn and Dave Smith (XRD)

Motivation for Research

- **Increasing efficiency of power generation requires system to operate at higher temperatures, pressures and in hostile environments (IGCC, SOFC, USC).**
- **COST EFFECTIVE METALLIC ALLOYS THAT CAN MEET PERFORMACE REQUIREMENTS (I.E., CREEP & CORROSION RESISTANCE ARE A KEY TO THE DEVELOPMENT OF ADVANCED POWER SYSTEMS.**
- **Strength and creep resistance is often obtained at the expense of corrosion resistance.**
- **NEED TO DEVELOP METHODOLOGIES TO IMPROVE HIGH TEMPERATURE COROSION RESISTANCE.**
  - ***Alloying additions***
  - ***Coatings***
  - ***SURFACE TREATMENTS***

Improving Oxidation Resistance with Reactive (Rare Earth) Elements

- **Well established small amounts rare earth additions improve oxidation resistance of a variety of metallic alloys**
  - Ce, La, Y, etc.
- **Characteristics**
  - Slow scale growth
  - Stabilize Cr_2O_3 scales at lower Cr levels
    - Lower Cr levels → lower alloy cost (especially for ferrous alloys)
  - Prevent oxide scale spalling

Improving Oxidation Resistance with Rare Earths

- **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 and have most benefit)
  - – "Extra" manufacturing step.
  - ? ***Long term effectiveness (as with any coating or surface treatment)***

Research Goal

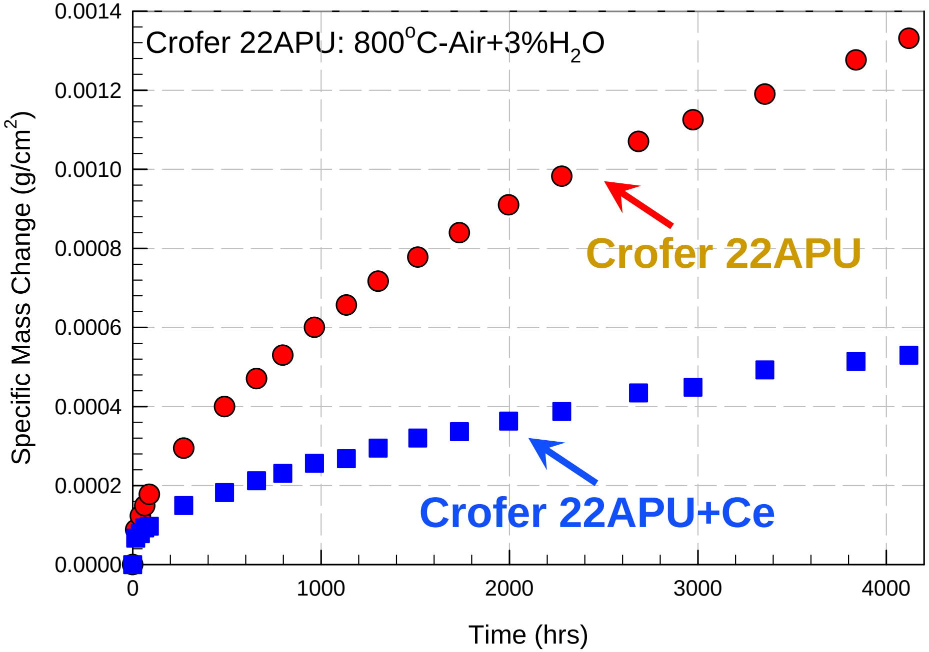
- **Investigate rare earth surface treatment for improving oxidation resistance of alloys for FE applications.**
- **Two different surface treatments investigated**
  - Developed at NETL
    - Similar to pack cementation: coated with a powder mixture containing CeO_2 or CeN and halide activator followed by heating in a controlled atmosphere (900°C-12 hrs), after which residual "pack" coating is washed off the surface.
    - Patent application filed with USPTO in September, 2005.
    - Applied to over 50 alloys.
  - Described in a paper by P.Y. Hou and J. Stringer (H/S)
    - J. Electrochem Soc., Vol 134, No. 7, July 1987, pp. 1836-1849
    - Coupons heated to 200°C were coated with a cerium-nitrate slurry (10w/o nitrate adjusted with HNO_3 to pH=2), followed heating in air at 400°C to decompose to CeO_2

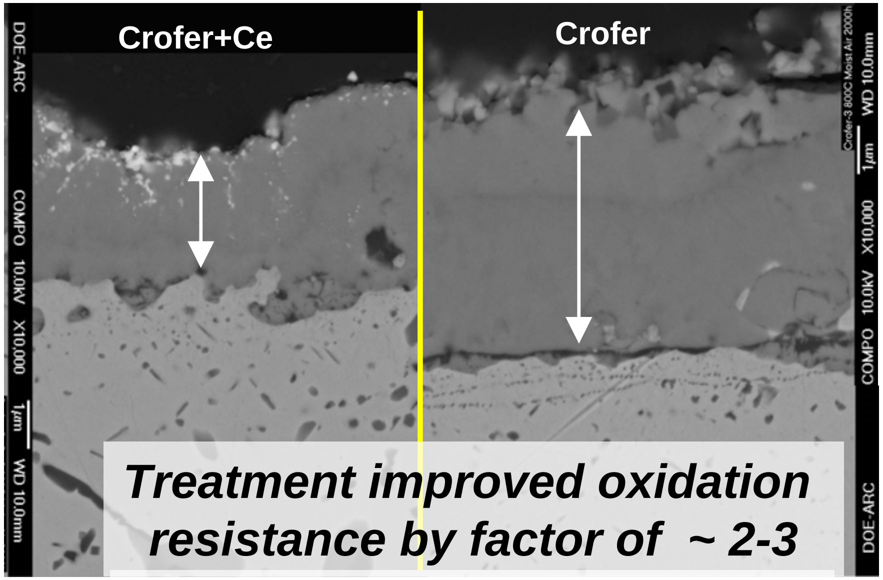
Oxidation Experiments


Typical furnace for oxidation testing

- **Coupons**
  - 25.4 x12.5 x thickness
  - placed in Al_2O_3 crucible (to collect any oxide spall)
  - Polished through 600 grit surface finish
- **Oxidation testing**
  - in dry air
  - air+3%H_2O (bubbling dry air through two ~ 1m water columns)
- **“pseudo-cyclical”**
  - coupons placed in pre-heated furnace; after pre-determined time interval coupons removed and weight change recorded; coupons were then replaced in furnace for next cycle

Crofer 22APU+Ce Surface Treatment

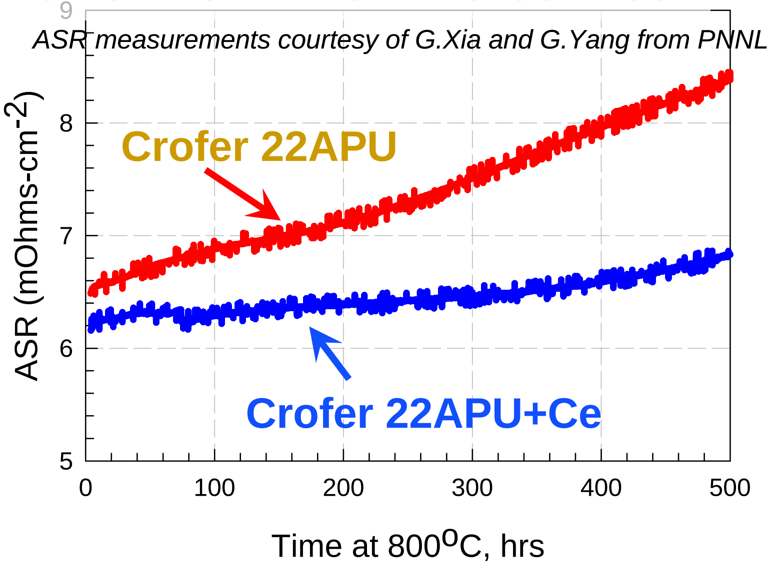




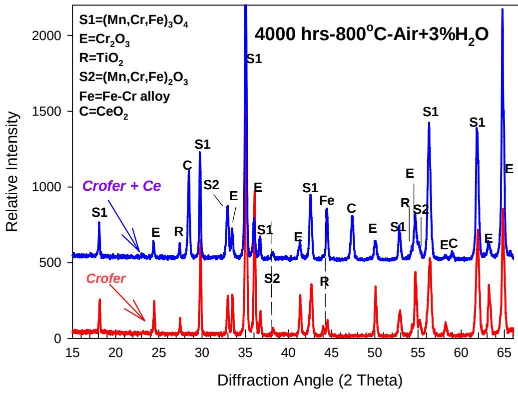
Treatment improved oxidation resistance by factor of ~ 2-3

Lower ASR ✓ for interconnect

ASR measurements courtesy of G.Xia and G.Yang from PNNL

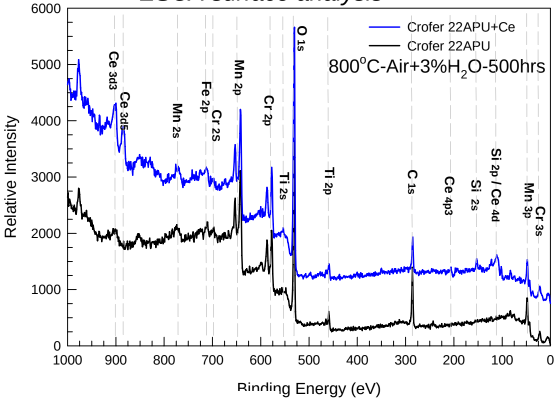


CeO_2 incorporated into scale



X-ray diffraction

ESCA surface analysis



Crofer 22APU is a "commercial" Fe-22Cr-0.5Mn ferritic steel developed for SOFC interconnect application at the Juelich Research Center and marketed by ThyssenKrupp.

