Bespoke Material Surfaces

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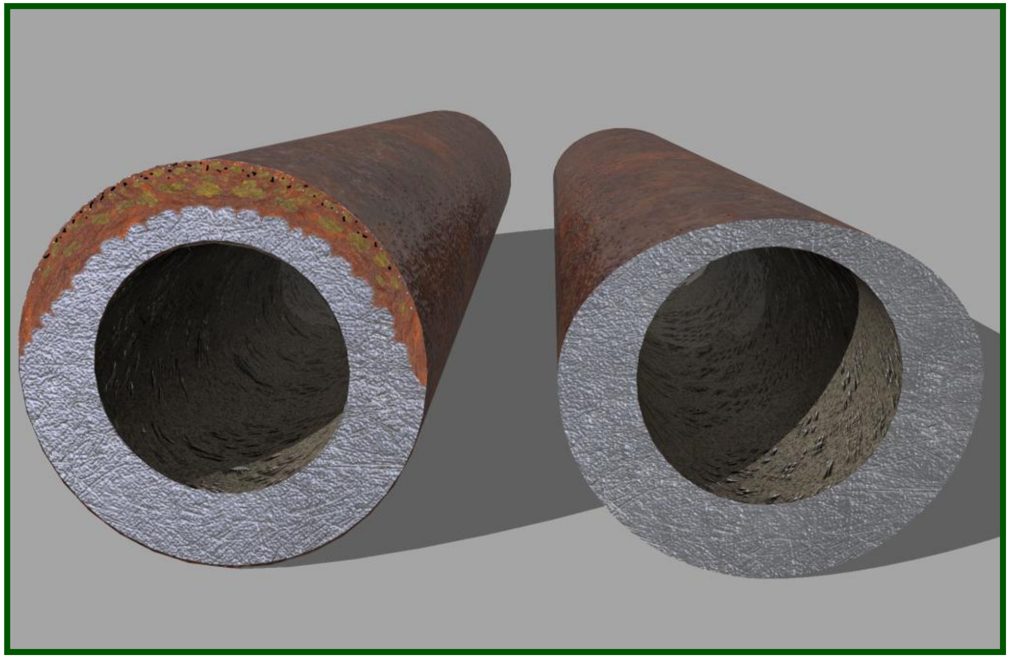
26th Annual Conference on Fossil Energy Materials
Pittsburgh, PA
April 17-19, 2012

Advanced Coatings for Fossil Energy Applications

- Temperatures up to 900°C
- Aggressive species
  - –Sulfur
  - –Steam
  - –High and low pO_2
  - –Alkali
  - –Ash



- Thermal fatigue cracking
- Need better methodologies for tailoring and producing highly protective surfaces that are cost effective

This Project Focus is Fireside Surface Protection

- Objective: *Develop approaches to synthesis of TAILORED material surfaces that have good adherence, high resistance to corrosion, limited adverse effect on thermal conductivity, and are easy and cost-effective to apply*
- Based on understanding and control of key factors affecting
  - synthesis
  - performance
    - sulfidation/oxidation resistance
    - thermal expansion match to substrate
    - effect on thermal conductivity
    - metal surface properties (roughness, microstructure, composition , etc.)

Approach

- Modeling to guide material selection and help explain observations
  - What are the stable alloy 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 application of slurry coatings to 2.25Cr-1Mo steel (Grade 22)
  - 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 Materials projects

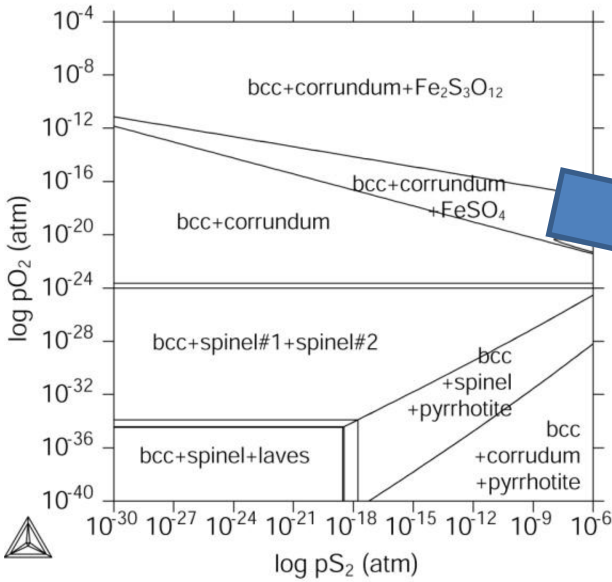
Started with Al-rich Coatings on Gr22 (2.25Cr-1Mo)

- Building on a foundation of previous FE-AM aluminide work at ORNL, ANL, Lehigh, Foster-Wheeler, EPRI using a variety of synthesis techniques
  - Good-to-excellent in highly reducing conditions, oxidation-sulfidation, water vapor
  - Problematic with ash
  - Modeling work supports further research in spite of mixed results
- Used ORNL's slurry 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 (but we've tried it before and it didn't work scenario…)
- Testing
- Refine and tailor
- Examine other compositions and structures

Modeling Leading the Composition Selection

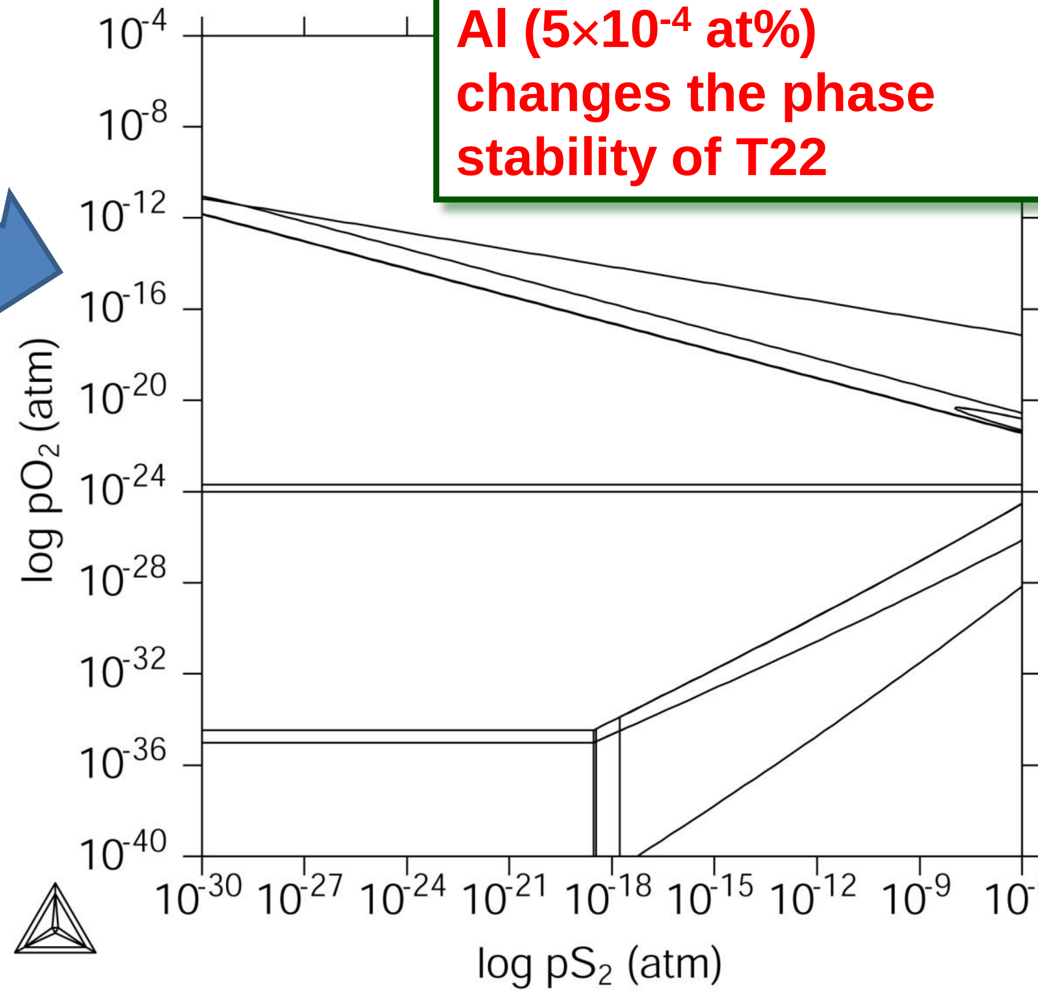
- Alumina and silica stability well known
- Even small additions of Al (5×10^{-4} at%) changes the phase stability of Gr22
- Al has large bcc phase field in Gr22
- Aluminum-rich surfaces were identified as the initial candidate material coating systems

