Bespoke Materials Surfaces

Beth L. Armstrong, Dongwon Shin,

J. Allen Haynes and Bruce A. Pint

Materials Science and Technology Division

Oak Ridge National Laboratory

28th Annual Conference on Fossil Energy Materials

Pittsburgh, Pennsylvania

May 21, 2014

This research is sponsored by
U. S. Department of Energy, Office of Fossil Energy
Crosscutting Materials Program

Fireside Corrosion, Particularly under Low NOx Firing Conditions, Limits Boiler Performance

- Temperatures up to 600ºC
- Aggressive species
  - Sulfur
  - High and low pO_2
  - Alkali
  - Ash
- Thermal fatigue cracking issues with some overlays
  - decreased heat flux

weld overlay

- Need better methodologies for tailoring and producing highly protective, thin, cost-effective surface treatments
- Project expected to use ORNL's experience in synthesis, high-temperature corrosion, and physical and mechanical properties to define material systems approaches to such

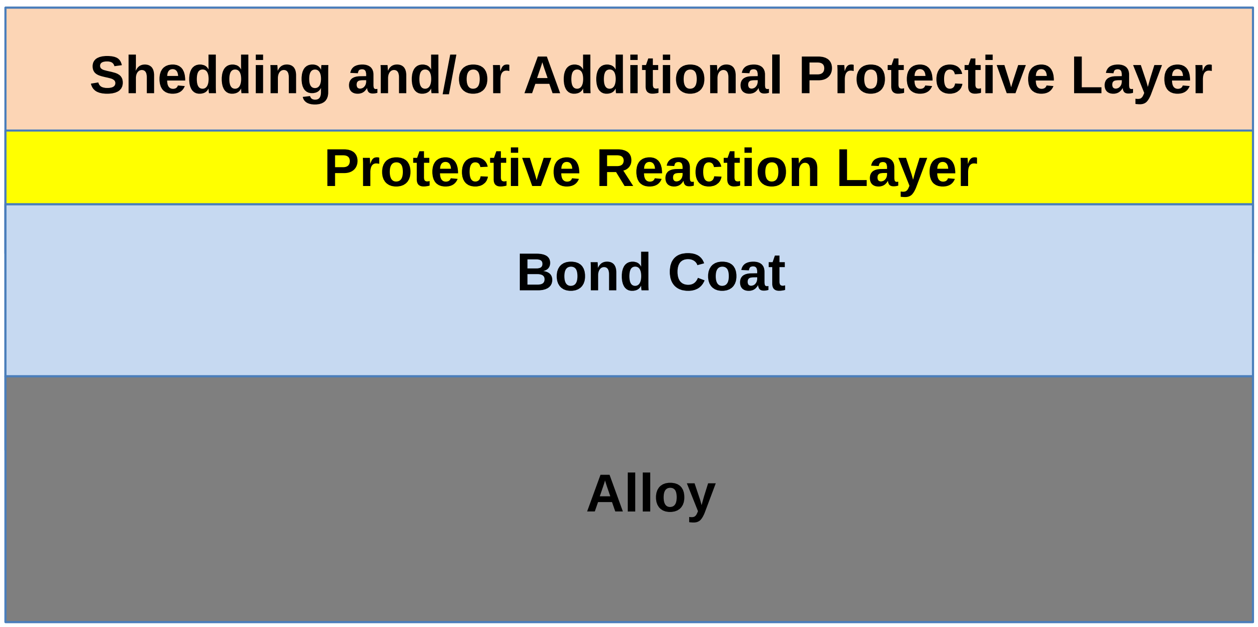
This Project Focuses on Fireside Surface Protection

- Objective: *Develop holistic system approaches to synthesis of TAILORED material surfaces that are corrosion resistant, have appropriate physical properties, and can be fabricated easily and economically*

- Based on understanding and control of key factors affecting
  - synthesis
  - performance
    - sulfidation/oxidation resistance
    - thermal expansion matches
    - thermal conductivity (thin oxide coating?)
    - ash/slag shedding (how to shed and remain durable?)

Overall Systems Approach to Achieve Properties Not Available in One Coating

Generic Example of a High-Temperature Corrosion Protection System



Approach

- Modeling to guide material selection and help explain observations
  - phase stabilities, reaction products
  - CALPHAD
    - Evaluate Gibbs energies of phases in the lower order systems
    - Extrapolate to higher order system to predict phase stabilities at any given conditions (T, P, wt. %, …)
- Experimental Verification – synthesis, characterization, performance evaluation
  - Focus on building an affordable coating system: slurry coatings
  - Initial experimental coatings guided by what we know works
  - Characterization of metal surface properties (roughness, microstructure, composition, etc.) and coatings thereon
  - Evaluation and testing of new candidate materials/surfaces
- Coordination with other Fossil Advanced Research Materials (ARM) projects

Project failed Go/No-Go milestone: Ending September 2014

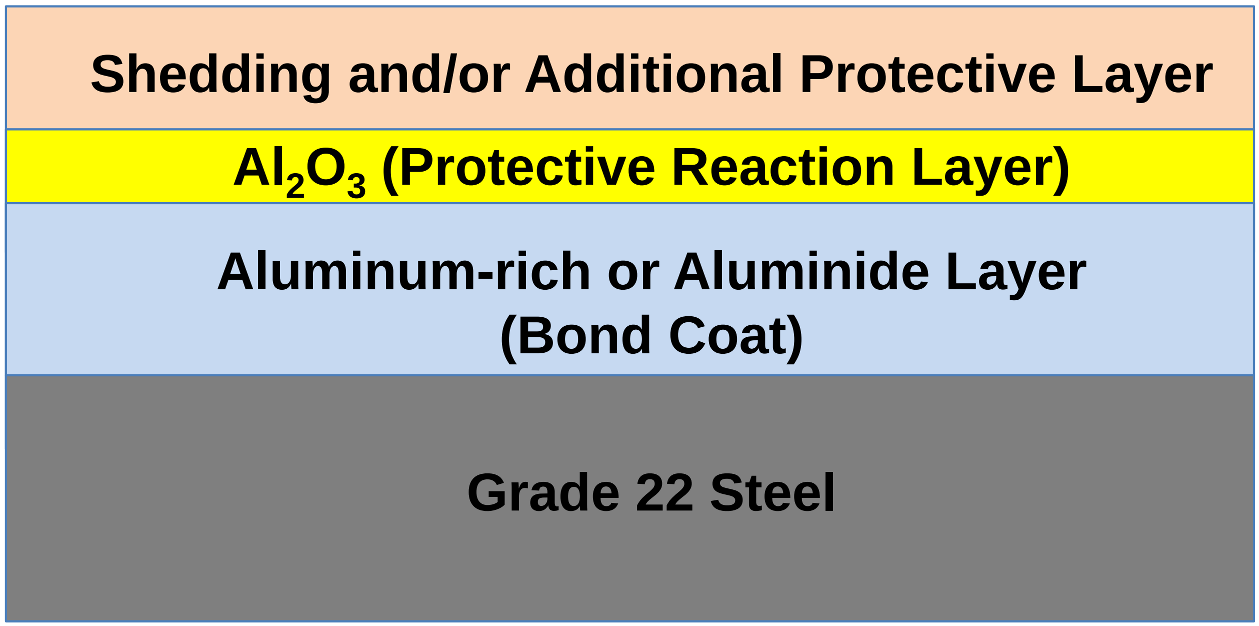
- Complete experimental and modeling work on approach to multi-functional surface modification of steels and produce first set of specimens using such. (8/30/13)
- Complete a Go/No-Go analysis on effectiveness of approach to multi-functional surface modifications (9/30/13)
- Complete a review paper of the major research worldwide as well as the state of the art commercial coatings for boiler and high temperature heat exchanger tubes (7/30/13)
- Complete evaluation of the physical properties and coal ash corrosion resistance of a set of surface modified steels and assess effectiveness. (9/30/13)
- Assess effectiveness of coating approach in proferring predicted performance improvement and define next steps (9/30/13)

This Project Focuses on Fireside Surface Protection

- Objective: *Develop holistic system approaches to synthesis of TAILORED material surfaces that are corrosion resistant, have appropriate physical properties, and can be fabricated easily and economically*

- Based on understanding and control of key factors affecting
  - synthesis ← work was hung up here
  - performance ← never got to here
    - sulfidation/oxidation resistance
    - thermal expansion matches
    - thermal conductivity (thin oxide coating?)
    - ash/slag shedding (how to shed and remain durable?)

Starting Point was Aluminum-Containing Bond Coating



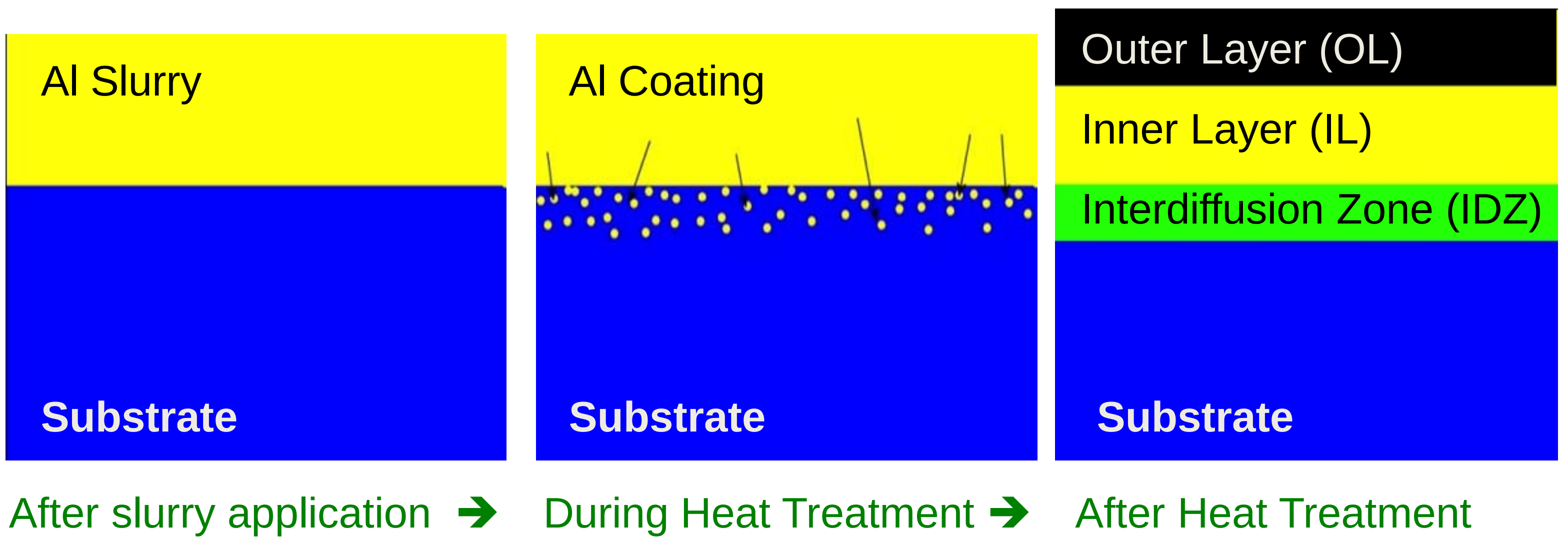
Slurry coating low Cr steel was easier said than done