Commercial Alloys Cerium Surface Treated

- IN100, MAR-M 247
- Haynes 230, IN625
- Haynes 242
- IN718, IN600
- 316, 321, 347
- AL-20-25+Nb
- MA965
- 446, EBrite
- Crofer22APU
- 441,430
- 409
- P91
- SAVE 12

Ni-base alloys

austenitic steels

ferritic steels

ferritic/martensitic steels

Alloy Compositions

Alloy	*Nominal Composition*	*Alloy Class*
IN625	**Ni-22Cr-10Mo-0.5Mn-4(Nb+Ta)**	**Nickel**
Al-20-25+Nb	**Fe-20Cr-25Ni-1.5Mn-1.5Mo-0.3Nb**	**Austenitic**
IN600	***Ni-18Cr-8Fe-1Mn***	***Nickel***
347	***Fe-18Cr-10Ni-2Mn-(Nb+Ta)10x(C)***	***Austenitic***
321	***Fe-18Cr-10Ni-2Mn-(Ti)5x(C+N)***	***Austenitic***
441	***Fe-18Cr-1Mn-0.5Ti-(0.3+9xC)Nb***	***Ferritic***

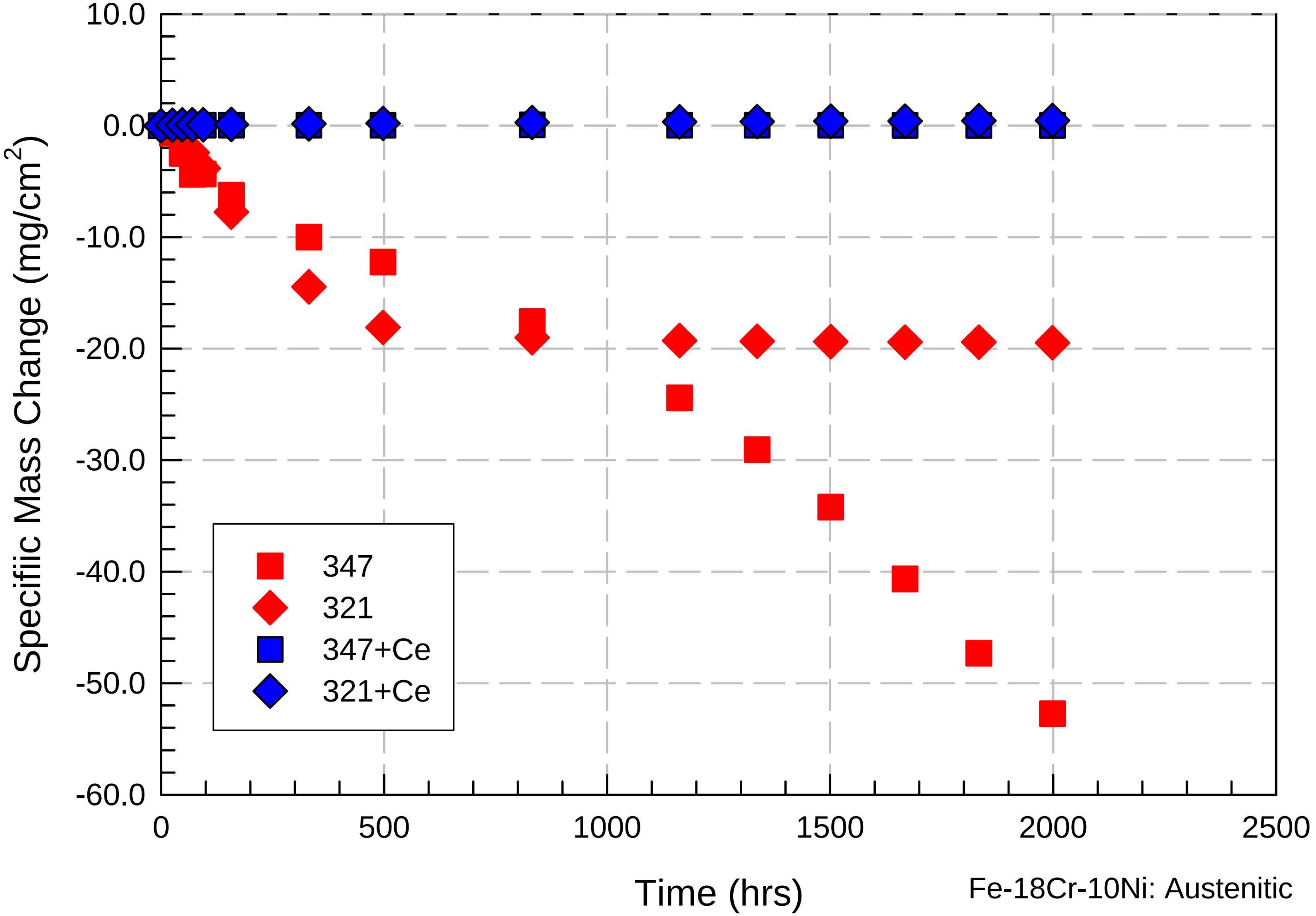
Chemical Composition (wt%, by XRF)

	Fe	Ni	Mo	Cu	Mn	Cr	Si	Al
Type321	68.92	10.18	0.13	0.16	1.63	17.49	0.55	0.075
Type347	70.57	8.99	0.20	0.16	1.17	17.49	0.40	<0.010
IN600	9.48	71.94	0.15	0.19	0.92	15.99	0.21	0.24
IN625	4.15	61.75	8.76	0.055	0.056	20.92	0.17	0.13

	Ta	W	Co	V	Nb	Ti	C
Type321	0.044	<0.010	0.030	0.020	0.001	0.69	0.08
Type347	0.034	<0.010	0.049	0.091	0.77	0.010	0.08
IN600	0.40	0.037	<0.010	0.011	0.18	0.26	0.01
IN625	0.34	0.032	<0.010	0.026	3.37	0.25	0.01

Type 347/321

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



Fe-18Cr-10Ni: Austenitic

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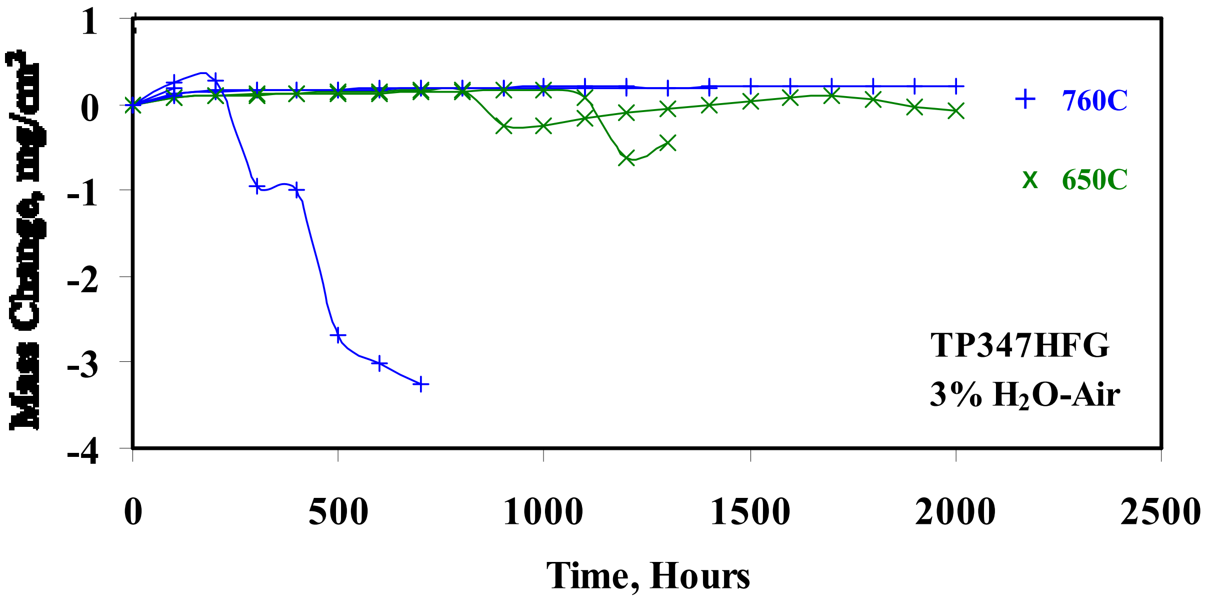
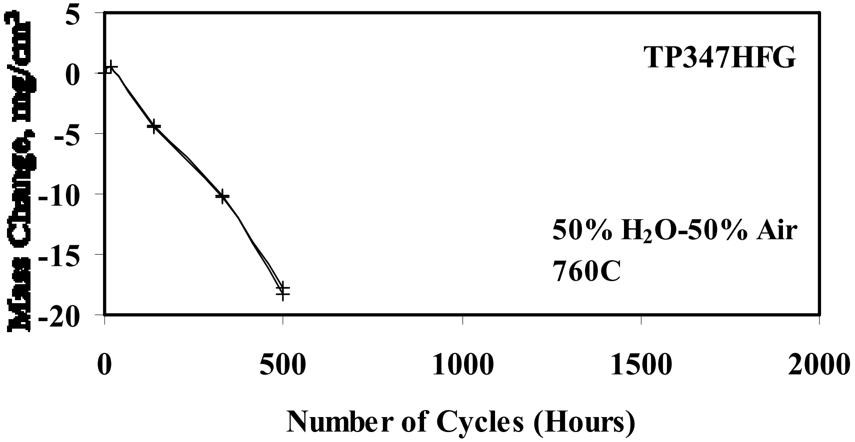
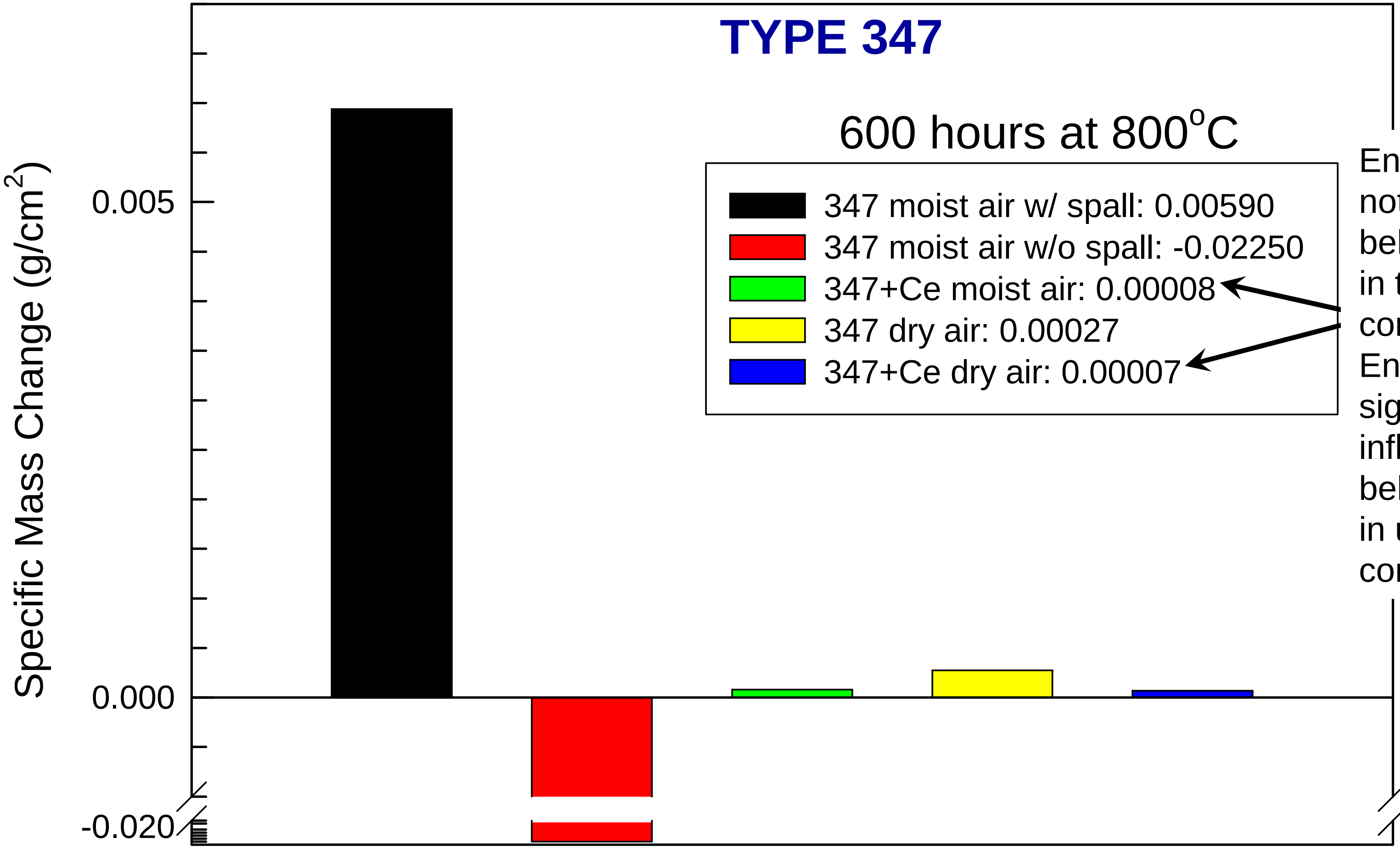
Oxidation of Type 347 HFG