Effect of Al on Phase Stability of Gr22



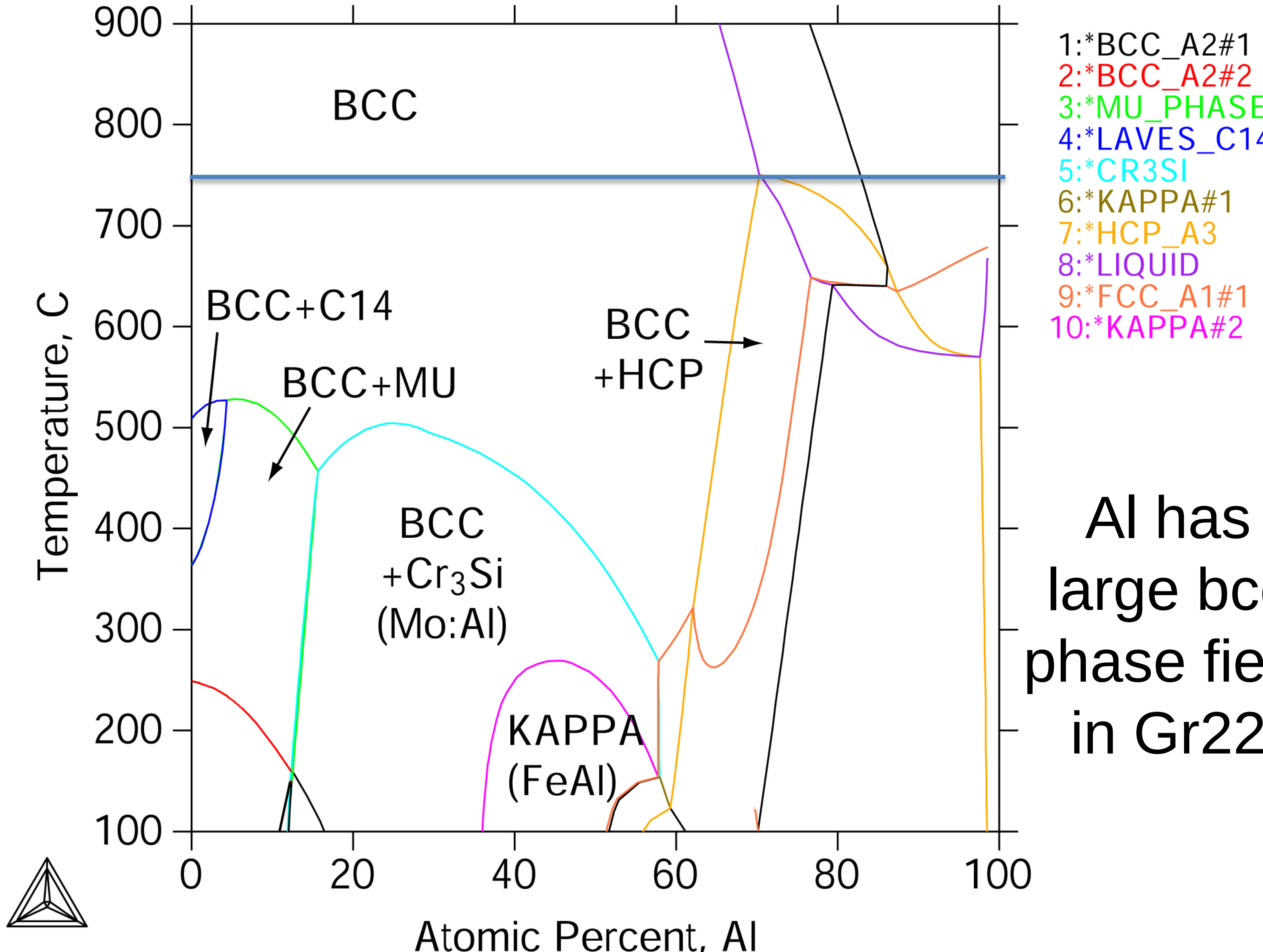
Al-free T22

400°C



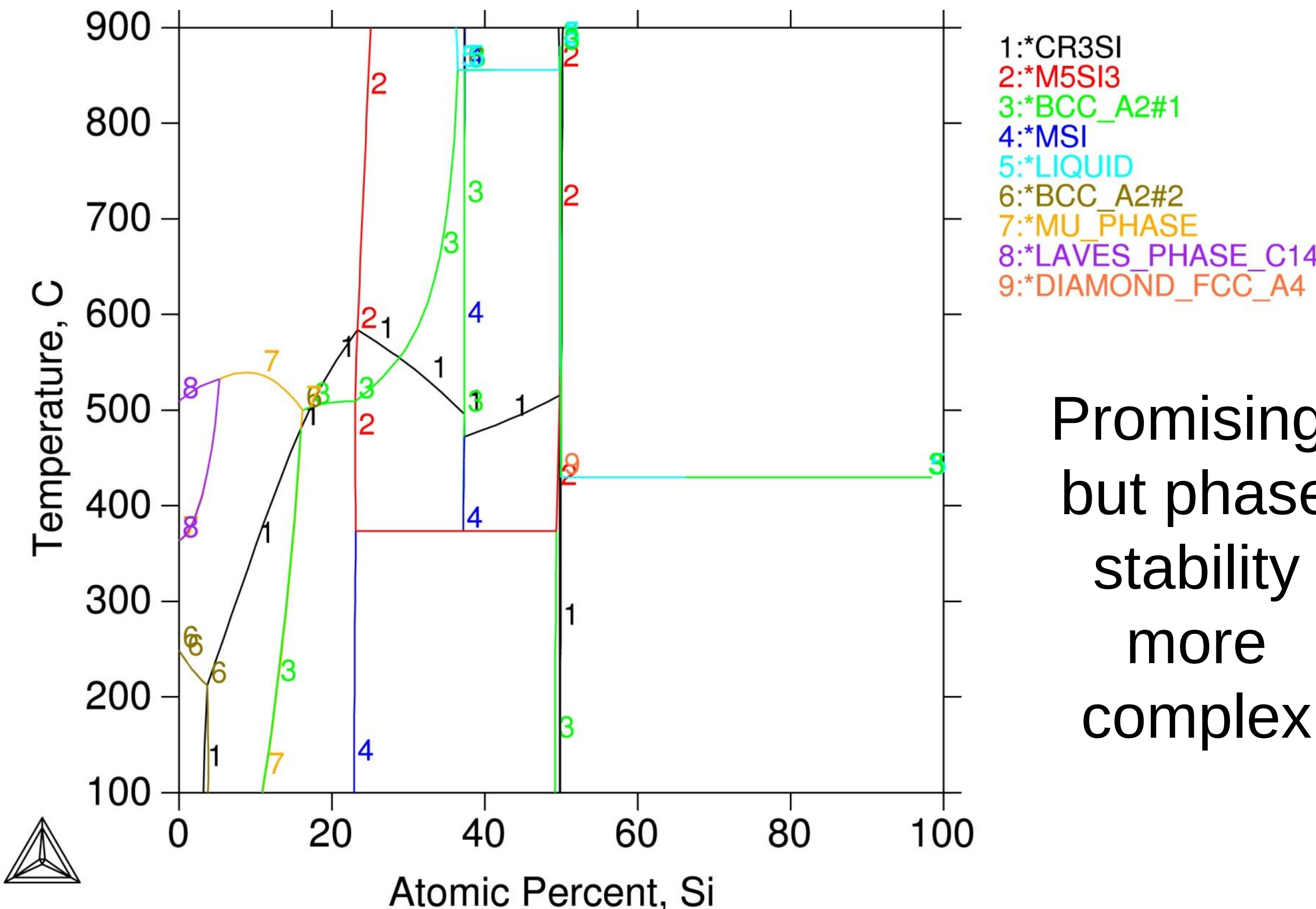
Even small addition of Al (5×10^{-4} at%) changes the phase stability of T22