First Layer: Al-rich Coatings on Gr22 Steel (2.25Cr-1Mo), Relevant to Waterwalls

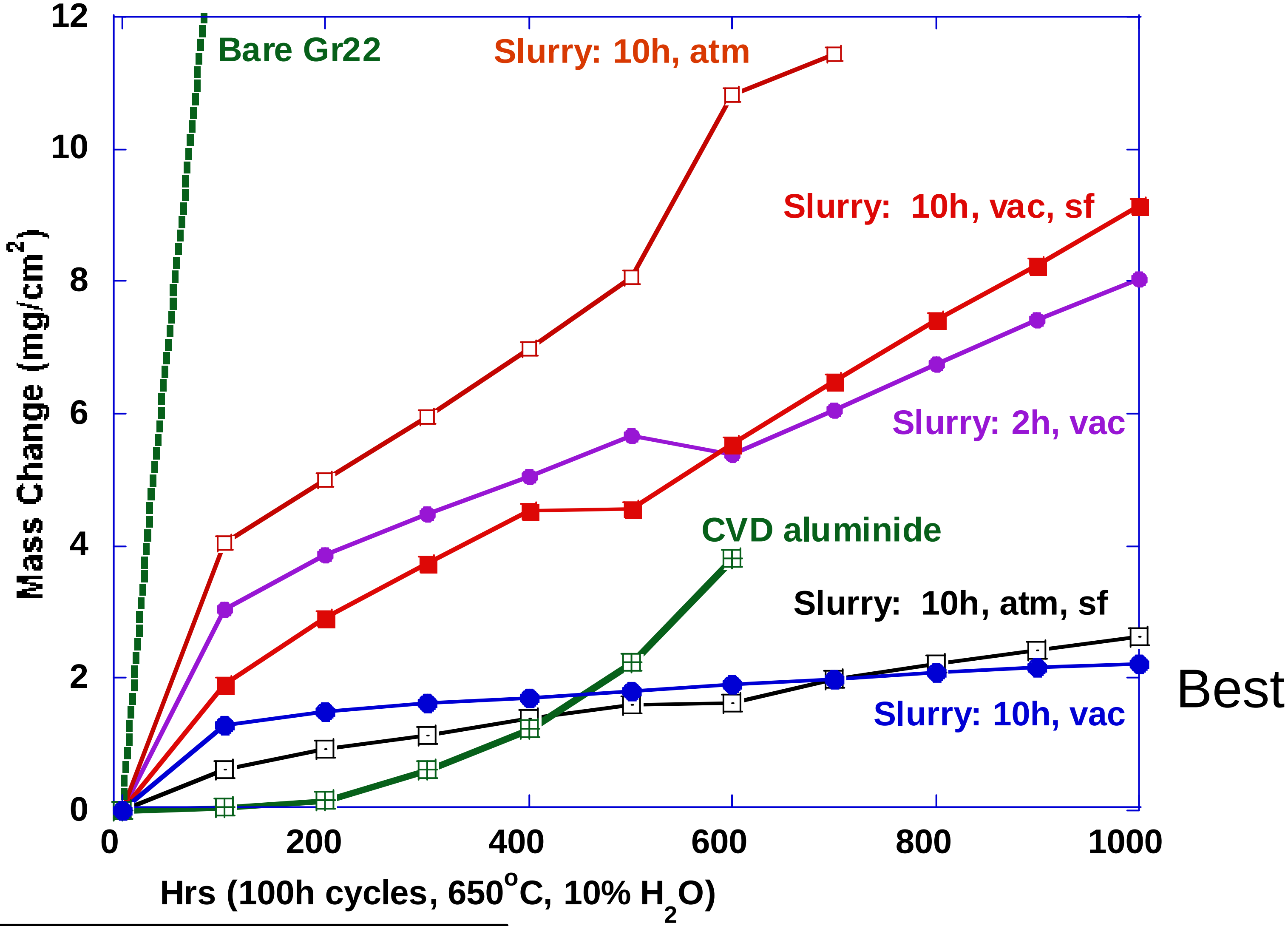
- Building on a foundation of previous FE-ARM aluminide work at ANL, ORNL, Lehigh, Foster-Wheeler, and EPRI using a variety of synthesis techniques
  - Good-to-excellent in highly reducing conditions, oxidation-sulfidation, water vapor
  - Problematic with ash
- ORNL's slurry aluminide coating process as an easy-to-apply route
- Examination of resulting microstructures
  - Formation of stable surface dependent upon processing conditions
  - Coating efficacy dependent upon alloy composition
- Testing
- Refine and tailor
- Examine other compositions and structures

Integrated Architecture is more complicated than earlier schematic

- Slurry is applied
- Heat treatment leads to diffusion of Al into the substrate (enriched surface and/or formation of another phase)
- Excess Al is removed after heat treatment
- In high-temperature environment, protective Al-rich scale forms

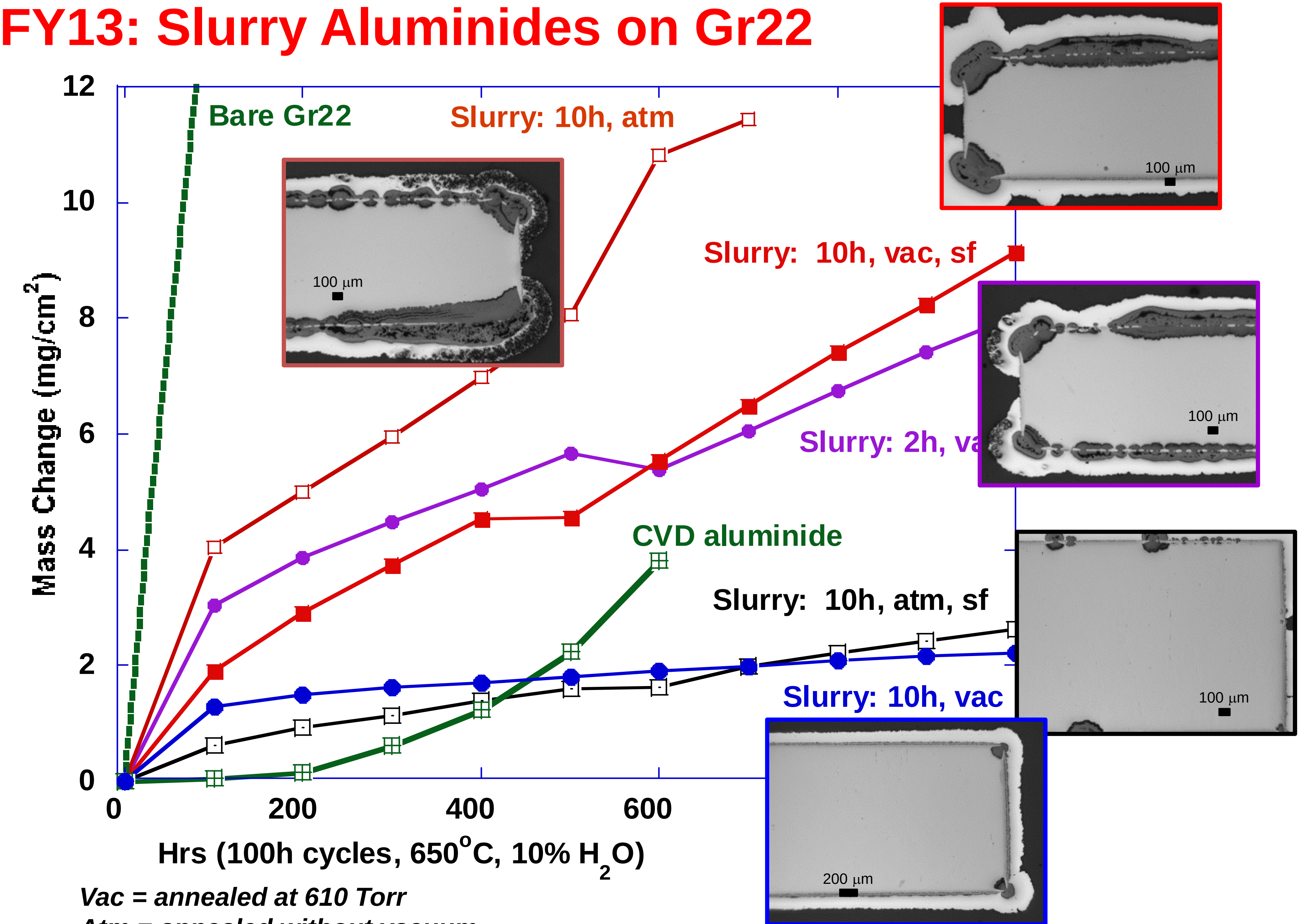


FY13: Parametric study of slurry coating process yielded no clear path forward



Vac = annealed at 610 Torr
Atm = annealed without vacuum
sf = surface finishing after annealing

FY13: Slurry Aluminides on Gr22



Vac = annealed at 610 Torr

Atm = annealed without vacuum

sf = surface finishing after annealing

FY14 Wrap-up Activities

Complete work by September 2014.

- 1. Prepare review article on state of the art for coatings for boilers and high temperature heat exchanger tubes (Milestone #1).
  - Completed January 2014 (submitted as ORNL TM report)
- 2. Additional fabrication, oxidation testing and characterization of slurry coatings to better define preferred coating strategies.
  - In progress
- 3. Complete a peer-reviewed publication highlighting the effect of the role of coating processing conditions on the efficacy of oxidation-resistant slurry diffusion coatings (Milestone #2).
  - September 2014
- 4. Proof of concept: Deposit slurry YSZ or mullite over an alumina-forming alloy for ash testing.
  - September 2014

Highlights from Literature Review

- Reviewed literature on slurry aluminides from 1960's to present.
- Slurry work in the1960's and 70's focused on coatings for Ni- and Co-based alloys.
  - Maxwell and Gabriel (United Aircraft Corp.) patented a FeCrAlY slurry coating for Ni- and Co-based superalloys for the USAF (D. H. Maxwell and J. M. Gabriel, "Slurry Coating Superalloys with FeCrAlY Coatings," U.S. Patent # 3,741,791, 1973).
  - Slurry Fe-Cr-Al could be an area of potential future interest.
- Very little literature in this area in the 1980's.
- In the 1990's United Technologies Corp. and Sermatech patented and published modifications to Al-based slurry technologies.
- In 1996, the National Research Council formed a committee on Coatings for High-Temperature Structural Materials and published a report on the trends and opportunities. Coatings for both metals and ceramic systems were highlighted. However, overlay coatings were the focus and slurry coating techniques were not discussed.

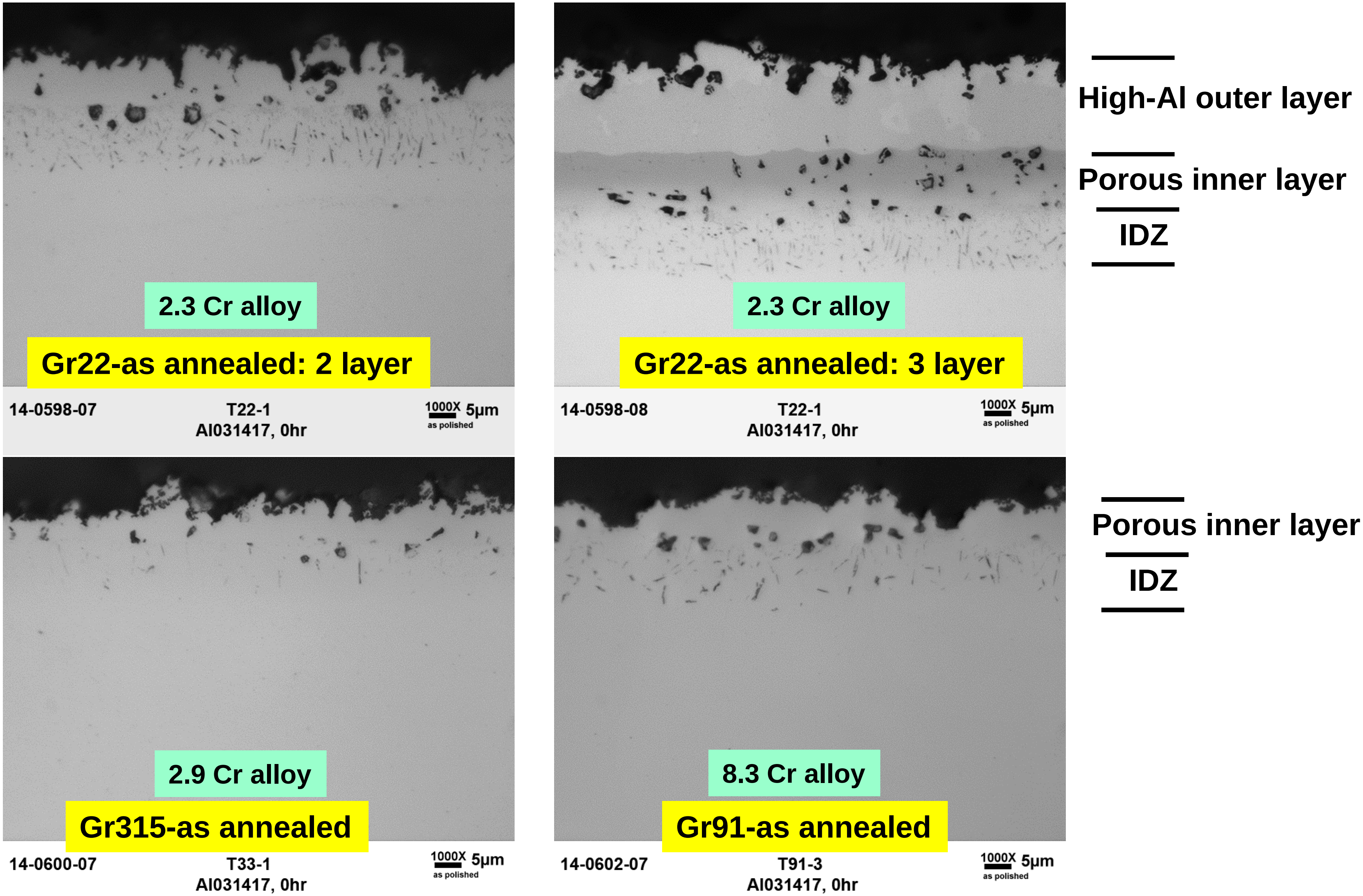
Highlights from Literature Review

- In the early 2000's, a move from superalloys to alternative, iron-based coatings for steel was evident - particularly for slurry-applied coatings on ferritic steels.
  - Work was driven primarily by the European COST Action 522: Ultra Low Emission Power Plant into the 21st Century.
  - The work of Agüero et al. at the Instituto Nacional de Tecnica Aerospacial in Spain demonstrated a resurgence of interest in slurry-based coatings for metallic substrates.
- DOE funded work on ceramic and metallic slurry coatings.
  - Included slurry aluminizing of cast austenitic stainless steels at ORNL.
- Sermatech introduced vapor phase slurry coating process.
- Slurry aluminizing of Ti-based alloys has been reported in the past decade.
- Sixteen currently active US industrial sources of slurry coating technology were identified in the review.