Courtesy of
Gordon R. Holcomb, NETL, 2006



Influence of Moisture on the Oxidation behavior of TYPE 347



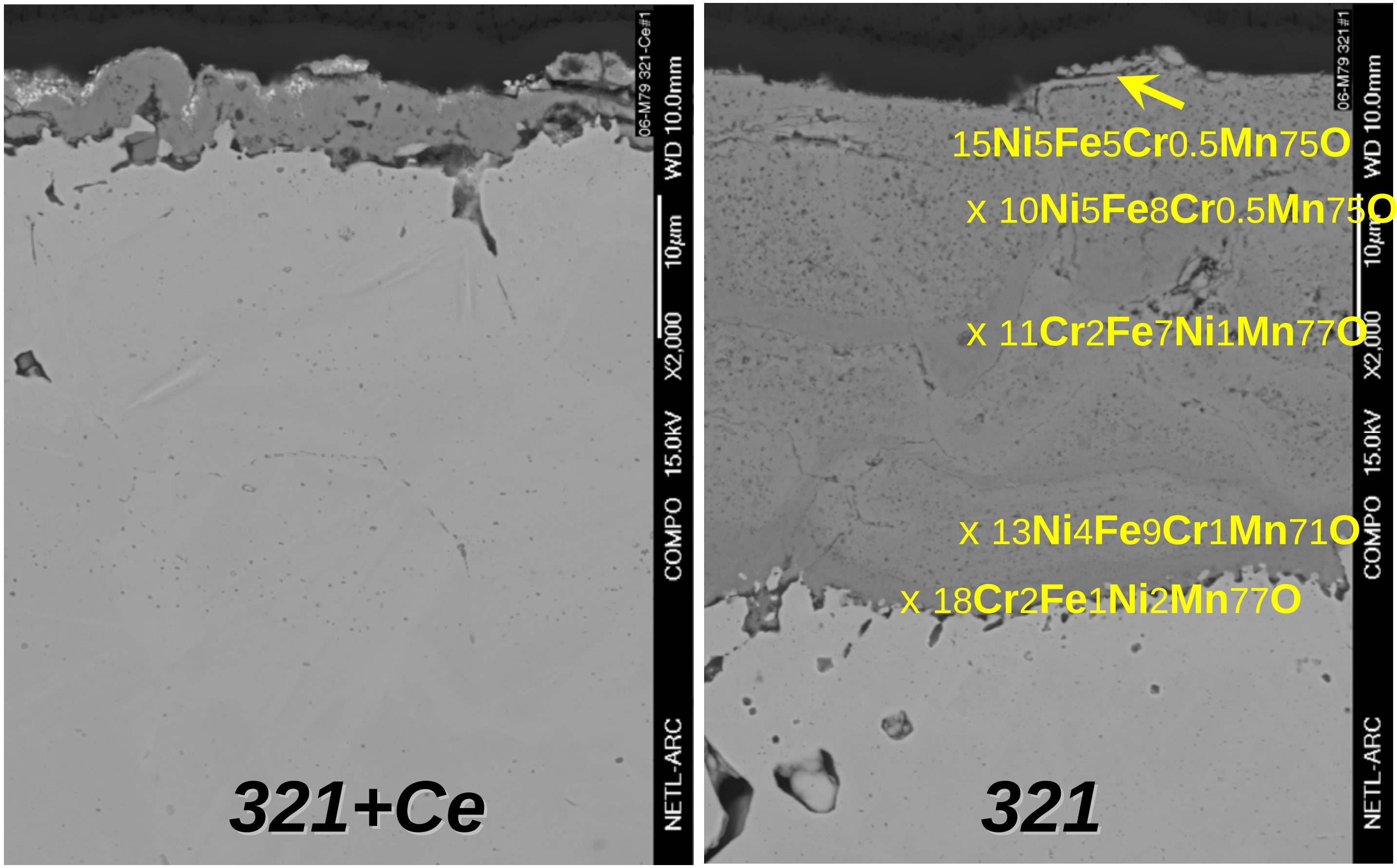
Environment did not affect behavior of alloy in treated condition. Environment significantly influenced the behavior of alloy in untreated condition.

Scale Formation During Oxidation of Type 347

	800°C Dry Air 600 hrs	800°C Moist Air 600 hrs	800°C Moist Air 2000 hrs
347	$Cr_{1.3}Fe_{0.7}O_3$ $Mn_{1.5}Cr_{1.5}O_4$	$FeFe_2O_4$(magnetite) $Cr_{1.3}Fe_{0.7}O_3$ *Fe_2O_3** *$NiCr_2O_4$**	$FeCr_2O_4$ Cr_2O_3 *Fe_2O_3** *$NiCr_2O_4$**
347+Ce	Cr_2O_3 $Mn_{1.5}Cr_{1.5}O_4$ CeO_2	Cr_2O_3 $Mn_{1.5}Cr_{1.5}O_4$ CeO_2	Cr_2O_3 $MnCr_2O_4$ CeO_2