Alloying Effect of Al on Gr22



Al has large bcc phase field in Gr22

Alloying Effect of Si on Gr22



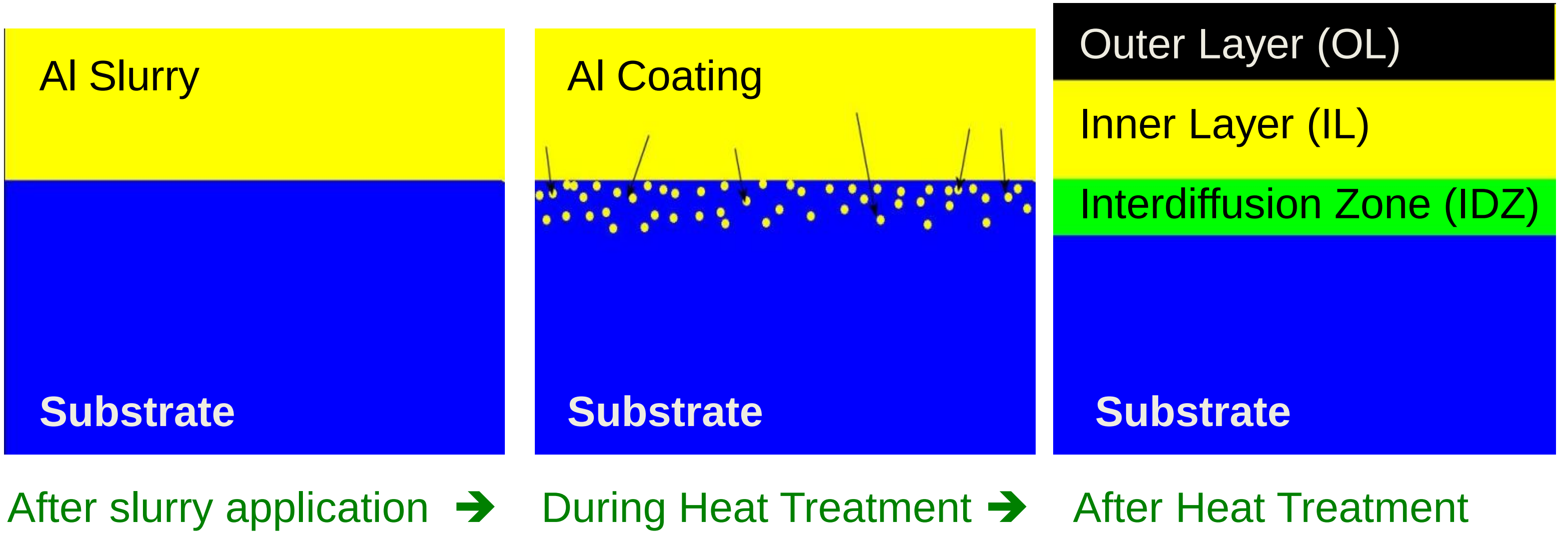
Promising, but phase stability more complex

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

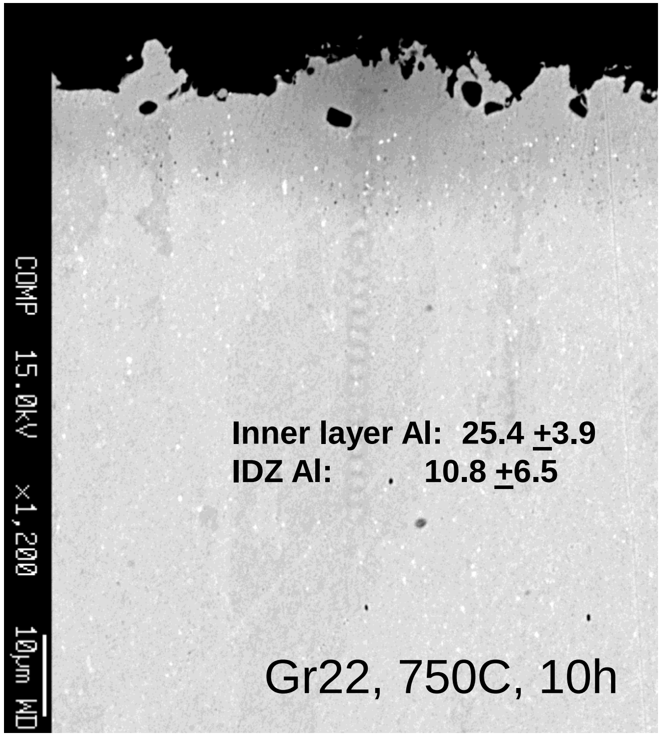
- Coatings/surfaces are dependent upon
  - Processing (resulting microstructure, density, contaminants…)
  - Substrate (composition, structure, CTE…)
- Our surface treatment approach
  - Solution or slurry based
  - Robust, non-line of sight, industrially viable (spray, dip, paint…)
  - Can be adapted 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

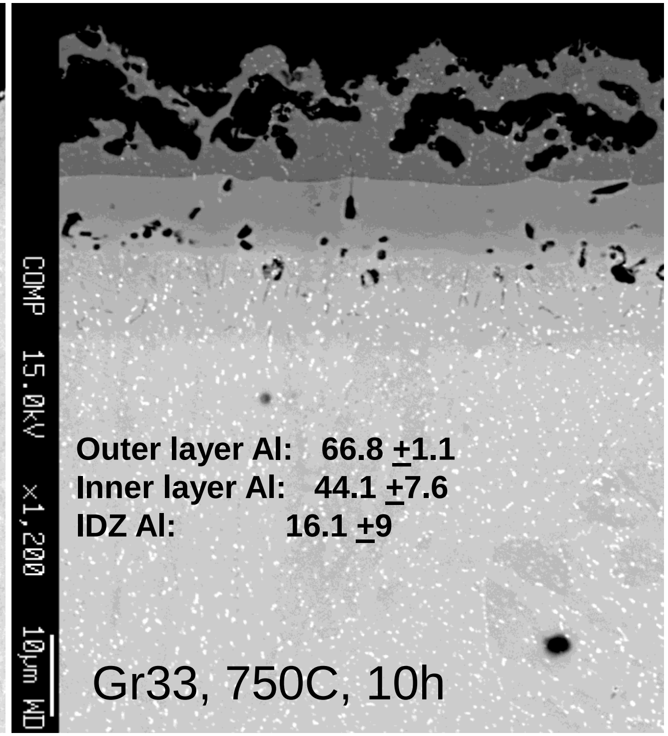
Formation of an Integrated Architecture Necessary for Tailored CTEs/Adherent Surfaces