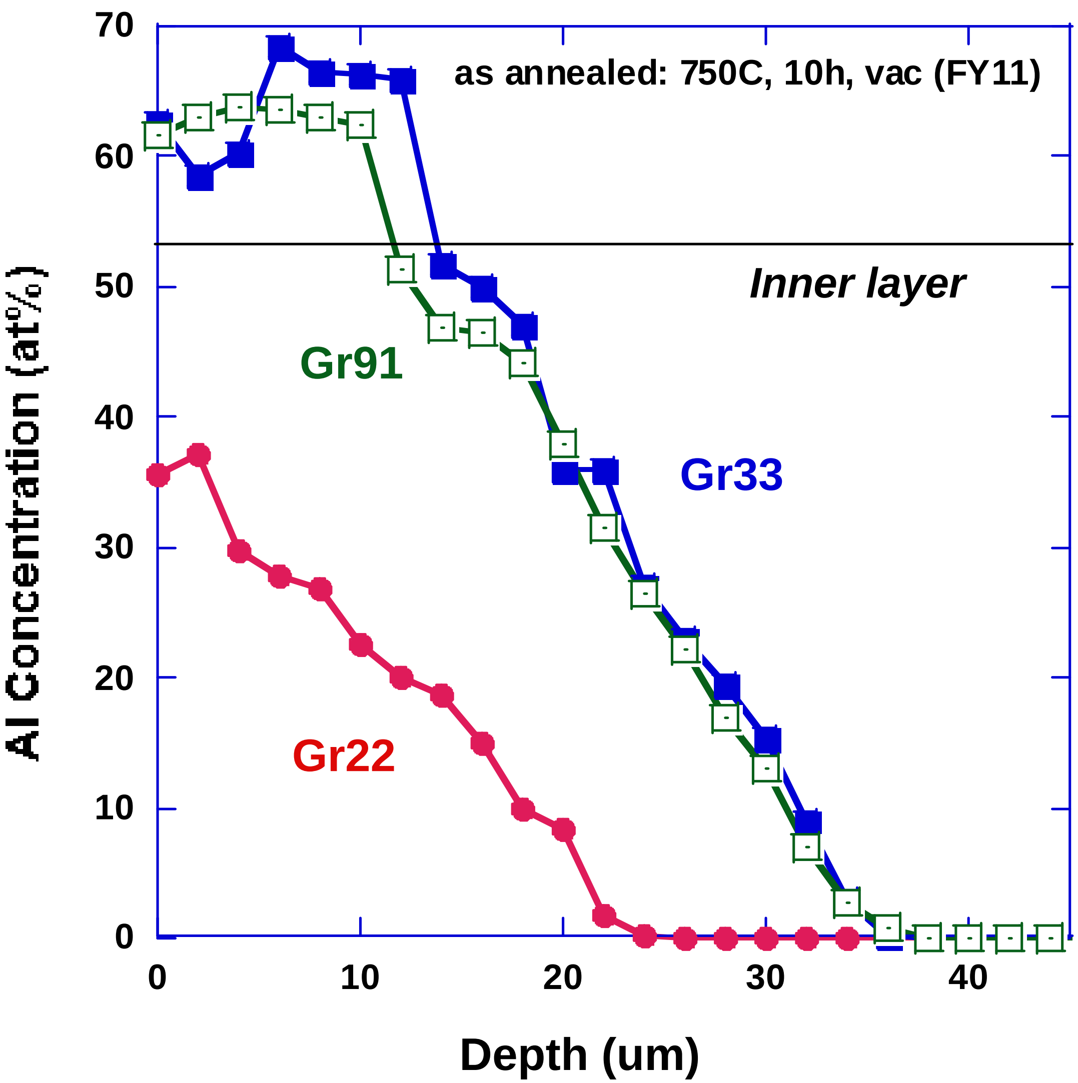
FY14: 650°C Cyclic Oxidation Evaluation

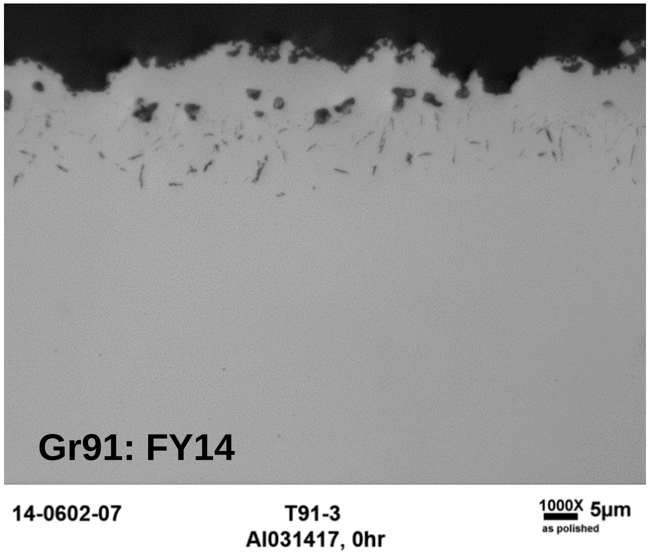
- Coatings: Slurry aluminide dip coatings (aqueous, ORNL)
- Alloys coated
  - Gr. 22 (Fe-2.3wt.%Cr-0.9Mo)
  - Gr. 315 (Fe-2.9Cr-0.7Mo-1.7W)
  - Gr. 91 (Fe-8.3Cr-0.9Mo)
  - CF8C-Plus (cast aust. steel) (Fe-19.2Cr-12.8Ni-4Mn-0.25N)
- Slurry coating heat treatment (best conditions from FY13)
  - Annealing: 750°C
  - Time: 10 h
  - Environment: argon (Ar) at 610 Torr
- Oxidation Testing Conditions:
  - 650°C, 100 h cycles, 10% water vapor
  - Low cost initial evaluation, rapid attack of base alloy in wet air

Microstructures of FY14 As-Deposited Slurry Aluminide Coatings (750°C, 10h, 610 Torr)

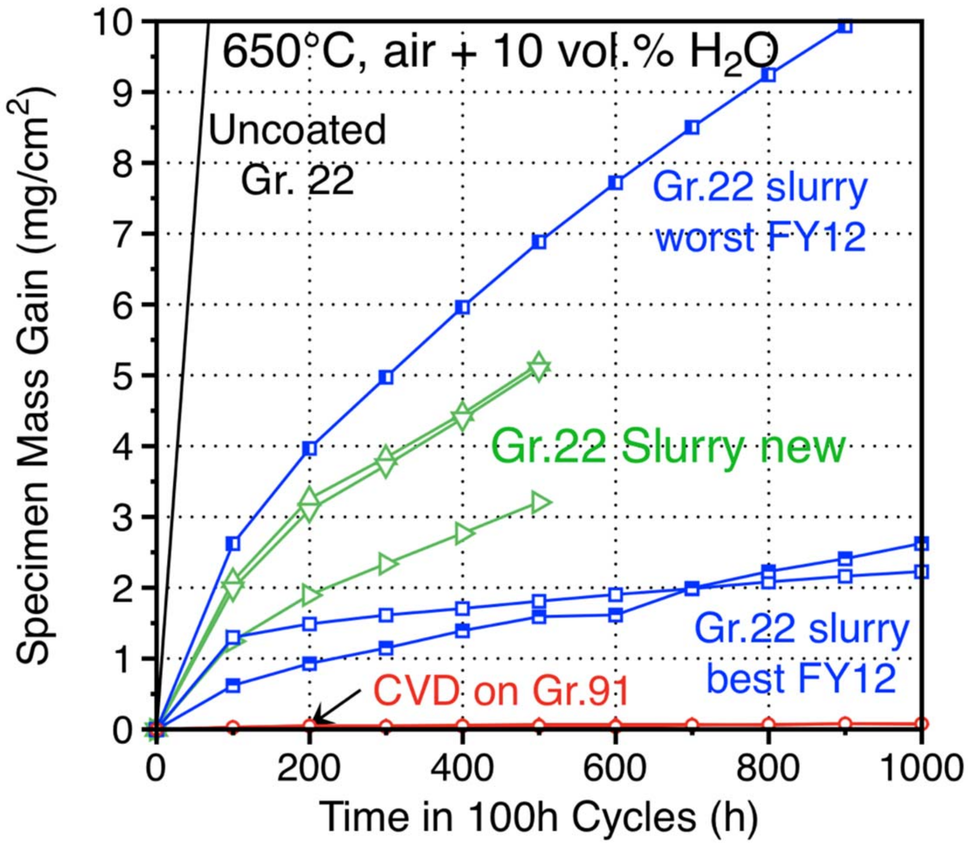


Elevated Al contents of slurry coating inner layer on higher-Cr ferritic steels





650° C oxidation behavior of slurry coated Gr.22 was similar to FY12 results

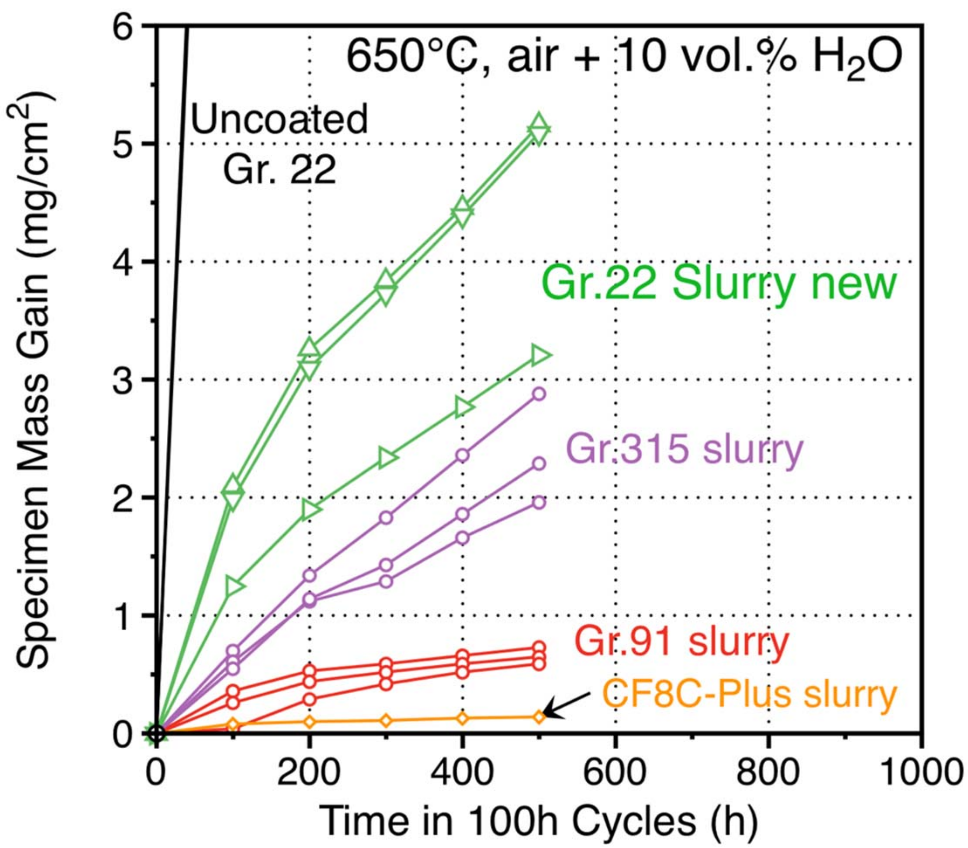


Air+10%H_2O:

- Rapid attack of uncoated Grade 22
- Quick indication of coating performance

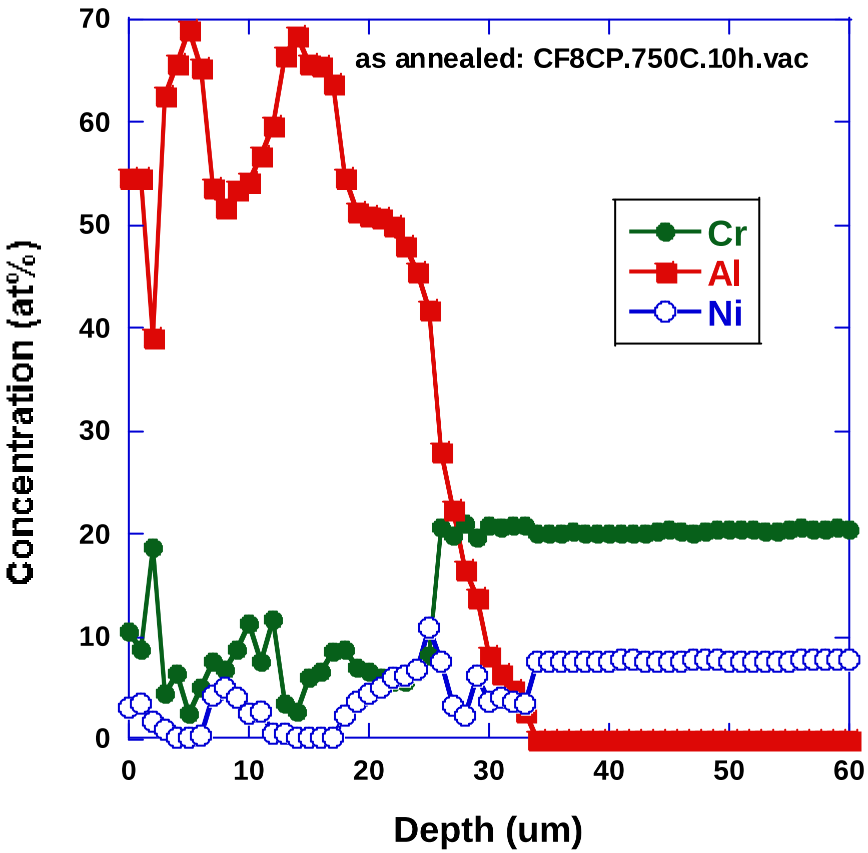
- FY14 slurry batch showed more rapid mass gains than best FY12 slurry coatings.
  - Variability: coating & surface preparation still not optimized