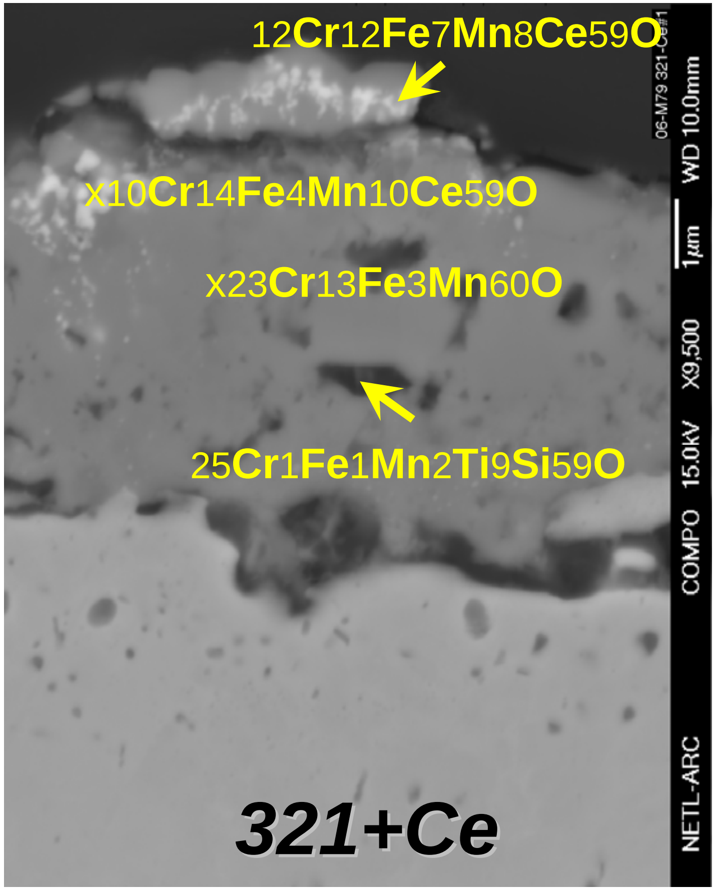
** found in spall*

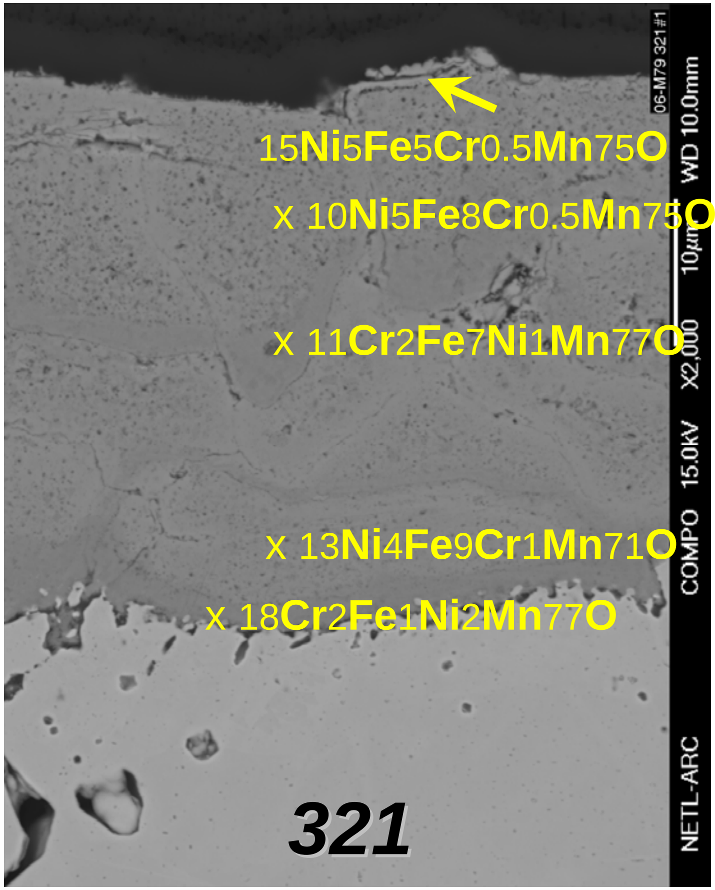
Scale Morphology



Compositions in at% determined by WDX analysis

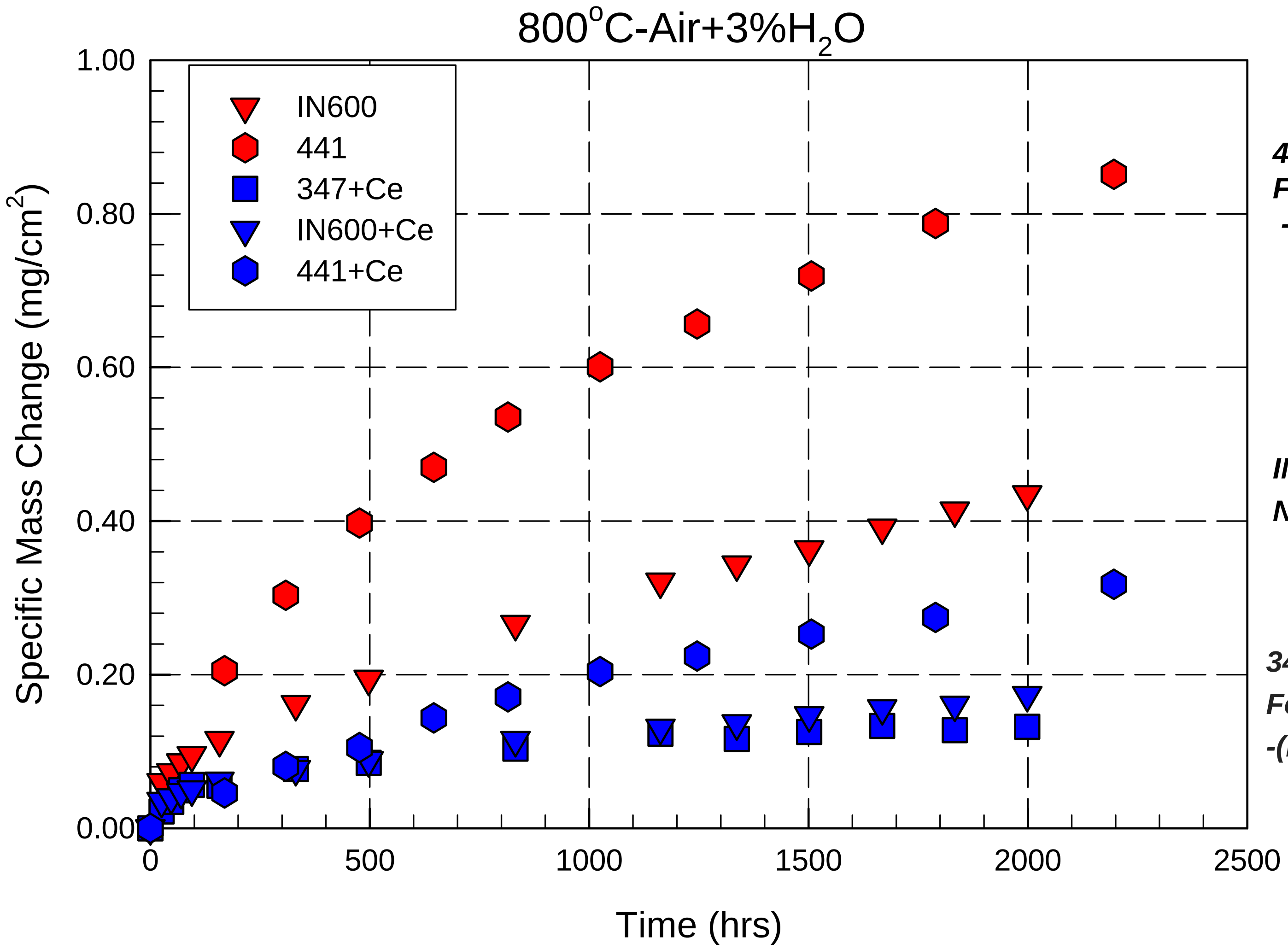
Scale Morphology





Compositions in at% determined by WDX analysis

18Cr Alloys



441: Ferritic
Fe-18Cr-1Mn-0.5Ti
-(0.3+9xC)Nb

IN600: Nickel Alloy
Ni-18Cr-8Fe-1Mn

347: Austenitic
Fe-18Cr-10Ni-2Mn
-(Nb+Ta)10x(C)