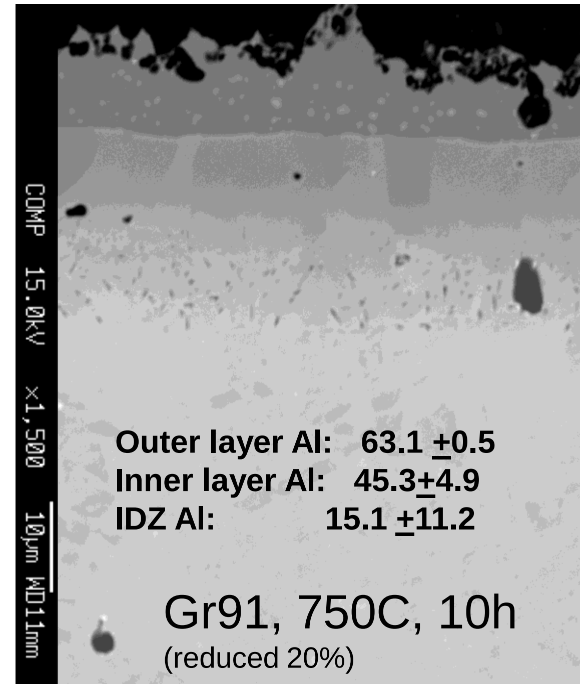
- Slurry is applied
- Heat treatment leads to diffusion of Al into the substrate (enriched surface and/or formation of another phase)
- Excess Al is removed after heat treatment
- Once exposed to an environment, a protective scale can form



Alloy Cr+ Content Affects Coating Formation/Microstructural Evolution







Apparent effect of Cr, but must consider as alloy system. Can heat treatment conditions produce a mechanically stable aluminide surface on Gr22?

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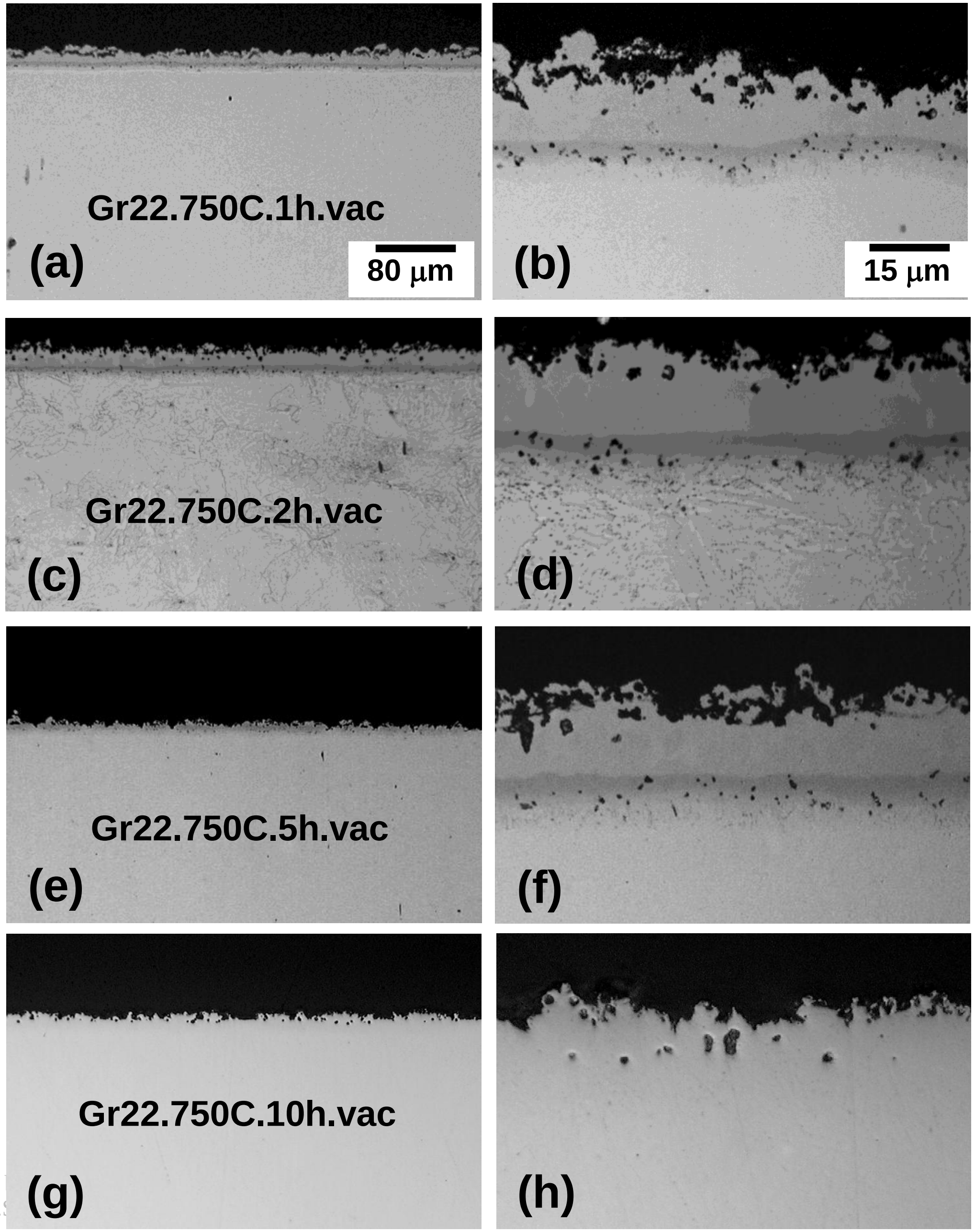
Processing Effects: Time at Temperature



