A Novel Low-Temperature Diffusion Aluminide Coating for Ultrasupercritical Coal-Fired Boiler Applications

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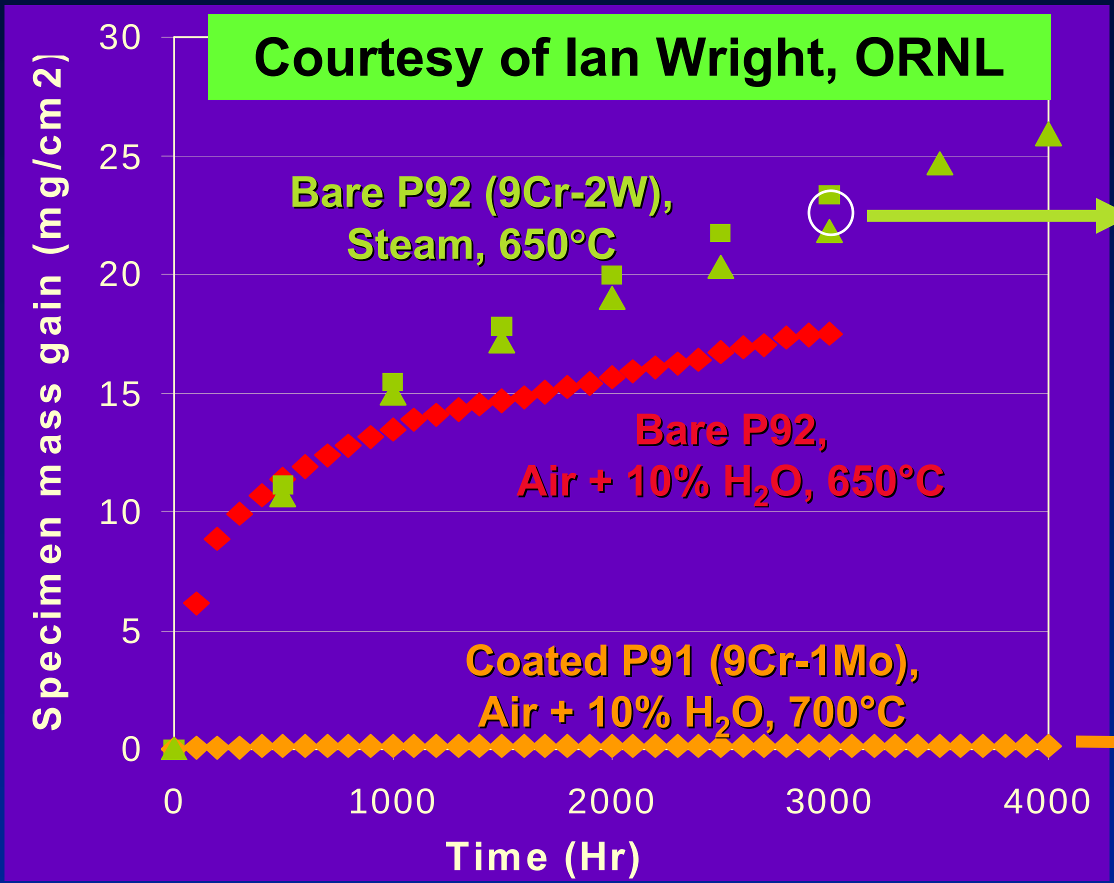
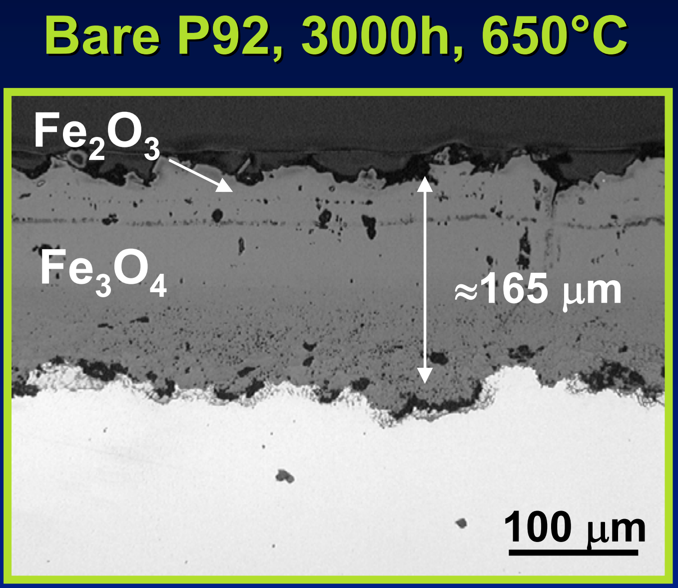
Why Iron Aluminide Coatings?