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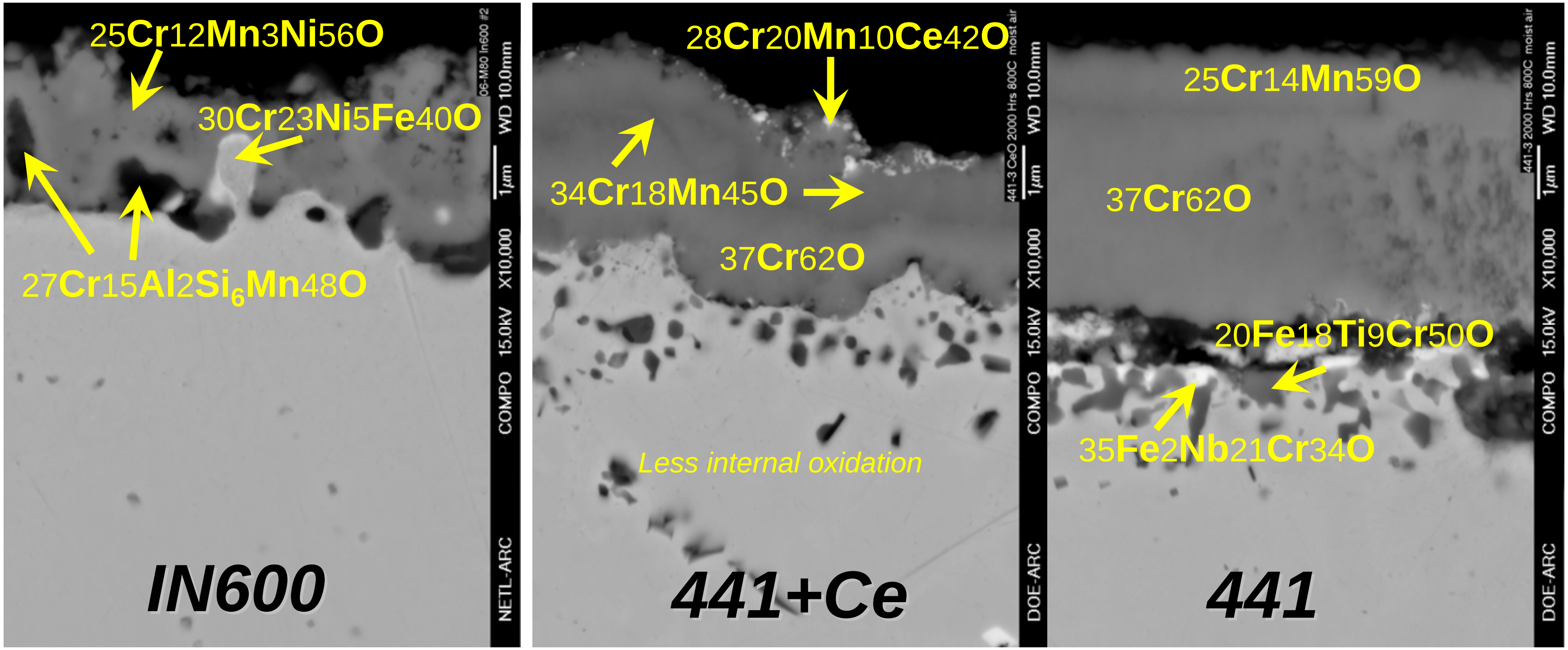
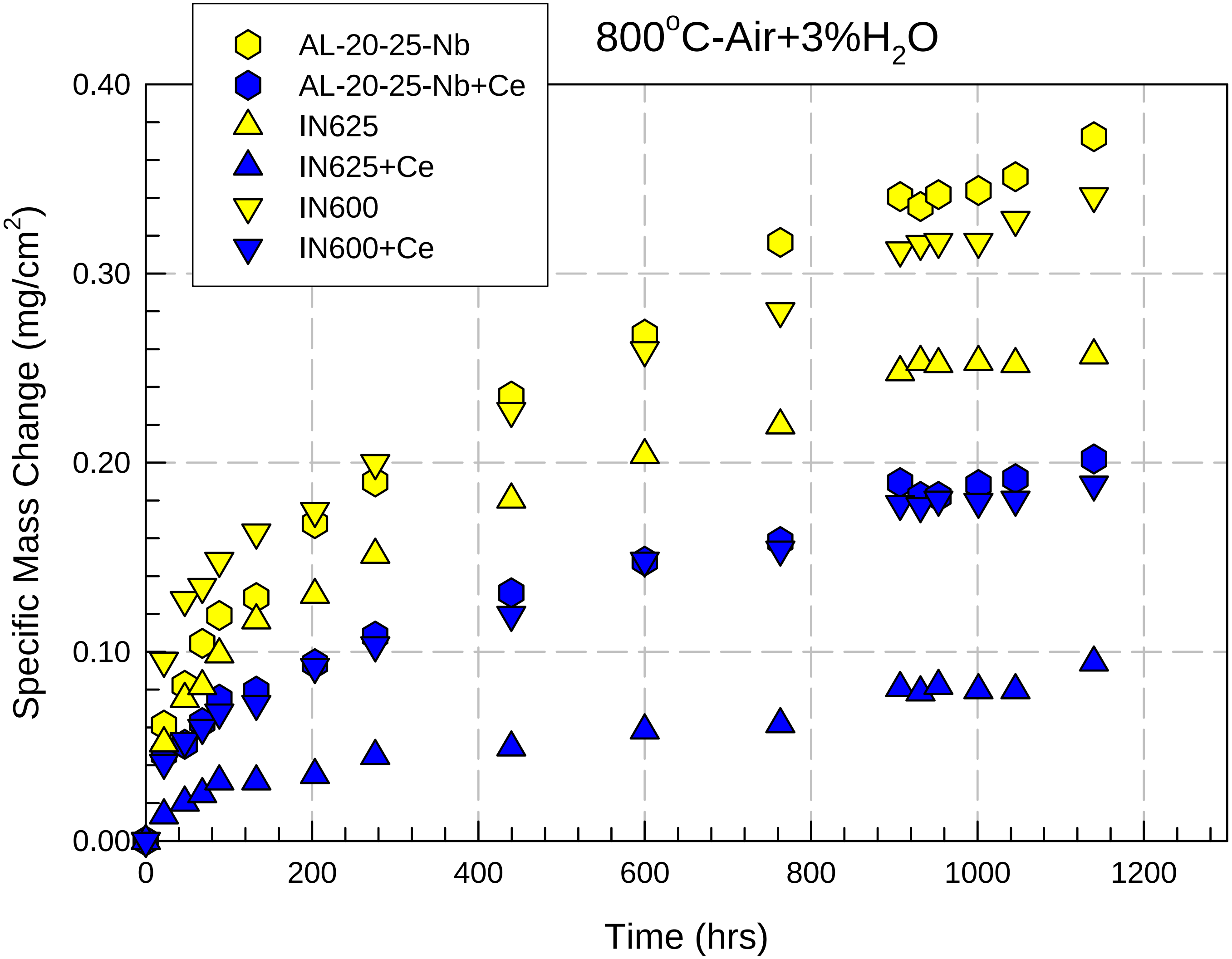
800^{o}C-Air+3%H_2O-2000hrs



Compositions in at% determined by WDX analysis

High Temperature Alloys



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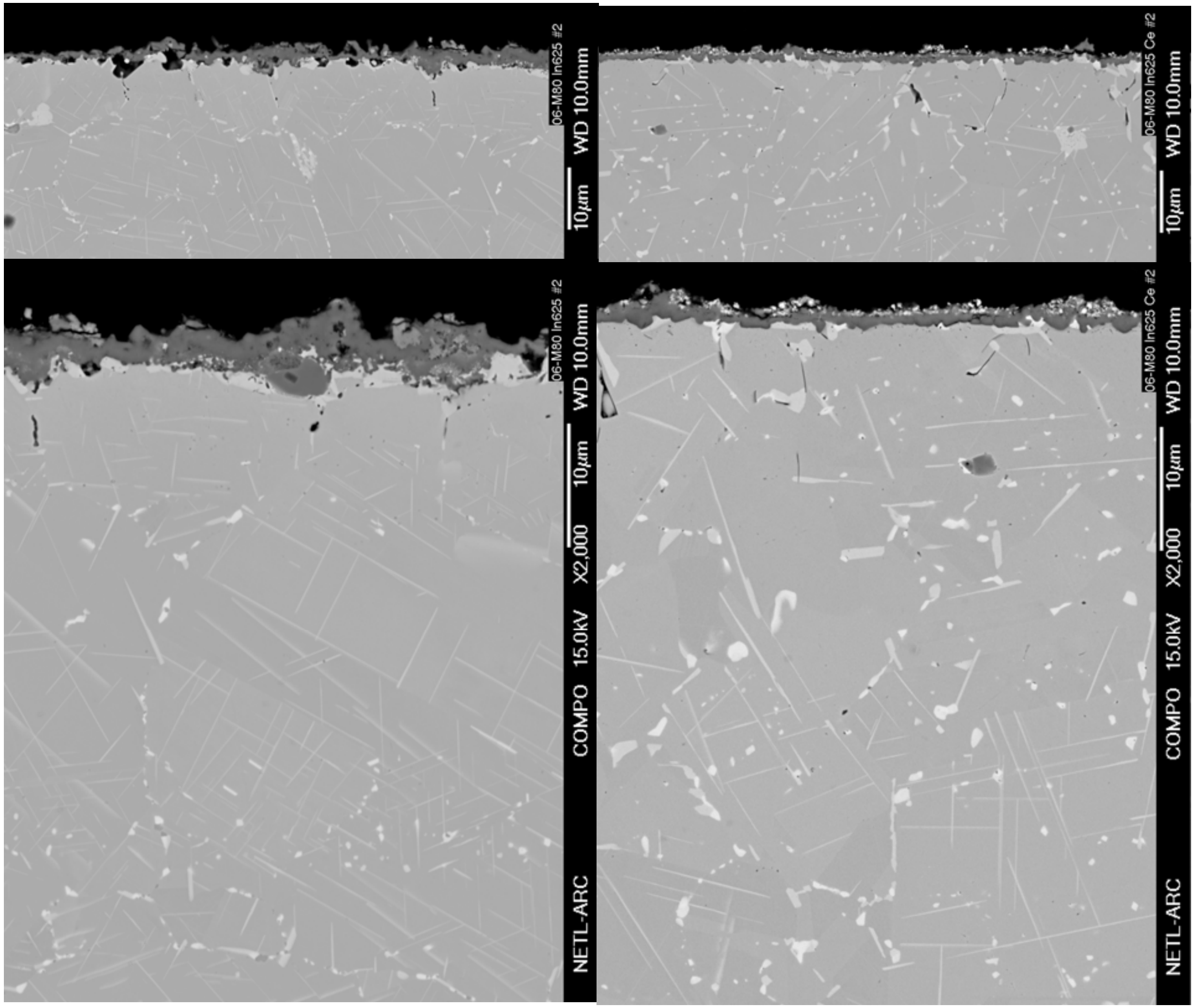
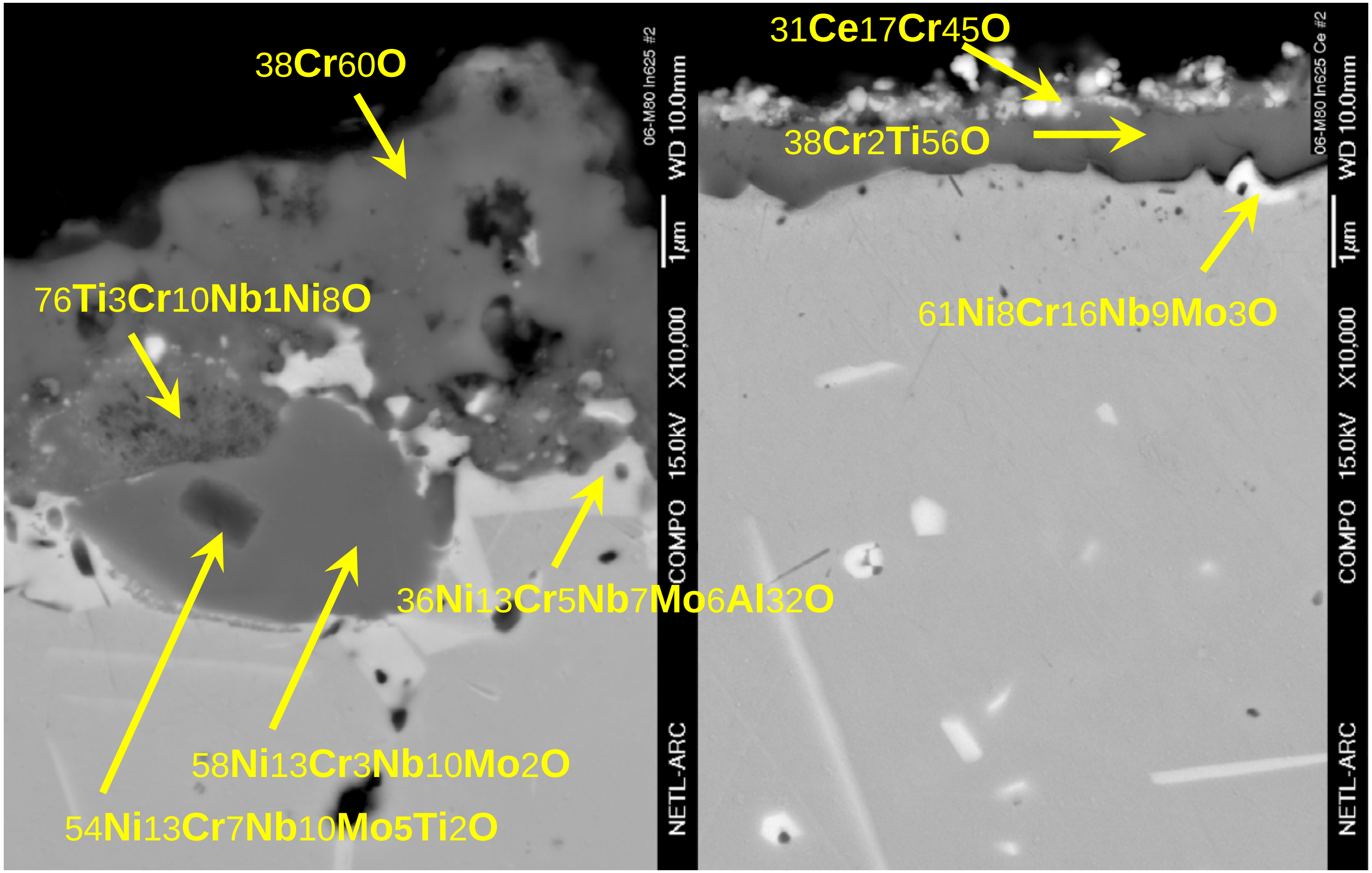
IN625:800^oC-Air+3%H_2O-2000hrs