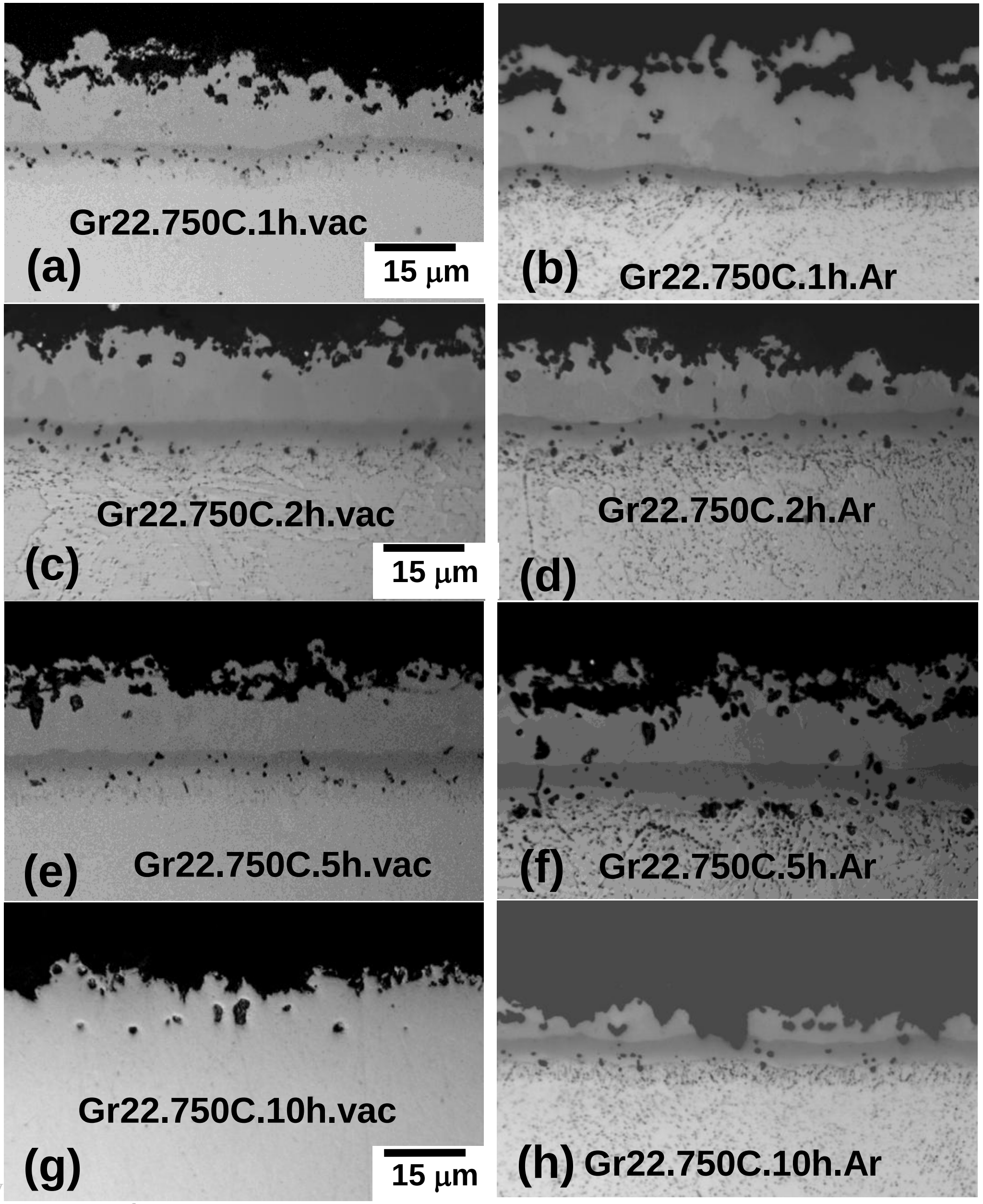
High Al outer layer, brittle

Low Al, Al decreases through inner layer and into IDZ

No abrupt phase transitions, reasonably ductile

Rough surface, good bonding surface

Processing Effects: Heat Treatment Environment



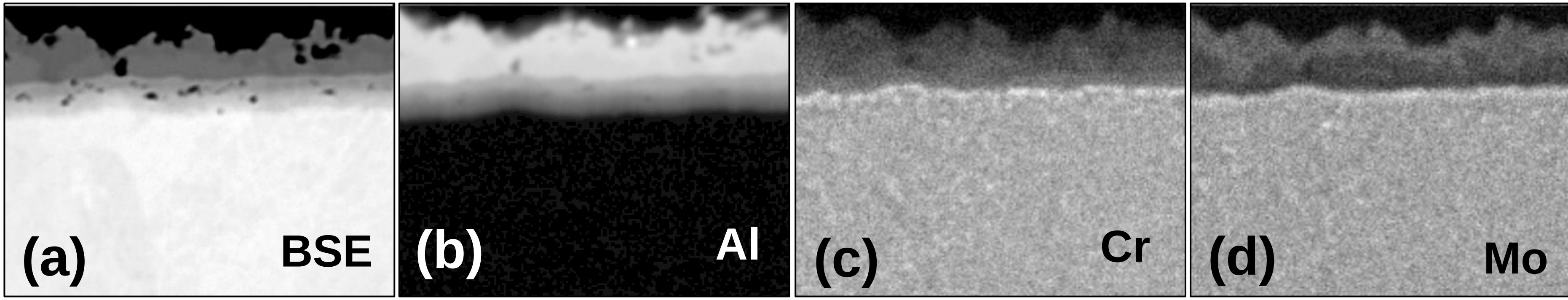
Similar Al diffusion trends

Al decreases in OL with increasing time

More porosity with atomspheric conditions

Inconsistent loss of OL, mechanical surface prep option/brushing?