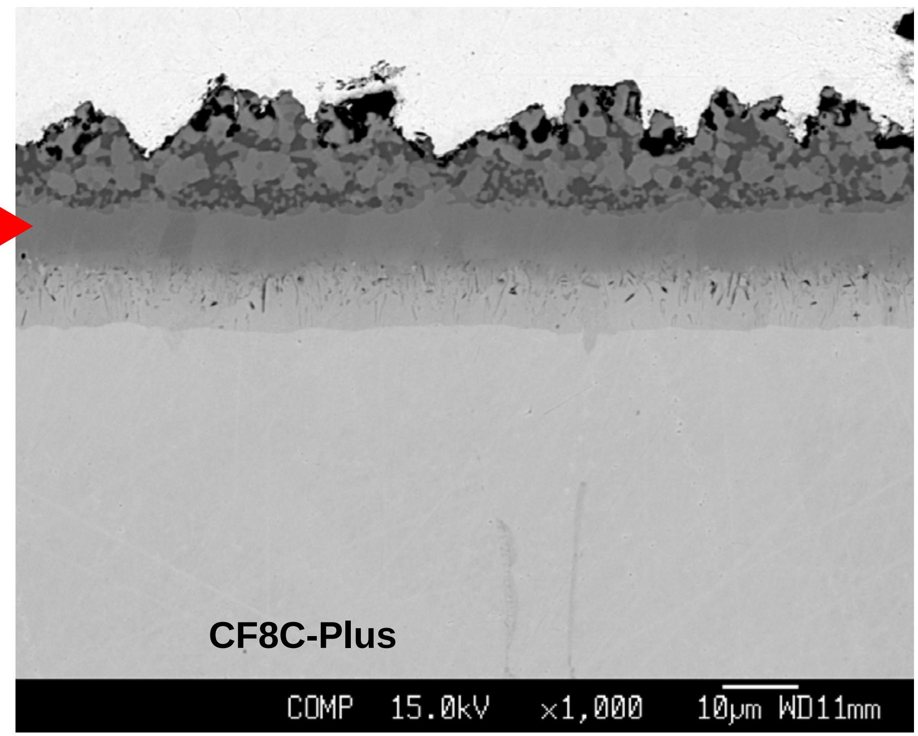
Substrate Cr content strongly influenced oxidation behavior of slurry aluminides at 650° C/air+10% H_2O



- Coatings on Gr.315 showed lower mass gains than the same slurry coating on Gr22.
- Slurries on Gr91 exhibited significant reductions in oxidation mass gain in short-term testing.
  - Suggests that Al-Cr slurry coatings may provide superior oxidation protection for Gr.22.
- Slurry aluminide on CF8C-Plus (austenitic) showed substantial further reduction in oxidation mass gain.
  - 19Cr, 13Ni

Composition profiles from a prior slurry coating batch on CF8C-Plus (750°C, 10h, 610 Torr)





Coating

Peak Al (inner layer): ~55 at%

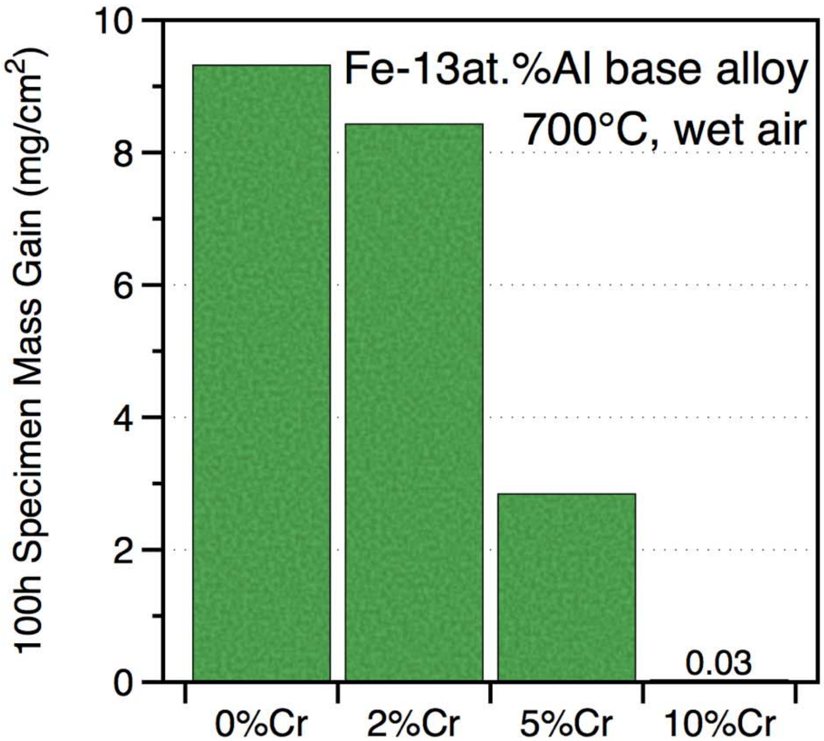
Avg Al (inner layer): 49.1±4.0 at%

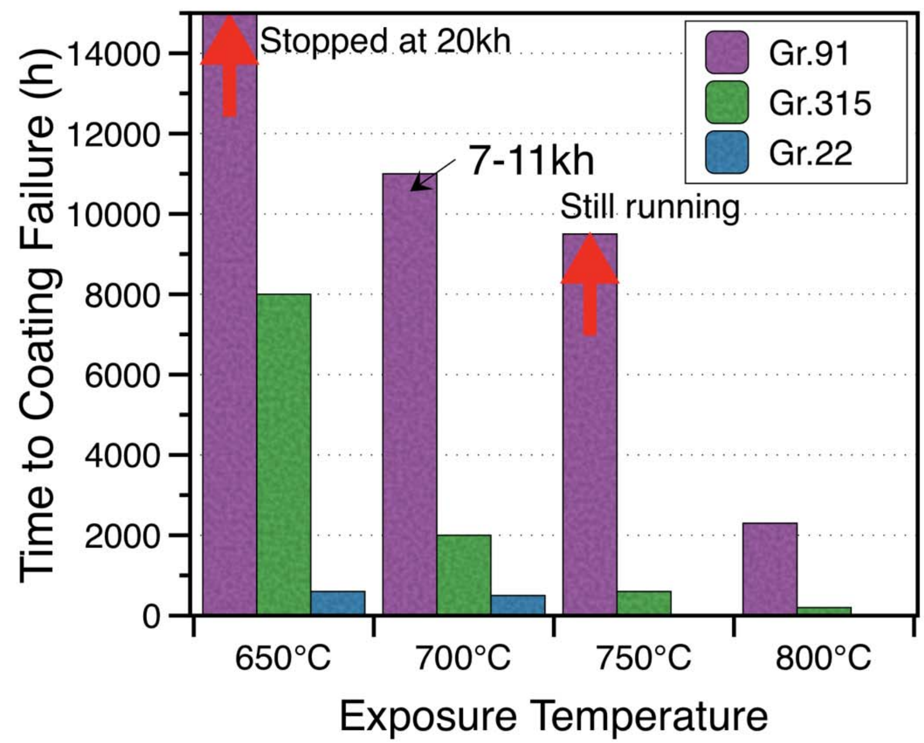
Avg Cr (inner layer): 6.8±1.1 at%

Summary of Slurry Coating Results

- Simple slurry aluminides were demonstrated to provide a paint-on, low-cost route to oxidation protection of steels, but may not be appropriate for long-term protection on low-Cr steels such as Gr.22 at 650° C.
  - Unclear why Al content higher on 3Cr and 9Cr substrates
  - An Al-Cr slurry should be investigated for Gr.22.
  - Fe-Cr-Al likely superior to Fe-Al but may cause problems in sulfidizing environments (negative effect of Cr)
  - Slurry process needs to be optimized.
- Current simple slurry aluminides show promise for higher-Cr alloys at 650° C

Effect of Cr has been studied previously

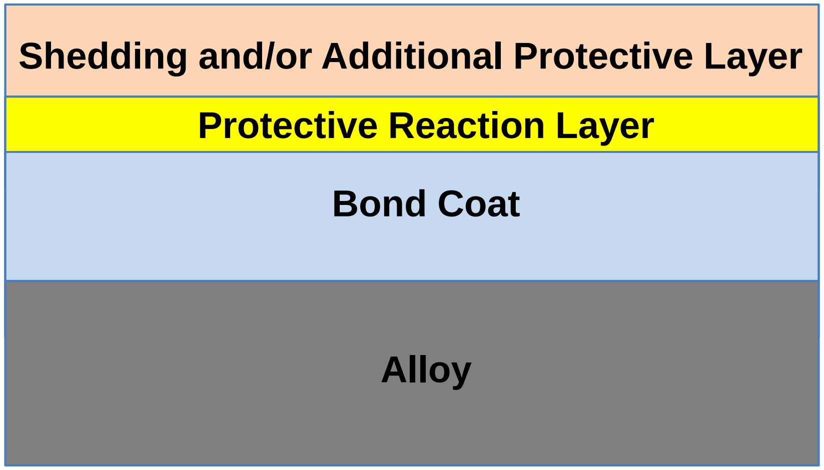




- Model alloys & CVD coatings both showed extreme effect of substrate Cr content at 650° -700° C using air+10%H_2O

Summary

- Modeling, synthesis, corrosion testing, and characterization
  - Project sidetracked by Gr.22 synthesis step
- Demonstrated that <u>simple</u> slurry aluminides can provide improvements in oxidation protection at 650° C vs. bare steel but may not be an adequate long term solution for low Cr alloys
  - Cr-Al coatings may be necessary for low-Cr steels
  - Processing & structure significantly affect efficacy of coating
- Conclude with proof of principle: A low-cost YSZ and/or mullite slurry coating deposited on a pre-oxidized FeCrAl rod for testing in coal-ash corrosion test.



Acknowledgements

Kevin Cooley, John Henry, Sebastien Dryepondt, Donovan Leonard, Jim Keiser, Dane Wilson
Peter Tortorelli at ORNL

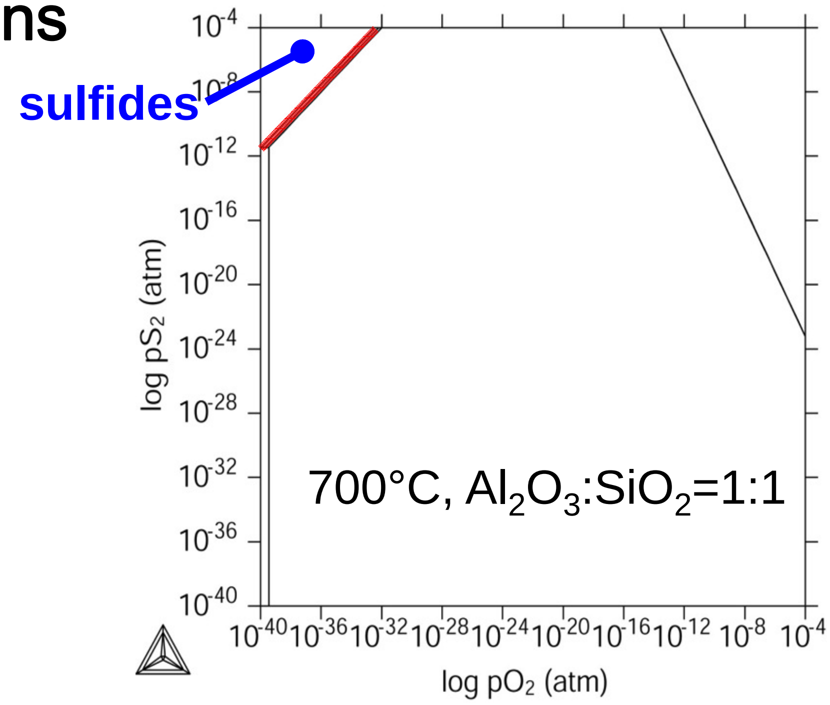
Vito Cedro at NETL

This research sponsored by
U. S. Department of Energy, Office of Fossil Energy
Crosscutting Materials Program

Backup Slides

Where Do We Go From Here?