IN625:800^{o}C-Air+3%H_2O-2000hrs



IN625 **IN625+Ce**

Compositions in at% determined by WDX

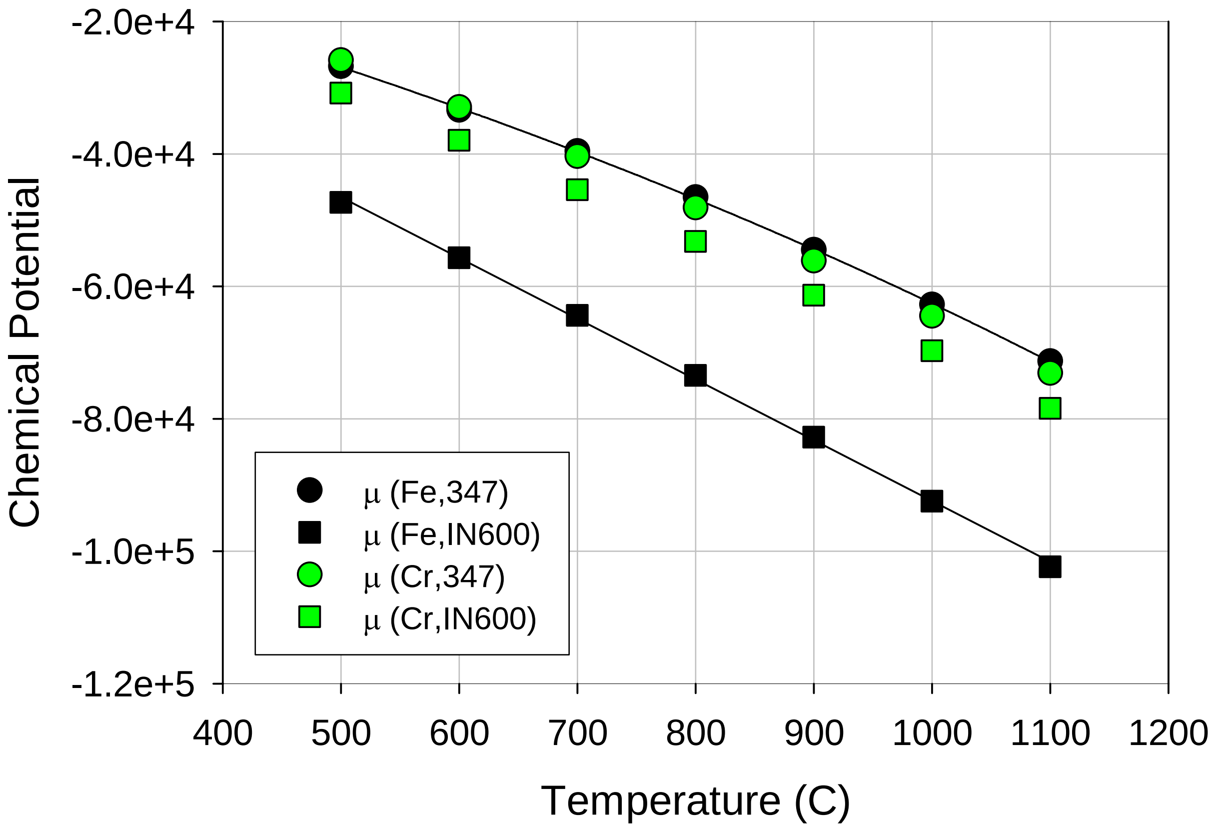
Base Alloy Behavior

- 347/321 (18Cr-10Ni) austenitic alloys → oxide scale spalled →Fe_2O_3 formation
- AL-20Cr-25Nb+Nb austenitic alloy → did not spall
- Ferritic alloy (441) and Ni alloy (IN600) → did not spall → Cr_2O_3 formation

? WHY?