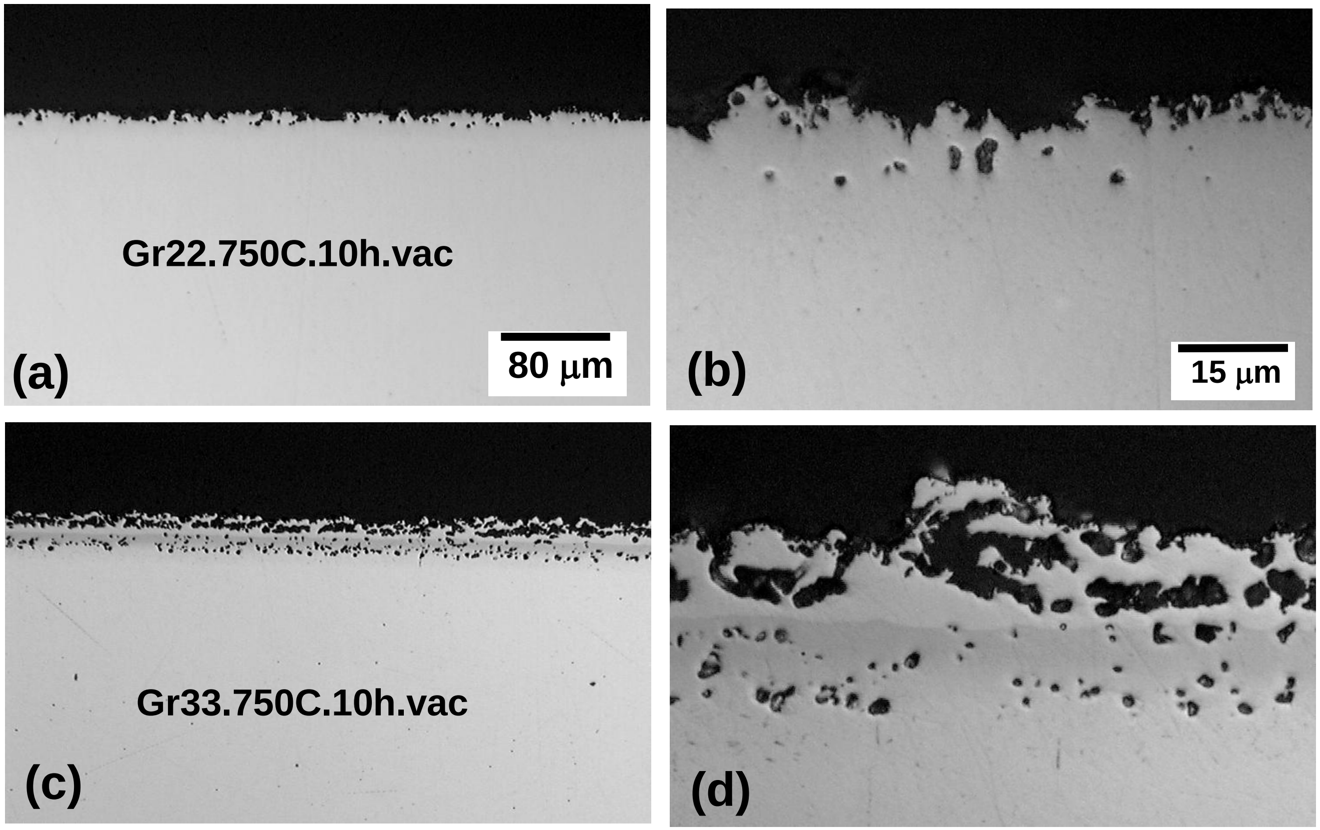
Preliminary Elemental Analysis



Gr22.750C.1h.vac

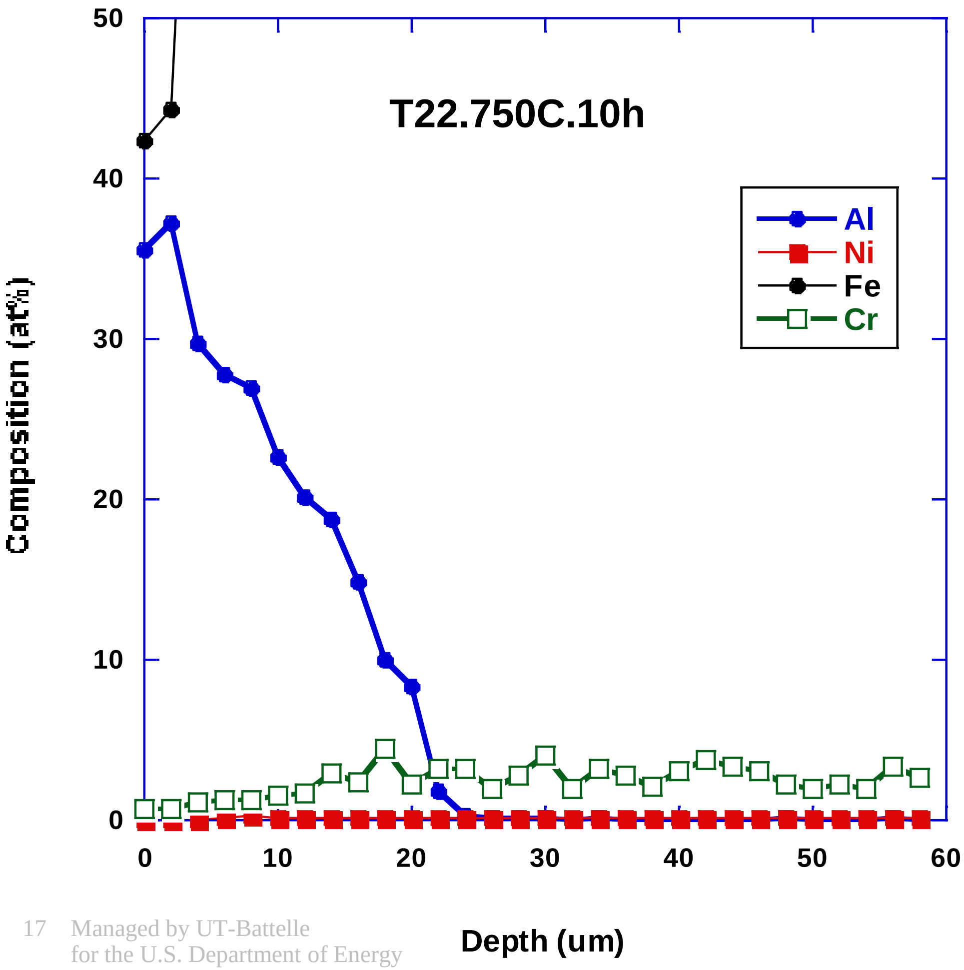
- 3 Al rich layers form during heat treatment:
  - Al rich OL, Al decreasing through IL and into IDZ
- Sub-stoichiometric Fe-Al composition, so good adherence predicted
- Analysis still on-going

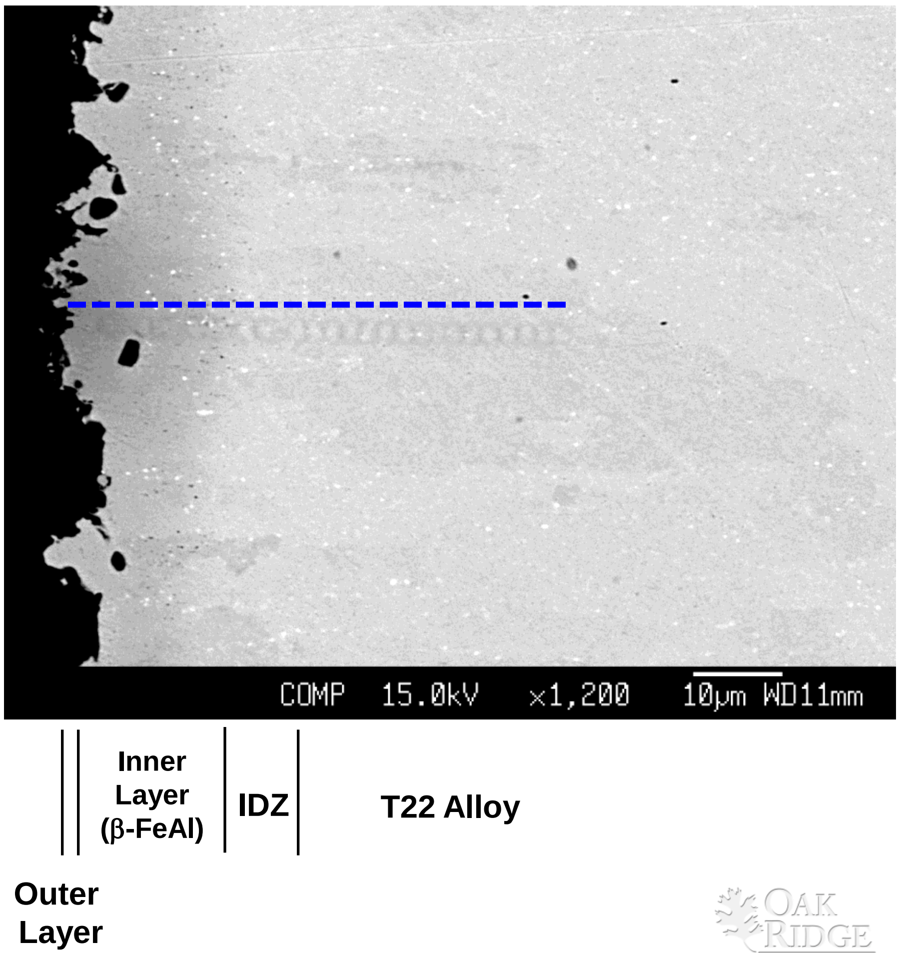
Microstructure Evolving Toward a Good Bonding Surface



ORNL Al Slurry on Gr22
(annealed: 750°C, 10h, 610 Torr)

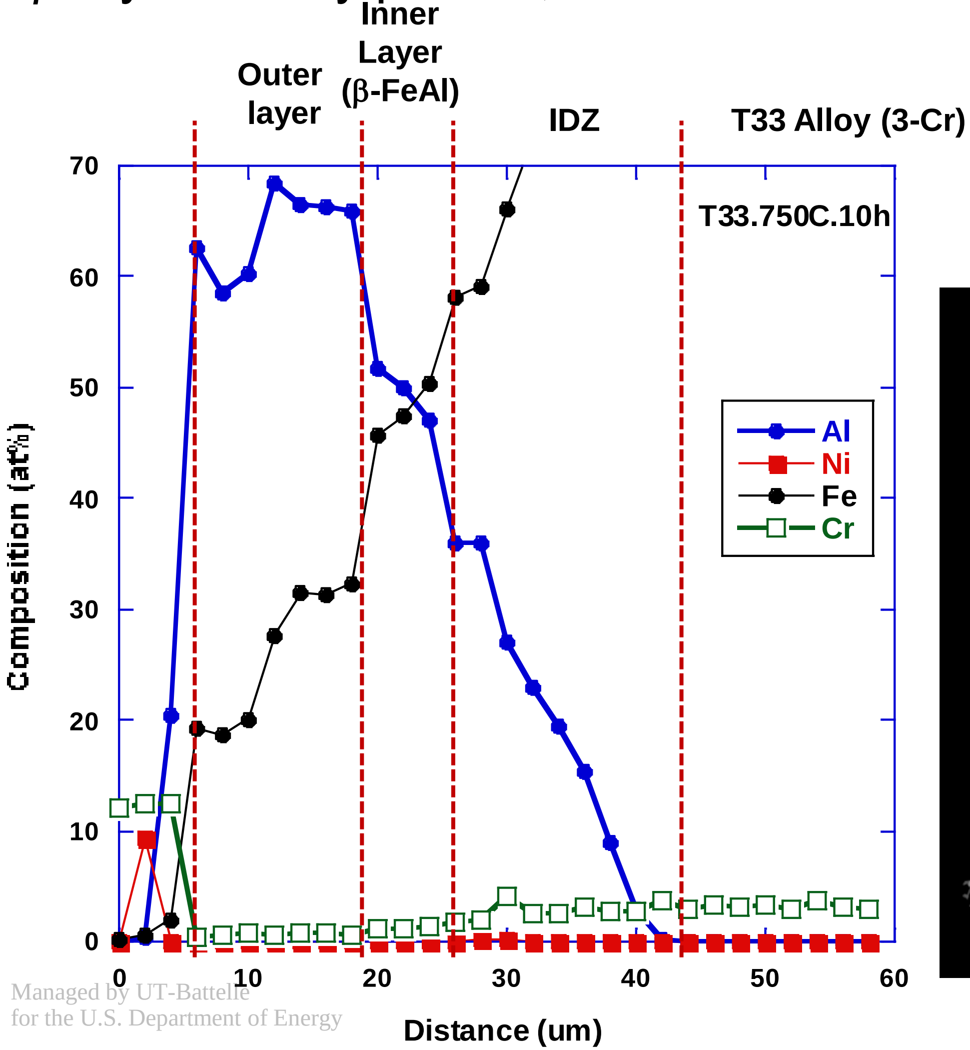
- thin, low Al, simple Fe-Al coating with a constant Al gradient
- <25 μm Al depth
- little if any intermetallic on surface