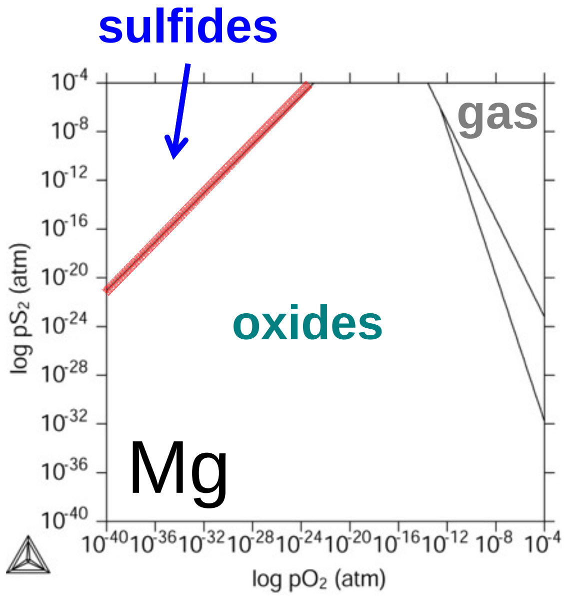
- Synthesis
  - Solution-based outer layer
    - o Examine/model incorporation of Cr, Mo, Si into existing coating for ash corrosion resistance
    - o Form additional protective oxide or sulfide scale
    - o Evaluate composite coatings (aluminide/silicide) and/or other compositions

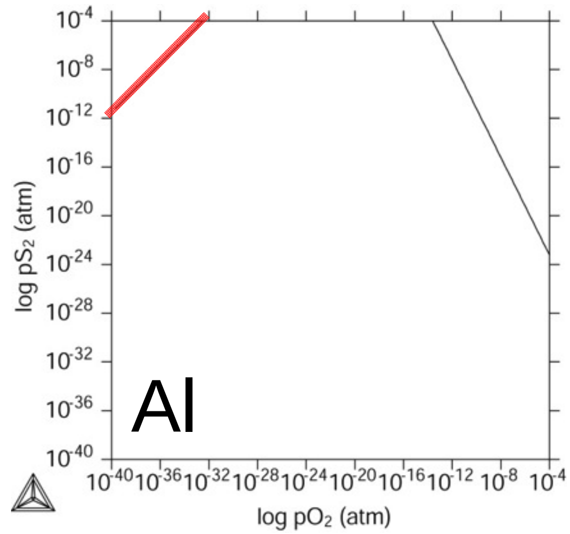


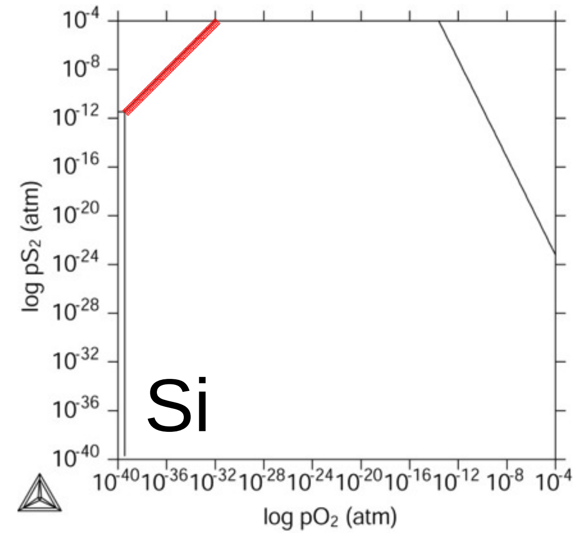
Where Do We Go From Here?

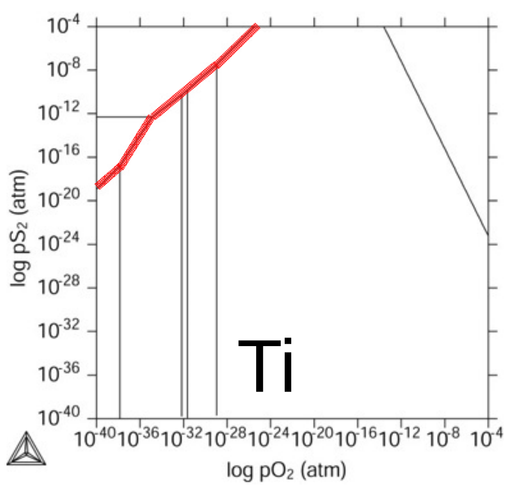
- Synthesis
  - Solution-based outer layer
    - Examine/model incorporation of Cr, Mo, Si into existing coating for ash corrosion resistance
    - Form additional protective oxide or sulfide scale
    - Evaluate composite coatings (aluminide/silicide) and/or other compositions
  - Examine surface structure/composition control as a non-stick approach, e.g., slag-shedding coatings
- Testing

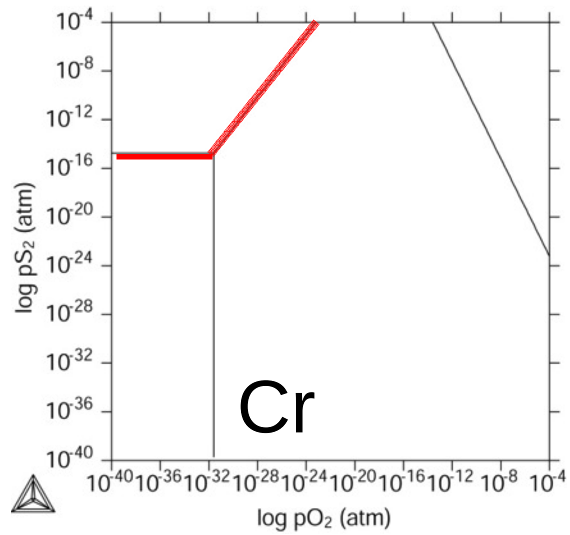
Calculation of Appropriate Metal-S-O Stability Diagrams (700° C)







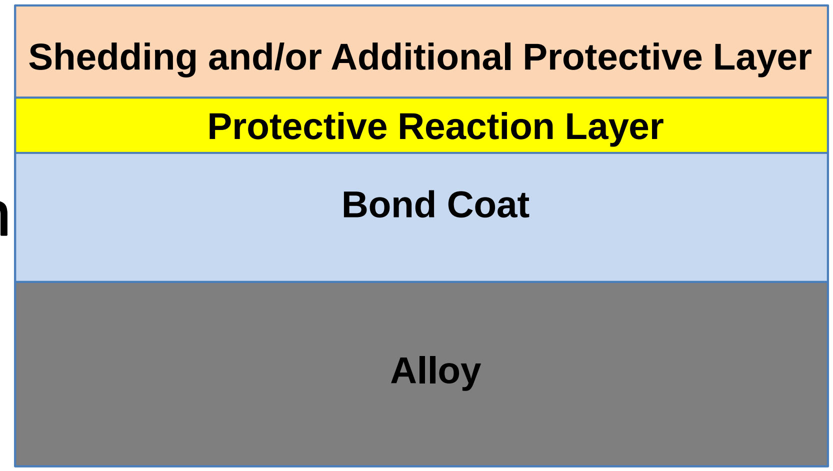




- 19 binary metal oxides considered
- Diagonal line represents oxide/sulfides phase boundary
- Al_2O_3 and SiO_2 are thermochemically stable

Future Work – Building and Tailoring the Protection System

- Sulfidation testing in $H_2/H_2S/Ar$ (4% H_2, 0.16 % H_2S and bal. Ar) environment at 650° C for 100 h 500 h, 1000 h, and potentially 2000 h
  - Bare Gr22
  - Slurry aluminide coated Gr22
  - Preoxidized slurry aluminide Gr22
  - Al_2O_3-SiO_2 formers
- Ash corrosion and top-coat shedding layers

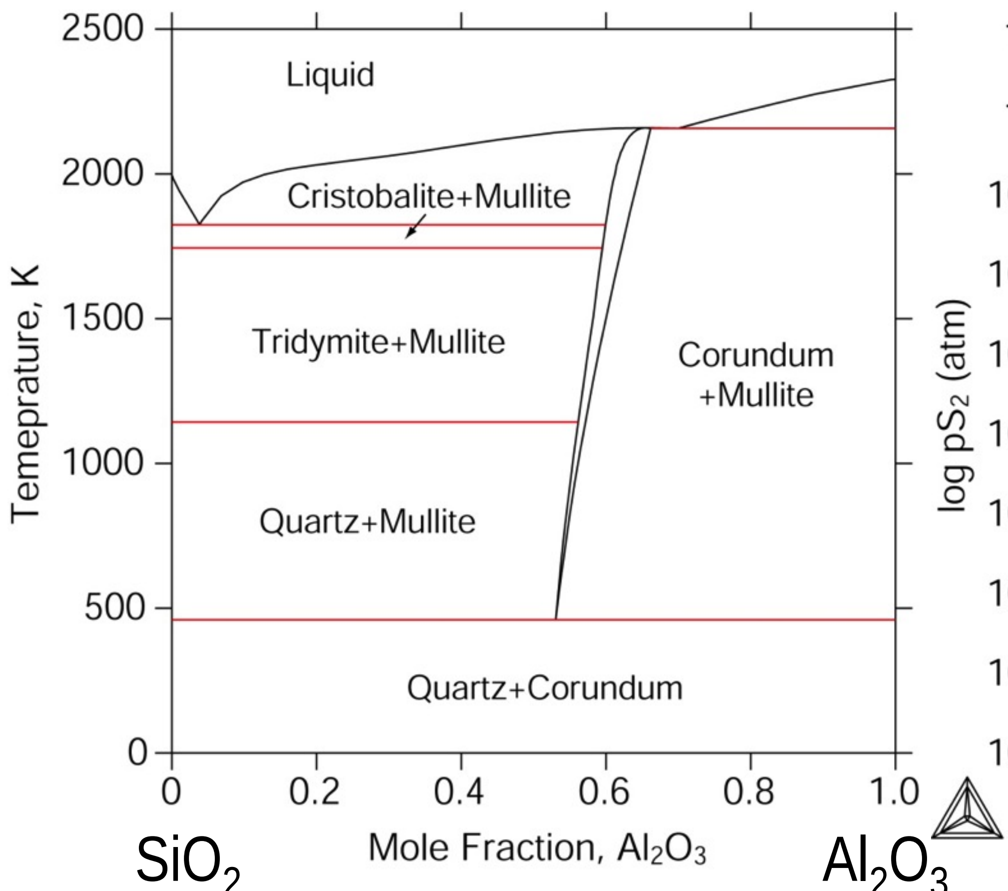


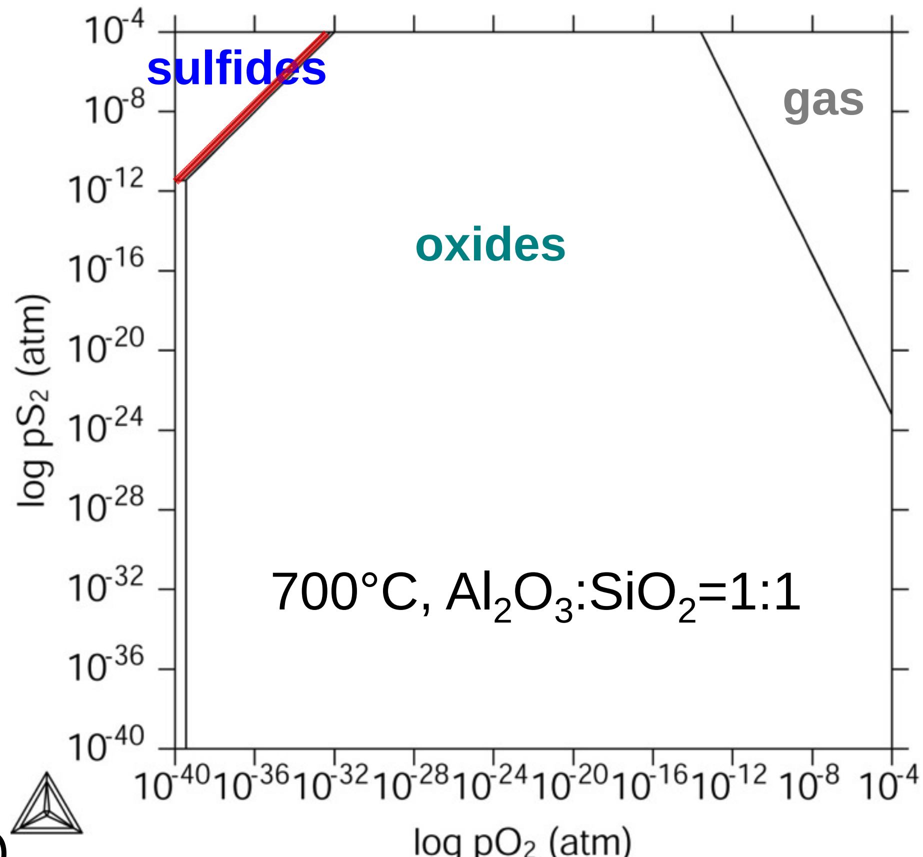
SiO_2 as the Sulfidation Resistant Layer

Thermochemical stability of Al_2O_3-SiO_2 was examined

Large phase field with SiO_2 polymorphs and mullite

Phase stability is not affected significantly by different Al_2O_3 and SiO_2 ratios