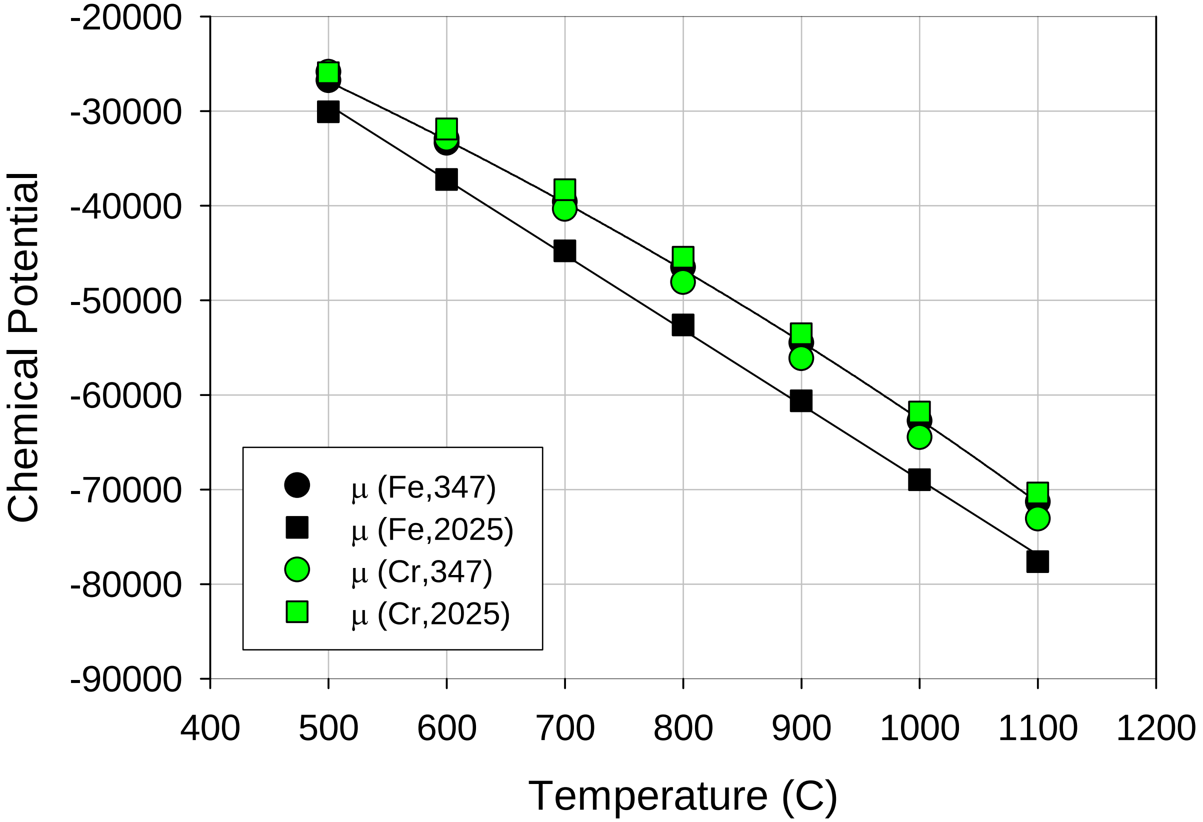
- Chemical Potentials and Diffusivities

Comparison of Chemical Potential



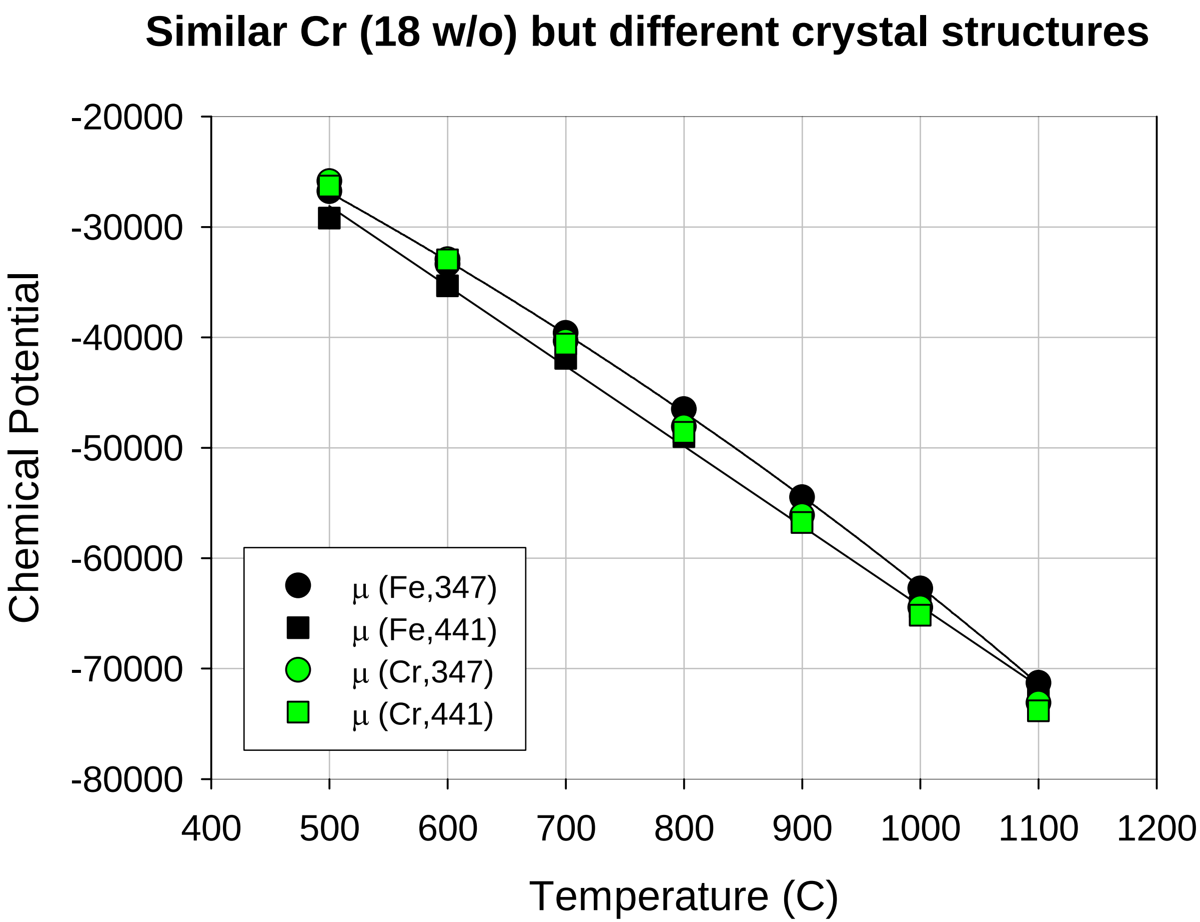
Note that the chemical potential for Fe and Cr are about the same in 347ss while in IN600 Cr has a much higher chemical potential.

Comparison of Chemical Potential



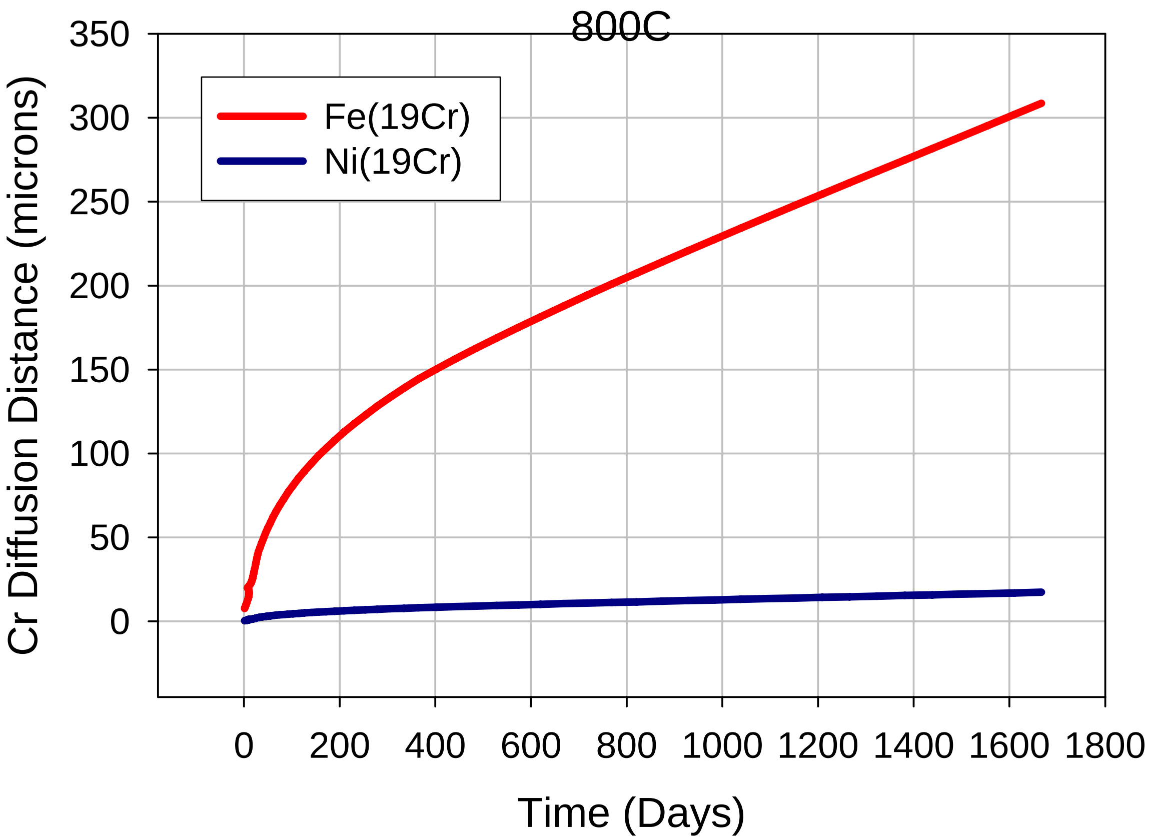
Note that the chemical potential for Fe and Cr are about the same in 347ss while in AL2025 Cr has a much higher chemical potential.

Comparison of Chemical Potential

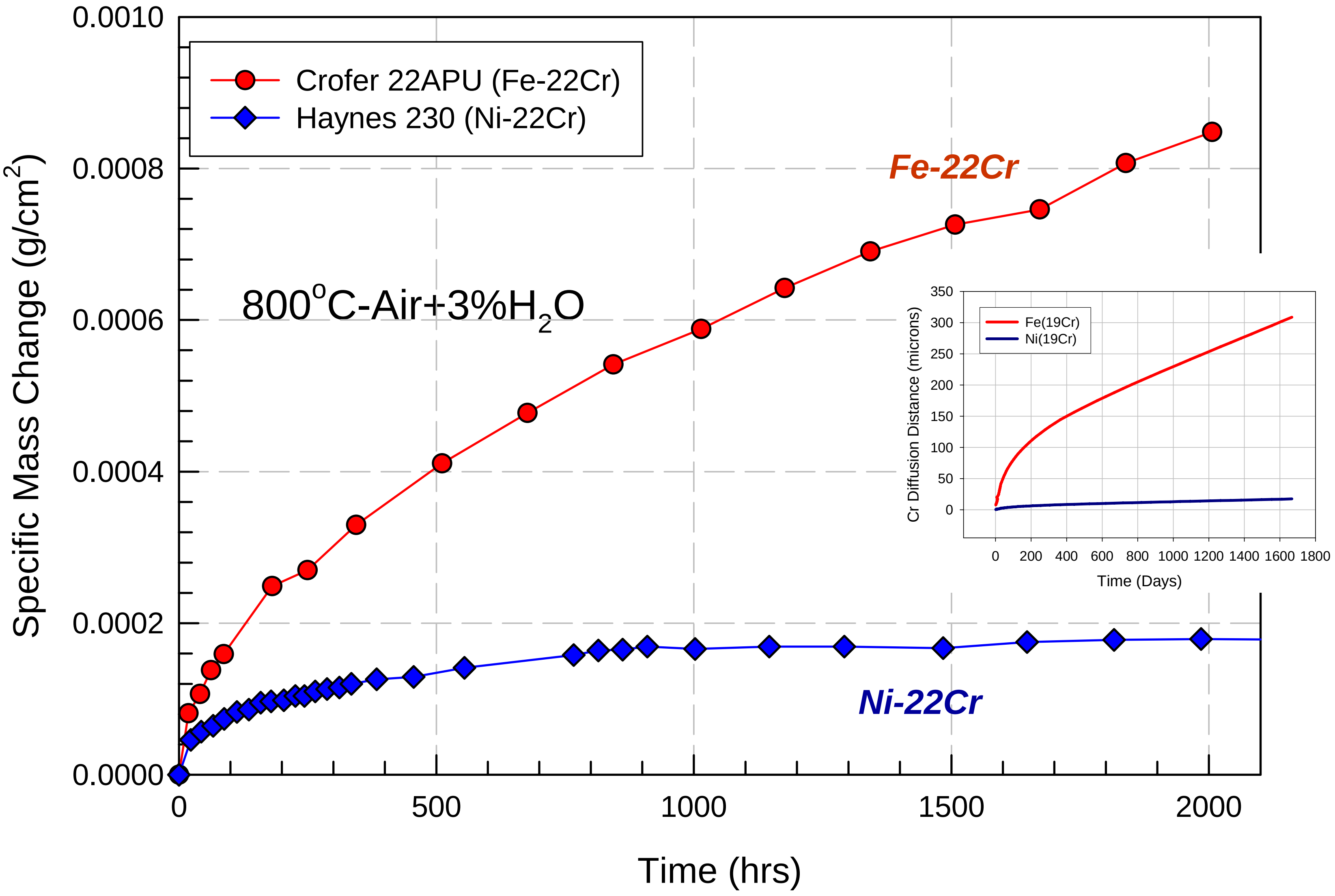

Similar Cr (18 w/o) but different crystal structures

Here we see that the chemical potential for Fe and Cr are about the same in 347ss and in 441ss. However, recall that the ferritic structure (BCC) allows for much greater diffusion rate thus providing a protective chrome rich layer.