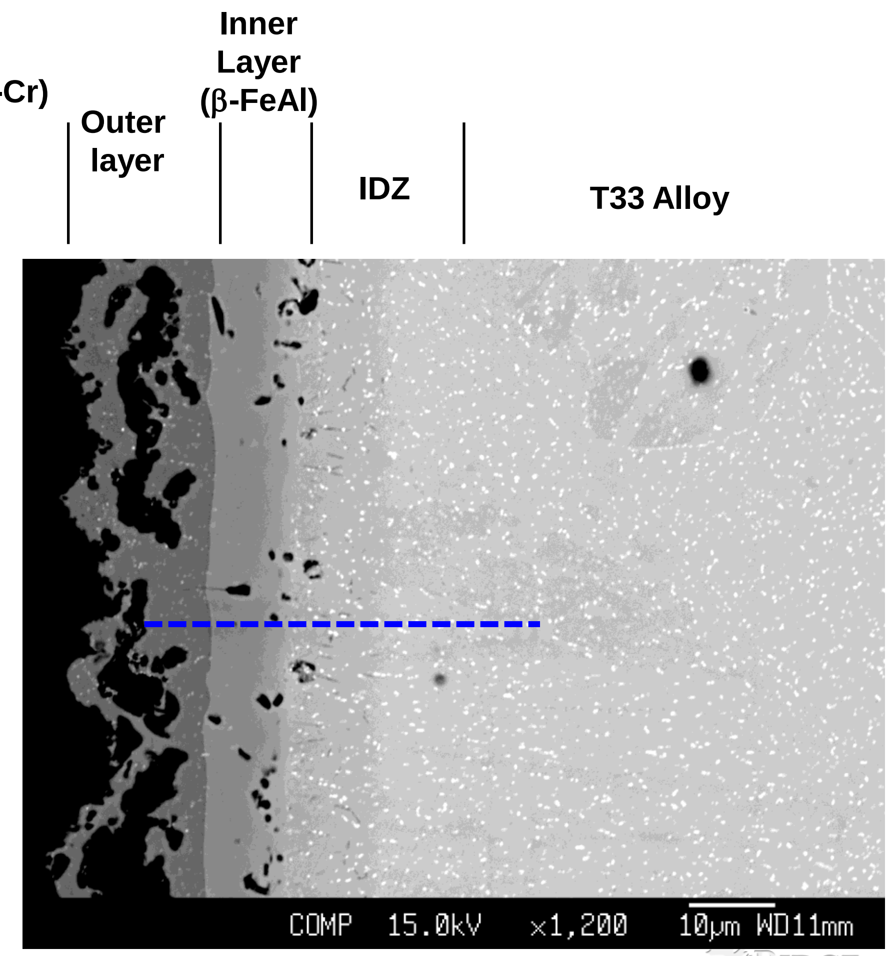




ORNL Al Slurry on Gr33
(annealed: 750ºC, 10h, 610 Torr)

- thin, high Al, multi-layer Fe-Al coating with ~40 mm Al depth
- porous, lacy intermetallic layer on surface
- β-layer is very porous, with some cracking visible



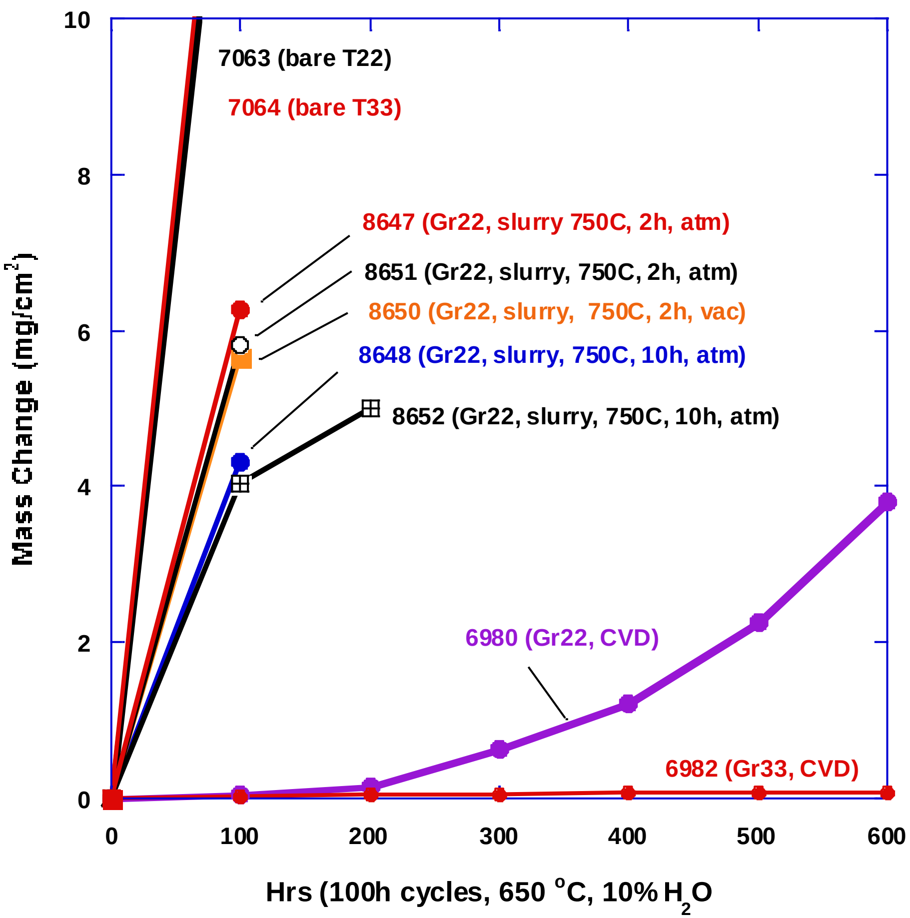


Testing Summary

- Evaluated the effect of heat treatment time at temperature and environment on coating microstructure (stability) development
  - Temp: 750°C
  - Times: 2 and 10 hours
  - Environments: argon (Ar) at and below atmospheric pressure (610 torr)
  - Testing Conditions: 650°C, 100 hour cycles, 10% water vapor
- Accelerated testing approach used as a screening tool to quickly evaluate materials

The Addition of a Coating Lowered Rates of Mass Gain as Compared to Bare Gr22 or Gr33

- Increasing heat treatment time at temperature lowers oxidation rate
- Contribution of atmospheric pressure?