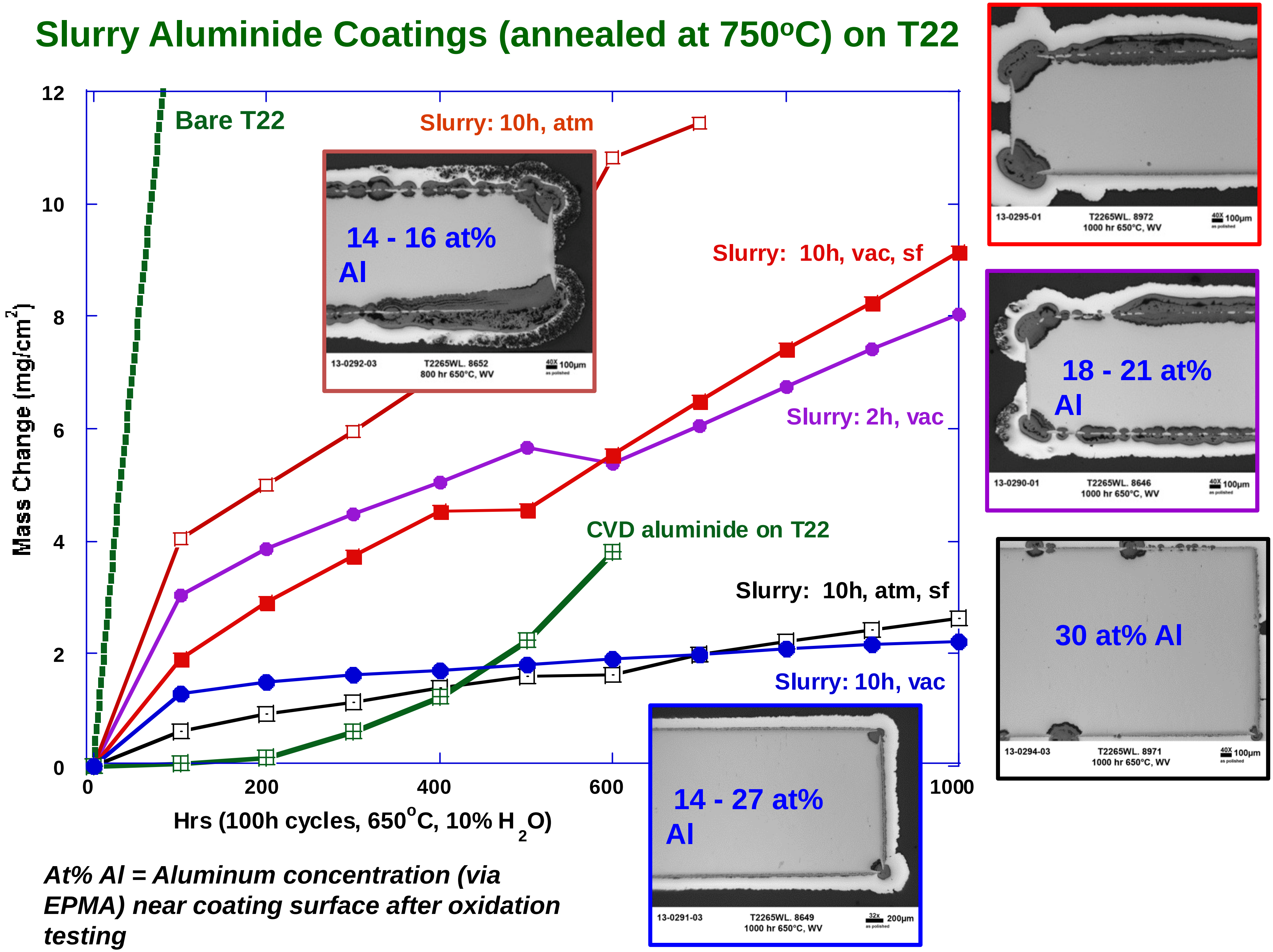




But We've Tried That Coating Before and It Didn't Work…

- Coatings/surfaces are dependent upon
  - Processing (resulting microstructure, density, contaminants…)
  - Substrate (composition, structure, CTE…)
- Our surface treatment approach
  - Slurry based
  - Robust, non-line of sight, industrially viable (spray, dip, paint…)
  - Can be adapted to multiple substrate and surface chemistries
  - Multiple layers feasible through diffusion, reaction and/or secondary applications
  - Control of processing variables are imperative for stability, i.e., success of resulting surfaces

Slurry Aluminide Coatings (annealed at 750°C) on T22

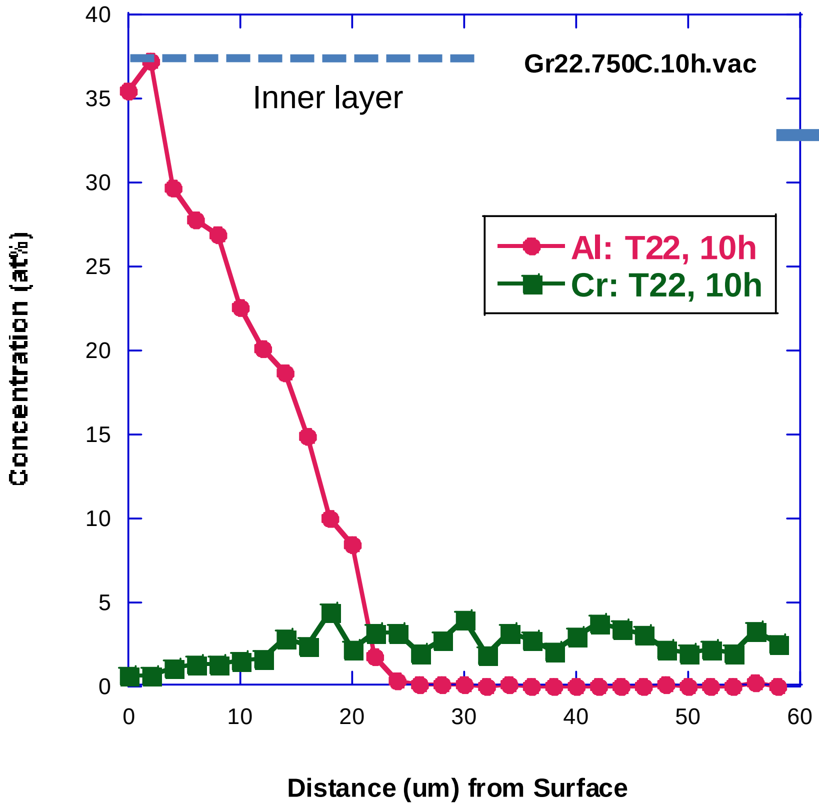


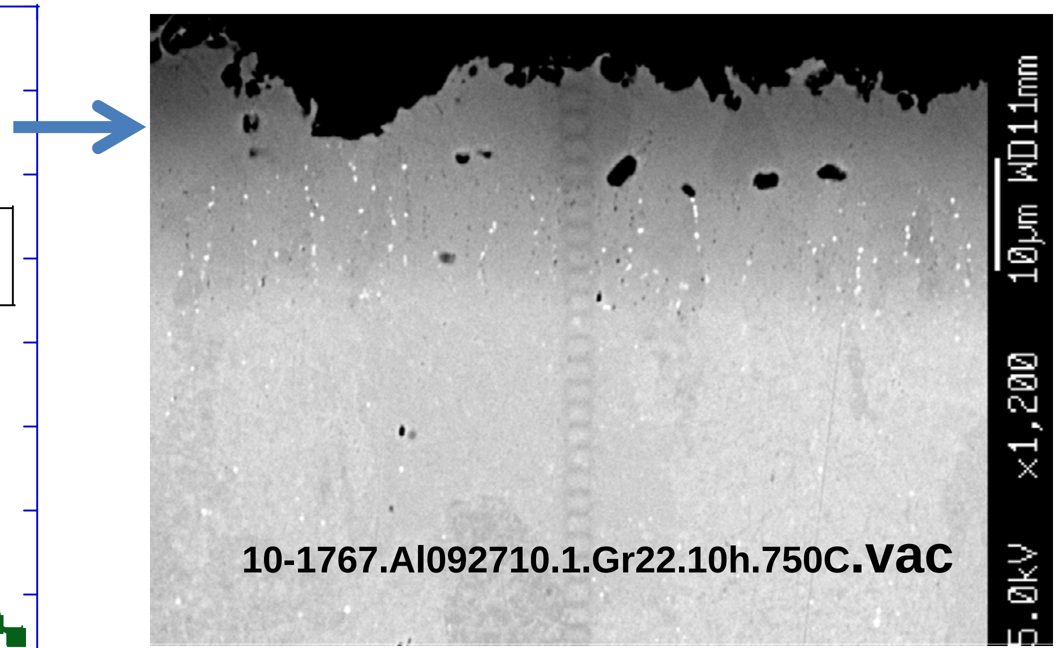
At% Al = Aluminum concentration (via EPMA) near coating surface after oxidation testing

Alloy Compositions

	Gr22	Gr315	Gr91	CF8CPlus
	wt %	**wt %**	**wt %**	**wt %**
Fe	95.5	93.4	89.7	61.8
Cr	**2.3**	**2.9**	**8.3**	**19.2**
Mo	0.9	0.7	0.9	0.33
Mn	0.6	0.3	0.3	**4**
Ni	0.2	0.1	0.1	**12.8**
W	<0.01	**1.67**	0.01	0.01
V	<0.01	0.21	0.3	0.05
Si	0.13	0.26	0.1	0.5
B	<0.001	<0.001	0.003	0.01
Nb	<0.01	<0.01	0.07	0.8
C	0.14	0.13	0.08	0.08
S	0.003	0.001	0.001	0.005
N	0.01	0.01	0.05	0.25
Cu	0.19	0.1	0.03	0.11
Al	0.02	0.01	<0.01	0.01

Composition profiles from prior slurry coating batch on Gr22 (750°C, 10h, 610 Torr)





BSE Image from FY11 slurry: high-Al outer layer spalled during annealing

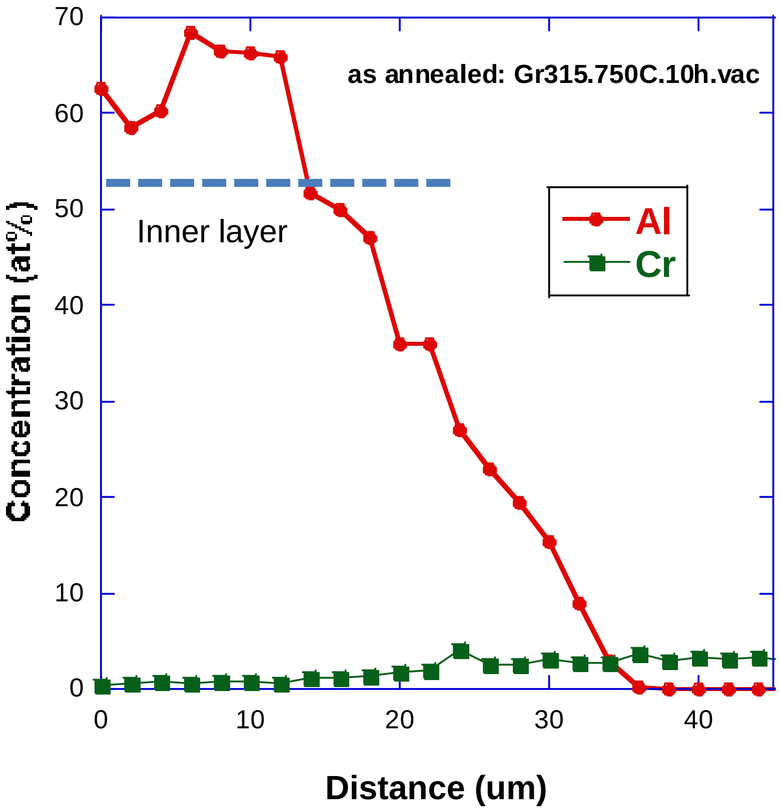
<u>Coating</u>

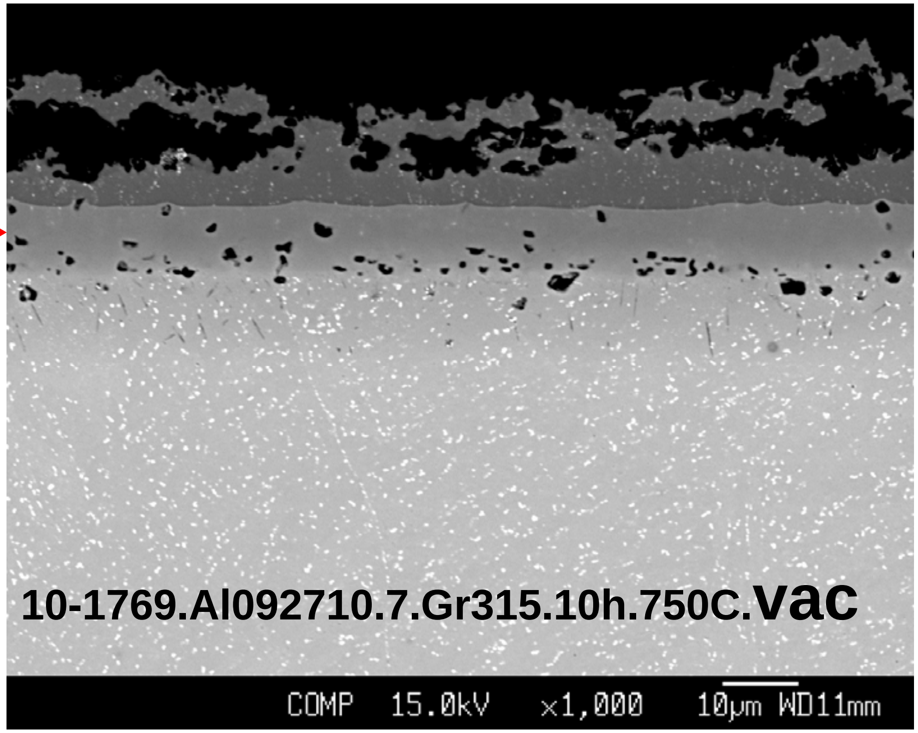
Peak Al: 38 at%

Avg Al: 29.7+7.5 at%

Avg Cr: 1.3+0.4 at%

Composition profiles from a prior slurry coating batch on Gr315 (750°C, 10h, 610 Torr)





BSE Image from FY11 slurry: initial optical microscopy indicates high-Al outer layer is not consistently present on FY14 batch