Cr Diffusivities In BCC vs. FCC Structures



Cr Diffusivities In BCC vs. FCC Structures



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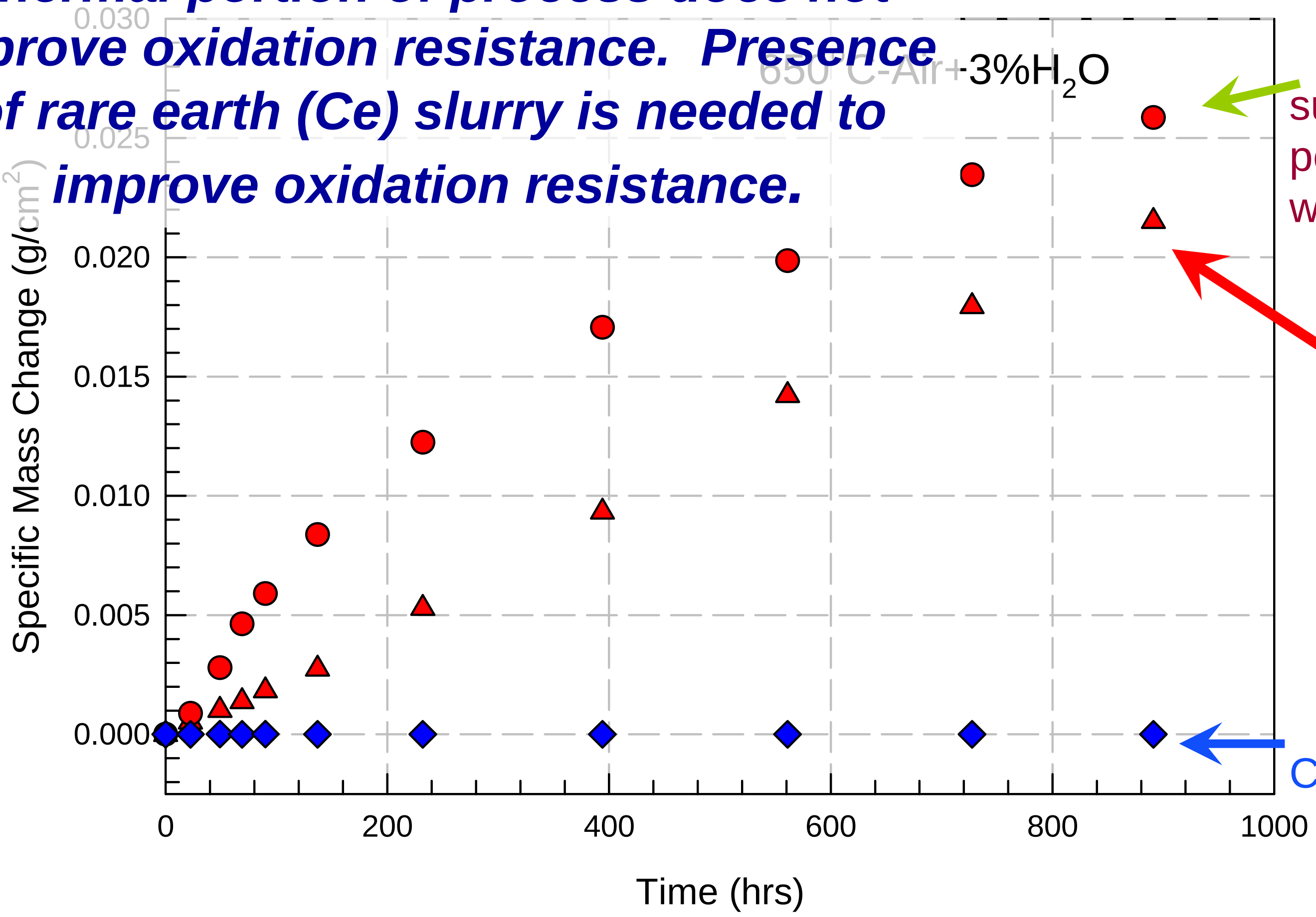
Influence of Thermal Portion of Surface Treatment

Thermal portion of process does not improve oxidation resistance. Presence of rare earth (Ce) slurry is needed to improve oxidation resistance.



HR 52-TC

subjected to thermal portion of treatment w/o Ce modification

HR 52

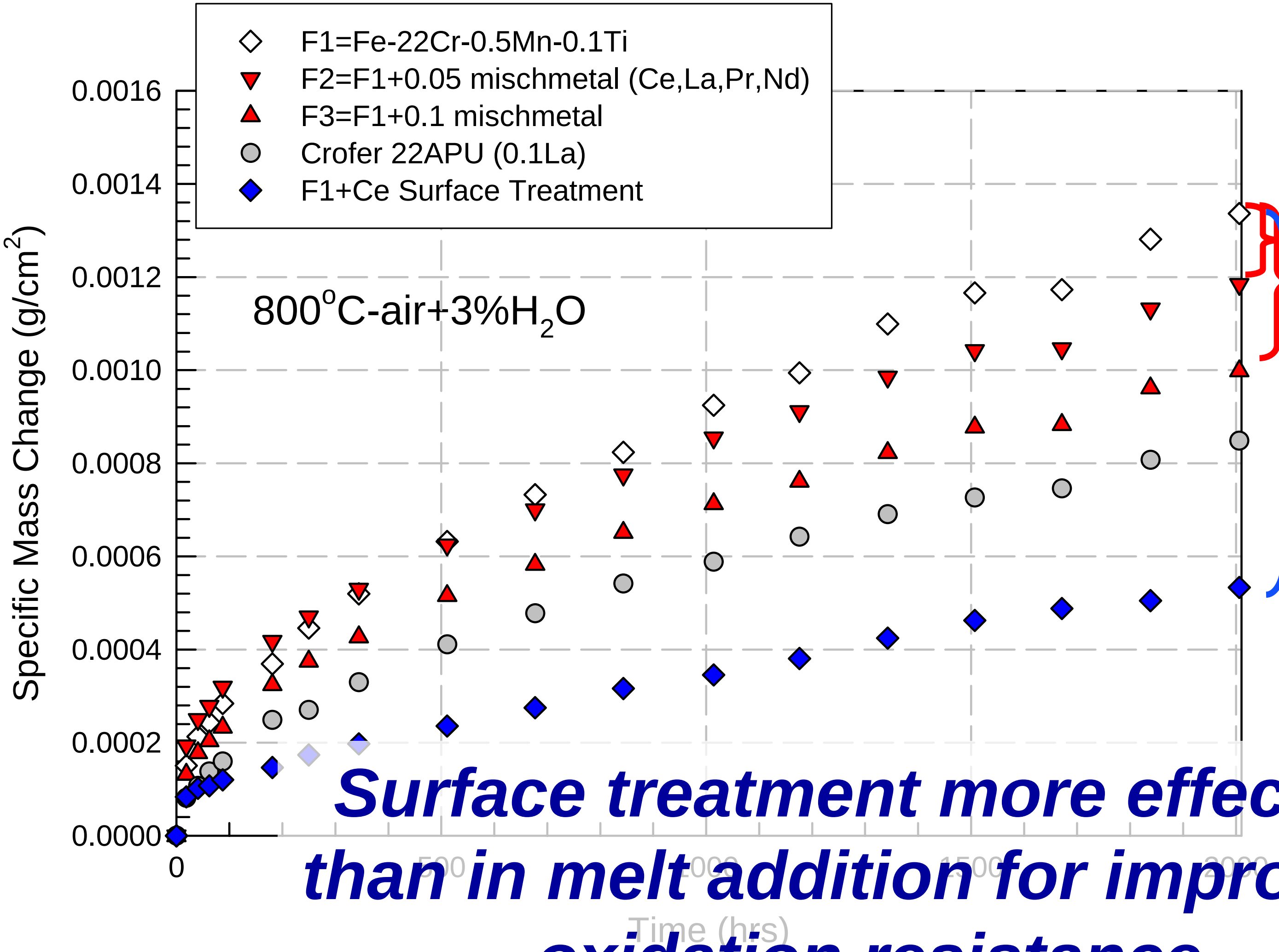
HR 52+Ce

Ce surface modified

HR52 & HR52TC → Fe_2O_3

HR52+Ce → Cr_2O_3

RE Alloying Additions vs. Surface Treatment



12 to 26% reduction in mass gain w/ melt addition

60% reduction in mass gain w/ surface treatment

Surface treatment more effective than in melt addition for improving oxidation resistance

Summary/Conclusion

- Base Alloy Behavior explained in terms of chemical potentials and diffusivities.
- Ce surface treatment → suppressed the formation of Fe_2O_3 formation in 347/321 → promoted formation of adherent Cr_2O_3 scales
- Ce surface treatment retard Cr_2O_3 growth rate and internal oxidation

? Why?

? CeO_2 surface particles that effect oxide nucleation→. promotes nucleation of Cr_2O_3 scales?????

? Chemical potentials of minor constituents are increased (such as Ti)→ slows subsequent diffusion????

Current and Future Work

- **LONG TERM EXPOSURES**
  - ACCELERATED TESTS ON CHROMIA FORMERS
- **BETTER CHARACTERIZATION OF SCALES**
- **MECHANICAL PROPERTIES AND CREEP BEHAVIOR**

Room Temp	σ_{UTS} (MPa)	σ_{YS} (MPa)	Elongation (%)
347	662	287	52
347+Ce	649	257	47

Courtesy of Karol K. Schrems, NETL, 2006