Bare Gr22 and 33

- Have extremely high oxidation rates

Slurry Gr22 and 33

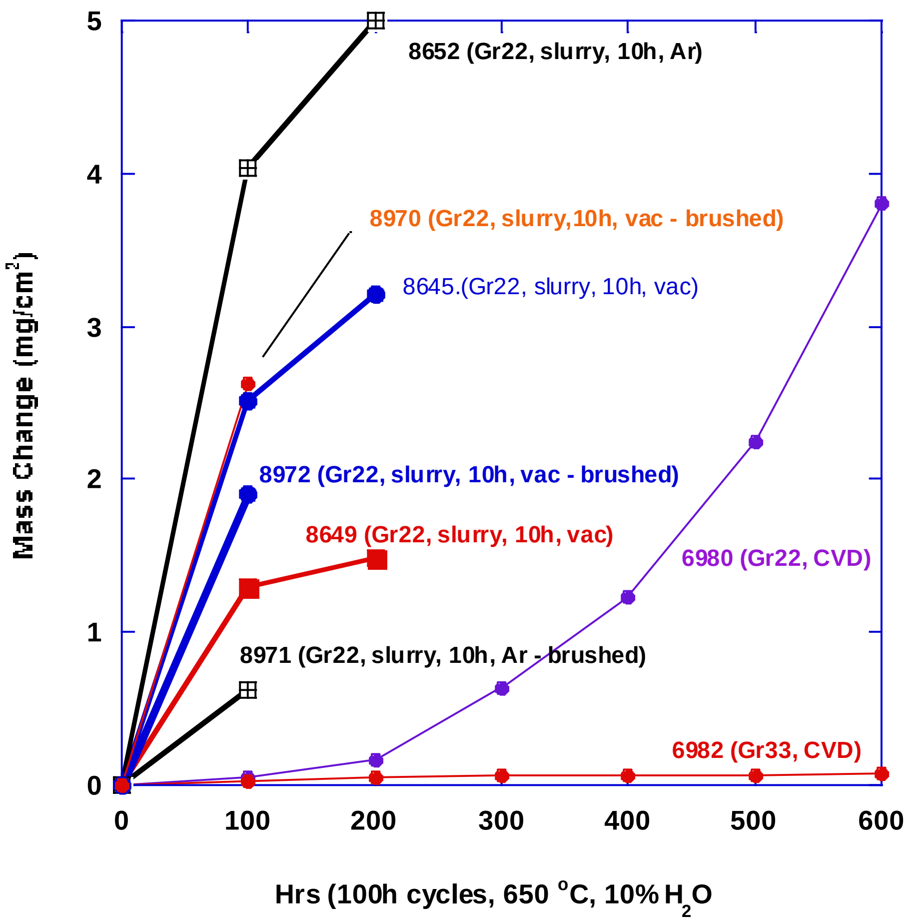
- Have high oxidation rates after 100h, but much improved over bare Gr22.
- Cracked, brittle outer layer is adherent

CVD Gr22

- Has much lower rate than slurries
- Rate increases at 300h

Coatings Annealed in Vacuum Showed Lower Rates of Mass Gain Than Bare Gr22 or Gr33

- Those annealed for 10h in vacuum were the lowest mass gains, as predicted.



Slurry T22 (750C, vac, 10h)
- further reduction in oxidation rates
- outer layer partially spalled

Slurry T22 – brushed
- even lower oxidation rates
- 10h, atm, lowest rate
- brushing likely removes more of OL

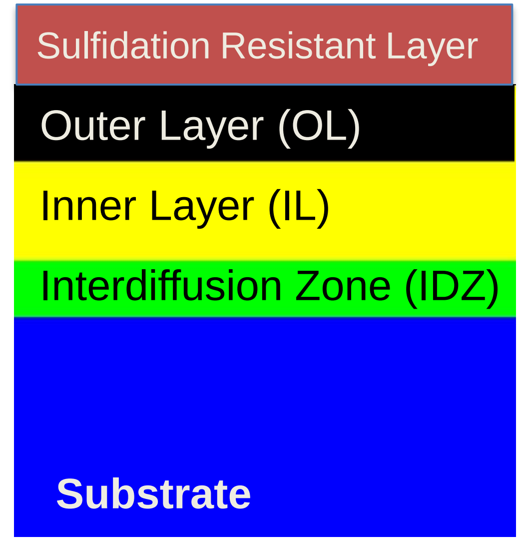
Slurry with OL mechanically removed may be good low-cost option as a “bond coat”

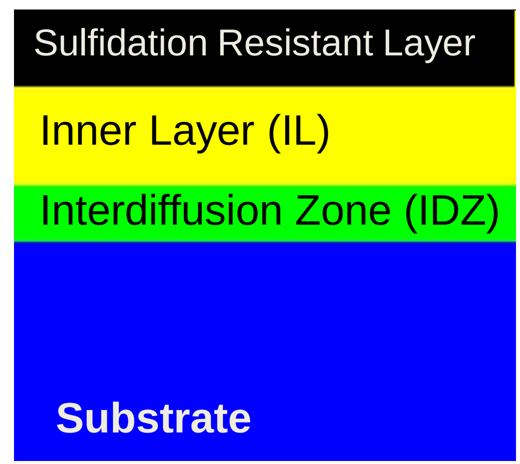
Why Al-rich Coatings on Gr22?

- Previous ARM work at ORNL, ANL, Lehigh, Foster-Wheeler, EPRI using a variety of synthesis techniques
  - Good-to-excellent in highly reducing conditions, oxidation-sulfidation, water vapor
- Slurry coating process has been demonstrated as an easy-to-apply route
- Potentially desensitizes Cr contribution
- Formation of a stable “bond” coat necessary for tailored CTE’s
  - Provides oxide bonding surface or another “reaction” surface for solution chemistry

Where Do We Go From Here?

- Begin development of a solution based outer resistant sulfidation resistant layer
  - Form semi-protective complex sulfide-oxide scale
    - Examine/model incorporation of Cr, Mo, Si (ash corrosion resistance?) into existing coating
  - From protective oxide or sulfide scale
    - Move on to other composite coatings (aluminide/silicide, ZrO_2) and/or other compositions
- Examine the modification of microstructure formation control as a non-stick approach, e.g., slag shedding coatings





FY 2011 and 2012 Milestones

- Complete computational evaluation of the thermochemical stability at the steel interface (9/30/11 – completed 6/30/11)
- Complete testing of coated steels and apply Go/No-Go criteria (12/30/11 - completed)
- Using modeling approaches, determine if a graded-property approach is feasible, and identify coating thicknesses necessary (9/30/12)
- Complete second iteration coatings based on results of FY2011 work. (9/30/12)
- Complete one-dimensional diffusion modeling (DICTRA to study surface kinetic behavior of candidate coating materials. (9/30/12)

Ongoing/Future Work

- Modeling
  - Feed results of experimental testing back into model and adjust for future work/sulfidation layer
- Experimental
  - Complete evaluation of aluminide: coatings with outer layer removed
  - Examine incorporation of Cr, Mo, Si into Al slurry or as separate slurry layer
  - Move on to other composite coatings (aluminide/silicide, ZrO_2) and/or other compositions
  - Evaluate slag shedding surfaces

Ongoing/Future Work (cont'd.)

- Testing
  - Continue/Complete air oxidation studies 10 hr/vacuum treated coated surfaces and "roughened" surfaces
  - Complete wet air oxidation studies on coated 2nd iteration and/or composite surfaces
  - Begin sulfidation and ash tests on best surfaces (can include monoliths) to date

Acknowledgements

John Henry, Larry Walker, Jim Keiser, Bruce Pint,

and Vito Cedro

This research was sponsored by
U. S. Department of Energy, Office of Fossil Energy
Advanced Research Materials Program

Questions?