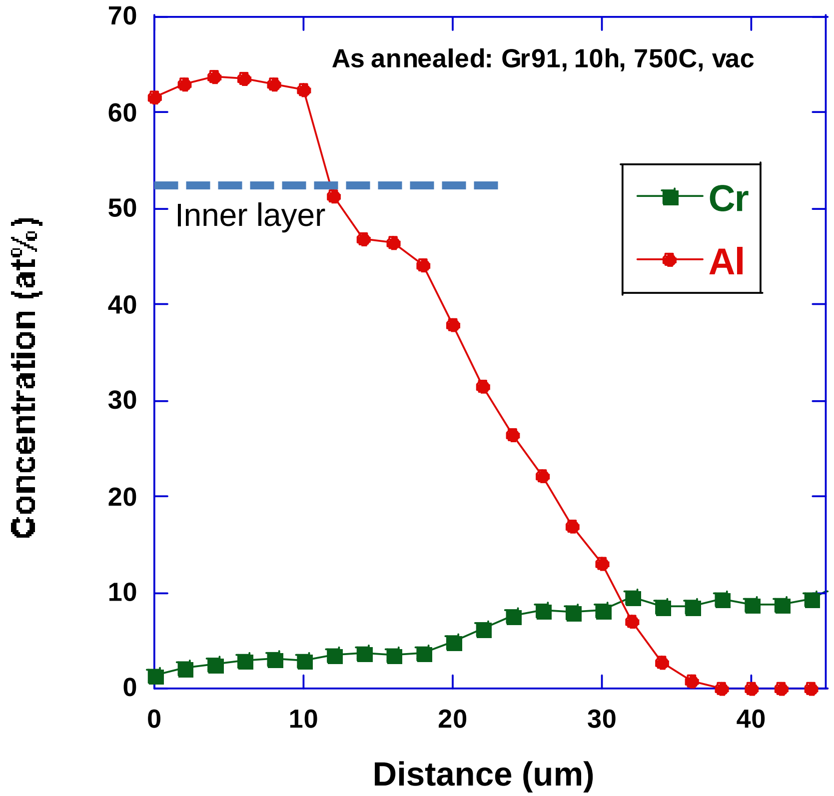
<u>Coating</u>

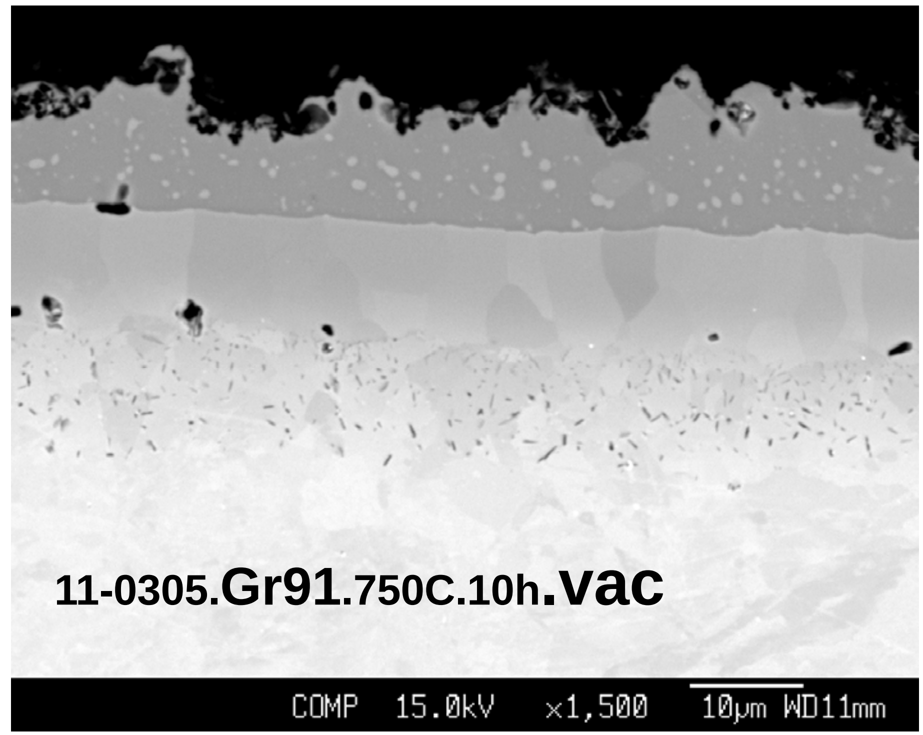
Peak Al (inner layer): 52 at%

Avg Al (inner layer): 41.3±9.8 at%

Avg Cr (inner layer): 1.9±1.1 at%

Composition profiles from a prior slurry coating batch on Gr91 (750°C, 10h, 610 Torr)





BSE image from FY11 slurry: initial optical microscopy indicates high-Al outer layer may not be consistently present on FY14 batch

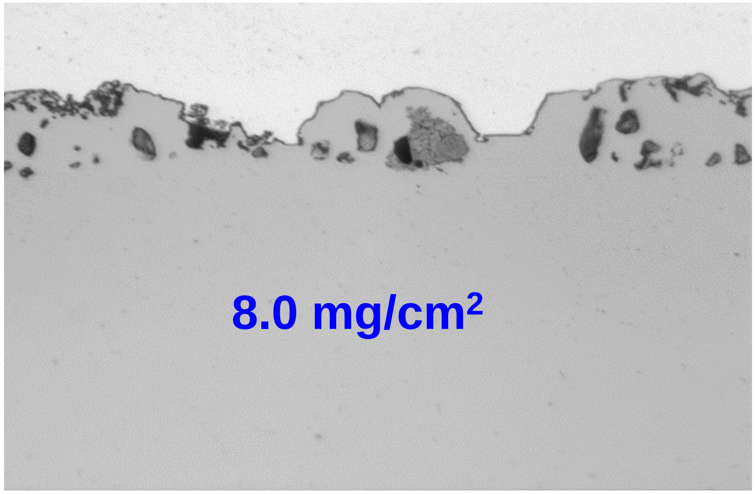
Coating

Peak Al (inner layer): 50 at%

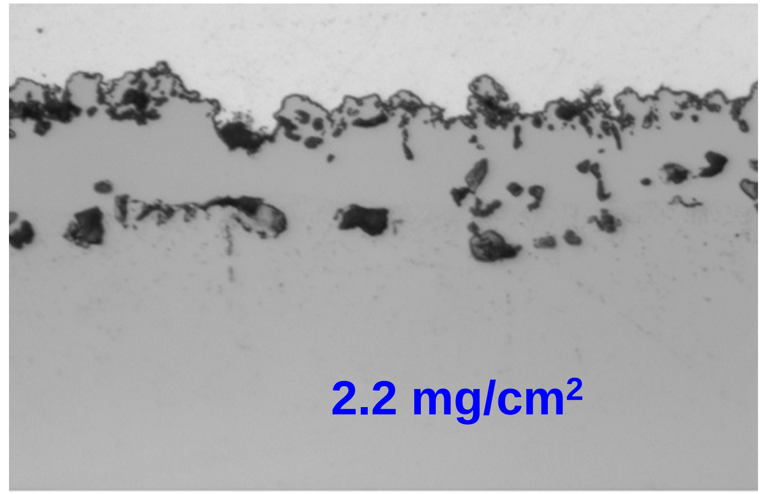
Avg Al (inner layer): 41.7±7.6 at%

Avg Cr (inner layer): 4.7±1.3 at%

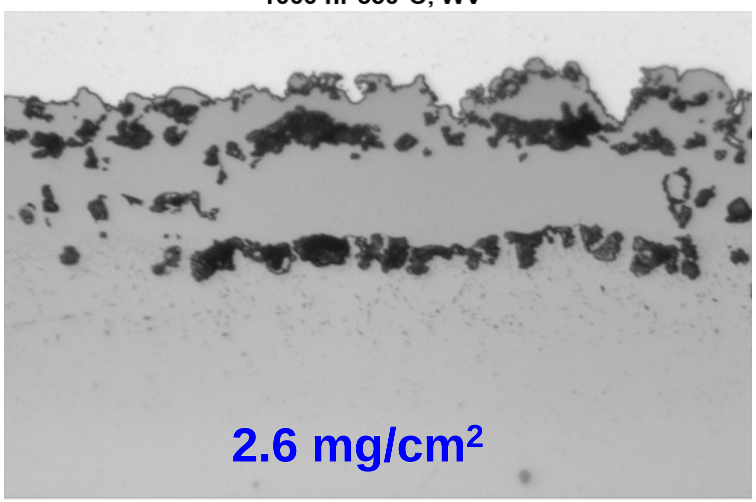
FY13: Intact slurry coating regions from various specimens after 1000h at 650°C



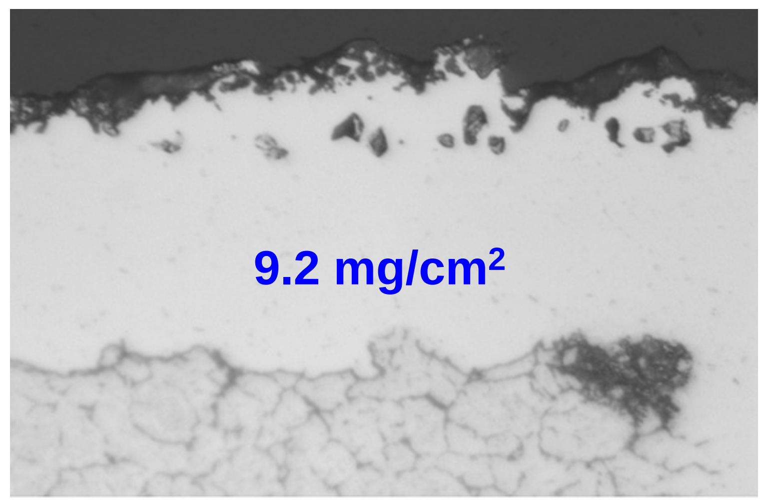
13-0290-08 T2265WL. 8646 1000 hr 650°C, WV 1000X 5µm as polished



13-0291-08 T2265WL. 8649 1000 hr 650°C, WV 1000X 5µm as polished

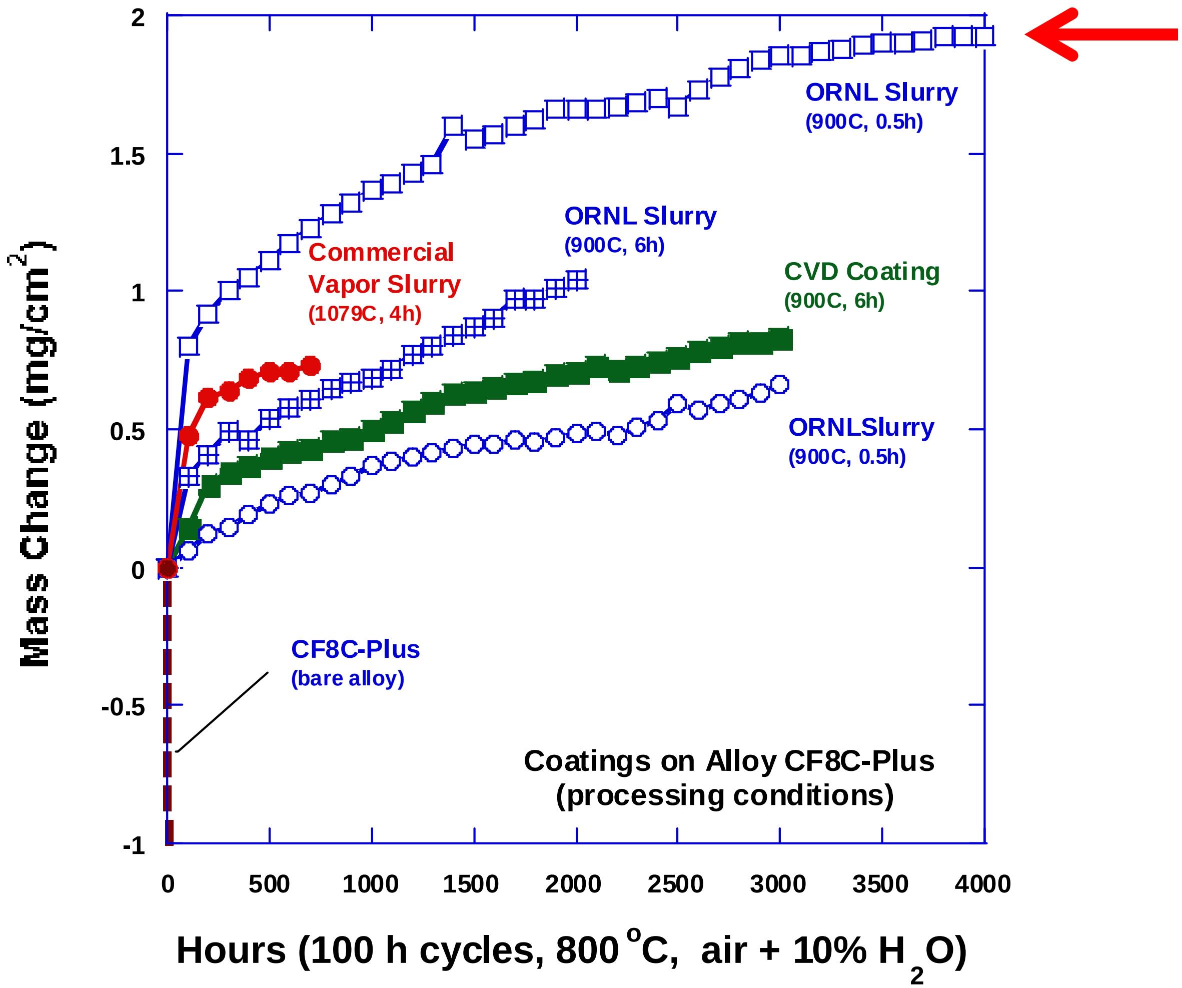


13-0294-07 T2265WL. 8971 1000 hr 650°C, WV 1000X 5µm as polished



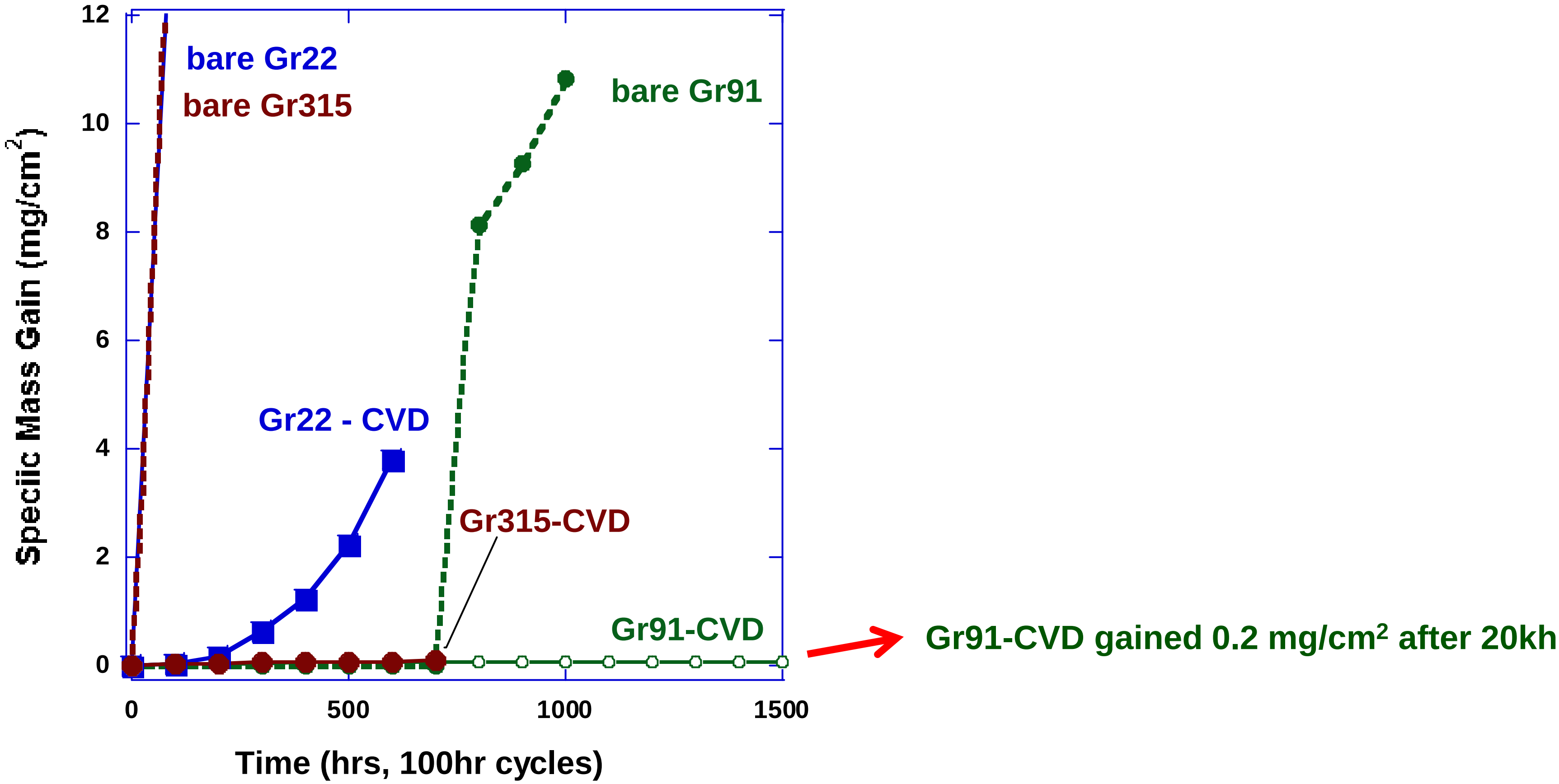
13-0295-07 T2265WL. 8972 1000 hr 650°C, WV 1000X 5µm as polished

ORNL simple slurry aluminides on CF8C-Plus austenitic stainless steel exhibited lifetimes of >4,000h at 800°C in water vapor

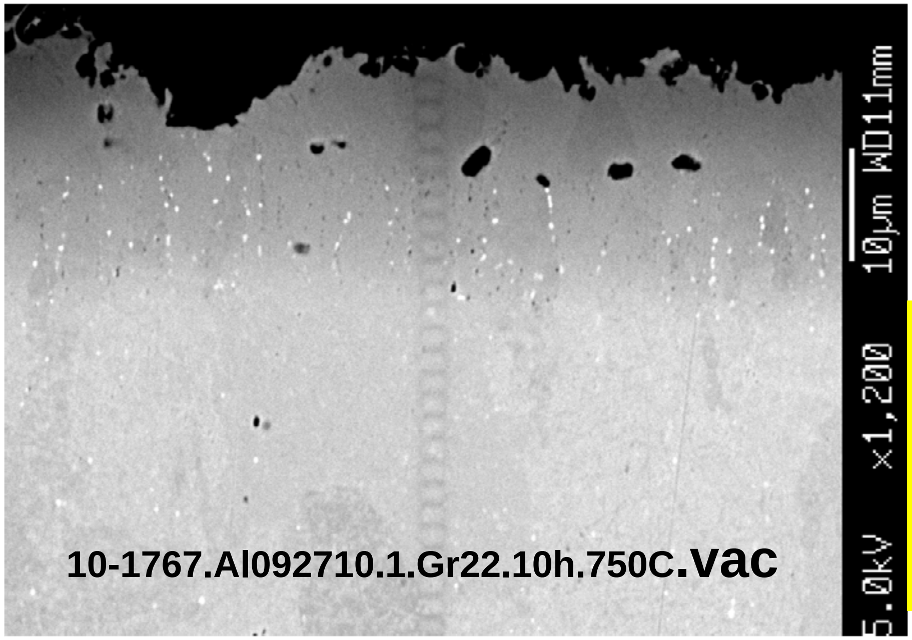


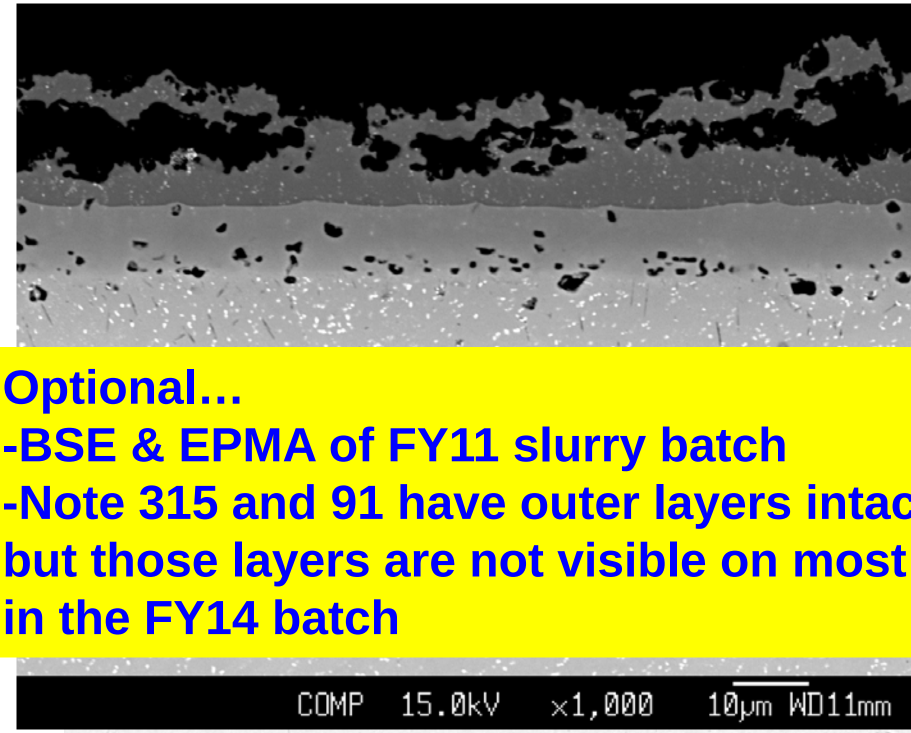
- CF8C-Plus: much higher Cr content, with Ni addition
- A variety of slurry processing conditions resulted in protective coatings.

CVD aluminides: Substrate composition influenced coating oxidation at 650°C (air + 10% H_2O)

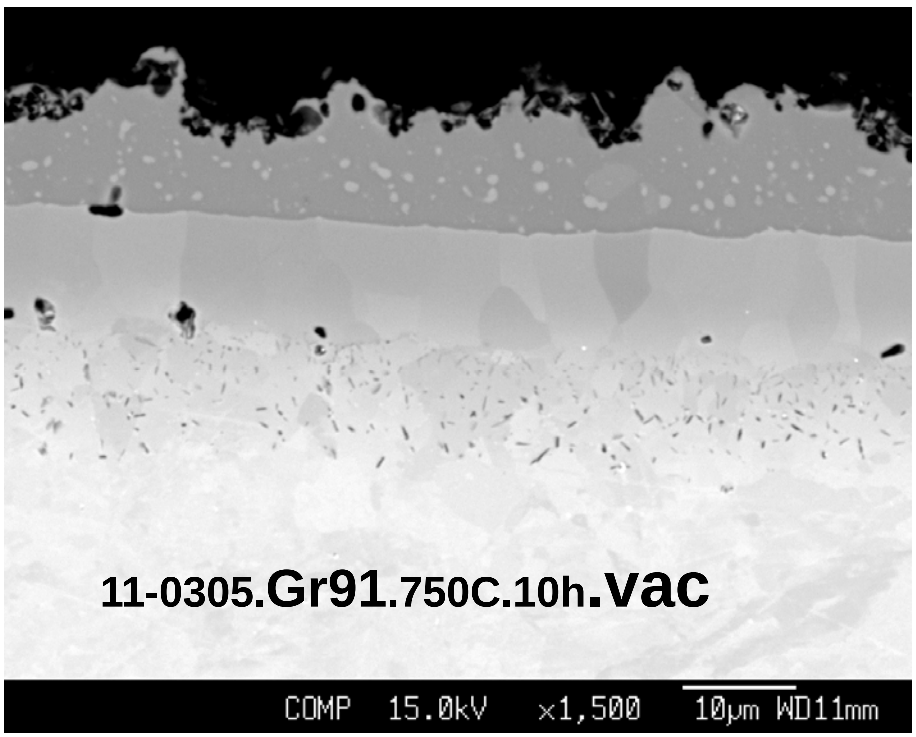


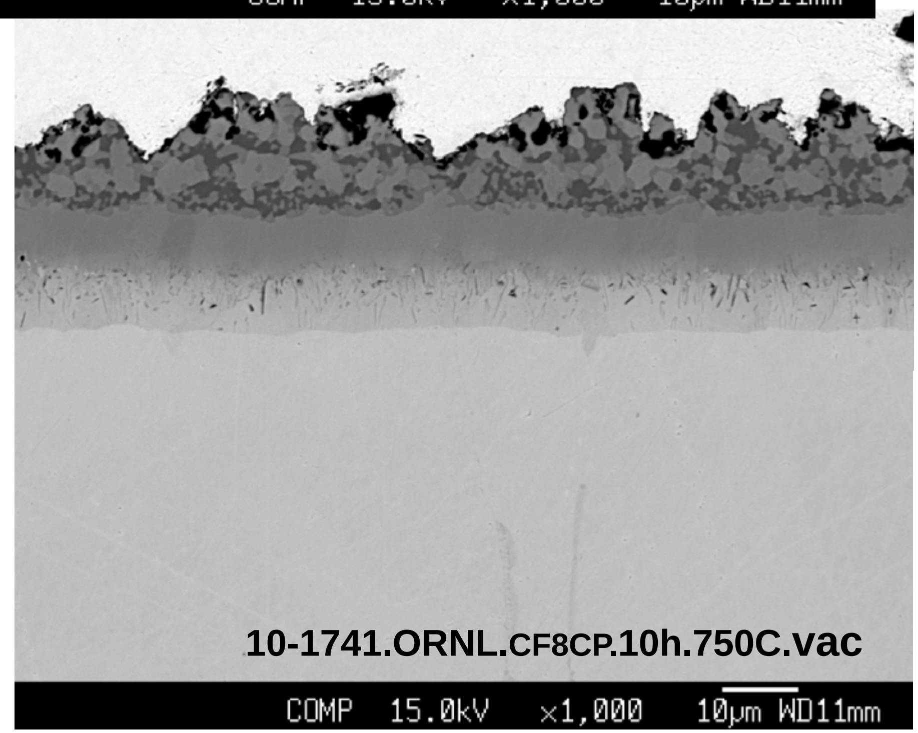
- Thin, high purity CVD aluminide on low-Cr Gr22 alloy provided minimal protection
  - Even a slight change (~0.6 wt.% increase) in Cr content of the substrate alloy exerted a noticeable effect on coating oxidation behavior.
- Early stage oxidation behavior improved substantially on Gr315
- CVD aluminide coating on 9-Cr alloy was stable to >20,000h





Optional…
-BSE & EPMA of FY11 slurry batch
-Note 315 and 91 have outer layers intact i
but those layers are not visible on most of
in the FY14 batch





What’s next

- Thin slurry YSZ on FeCrAl (as a model alloy) for ash testing
  - Fired at 1325 – 1400C
  - June activity
- In application the YSZ might be fired via a plasma-arch lamp or other portable high temperature flash device…
  - Add schematics for flash lamp fired YSZ
- Finish slide