- Improvement of coal-fired power plant efficiency requires increase in steam temperature & pressure
- Advanced 9%Cr ferritic/martensitic alloys may be creep resistant up to 650°C but they will suffer extensive steam-side oxidation

- Aluminide coatings have been shown to drastically reduce the oxidation rate in exhaust/steam environment

Effect of Aluminide Coatings



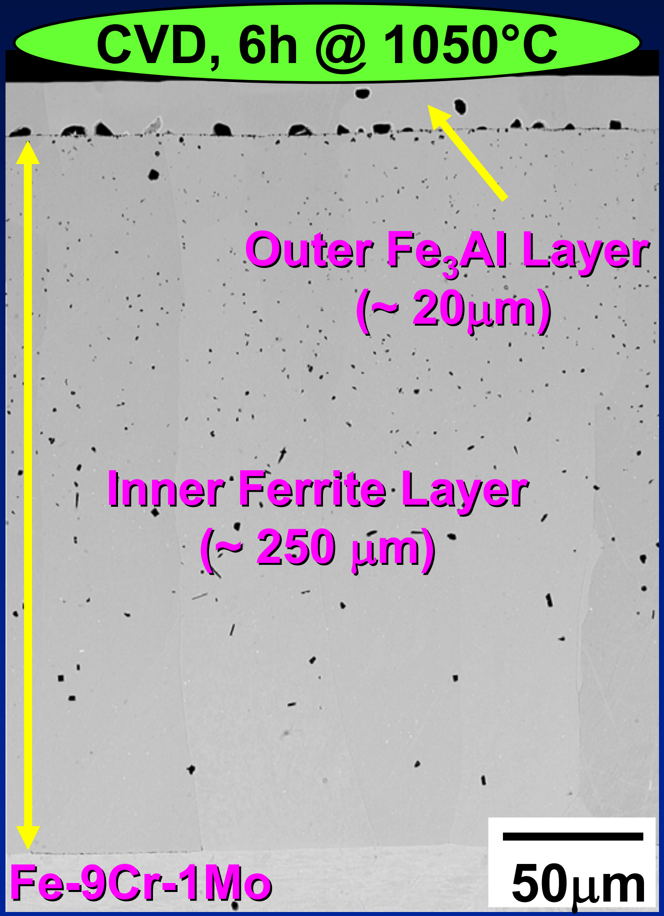


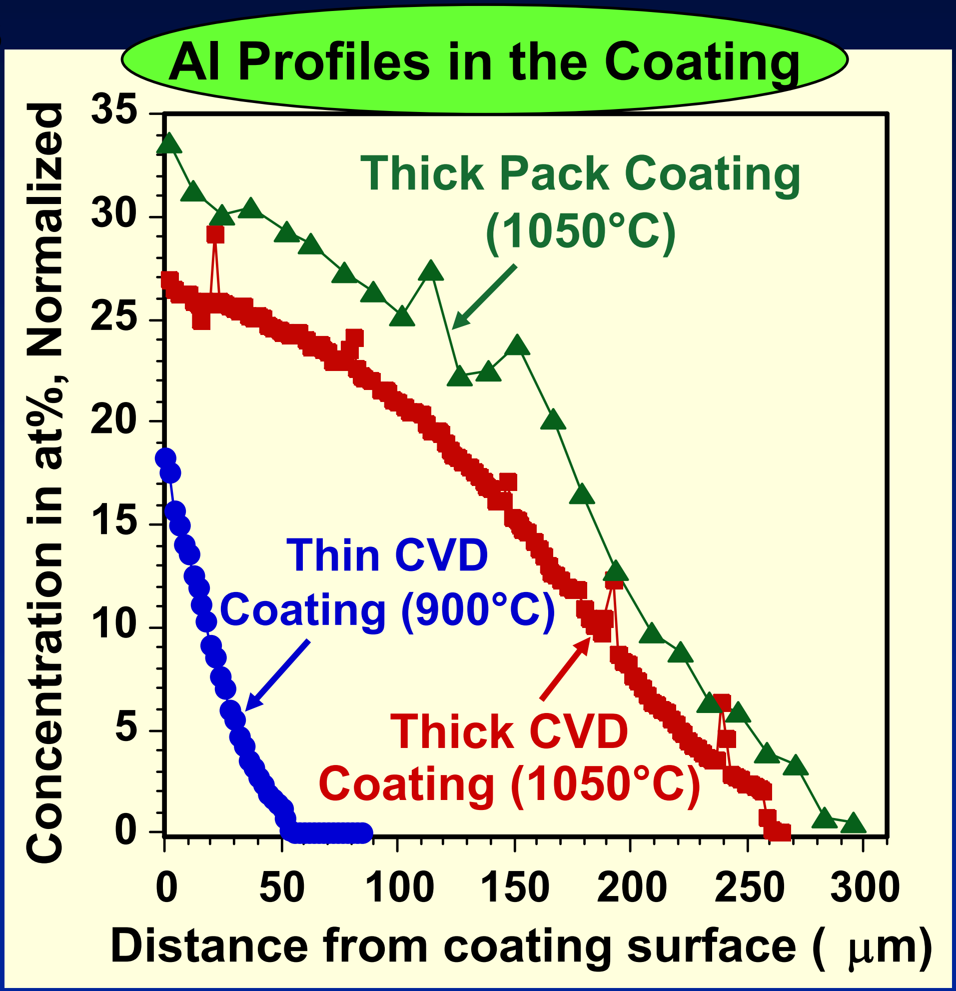
oxide scale
< 2 μm thick

- Unlike in dry air, many Fe-base alloys are rapidly oxidized in steam/humid air when not coated
- Testing in an environment of air + 10 vol.% H_2O can be used as a low cost method for determining coating performance

Aluminide Coatings Fabricated at 900-1050°C via Chemical Vapor Deposition or Pack Cementation

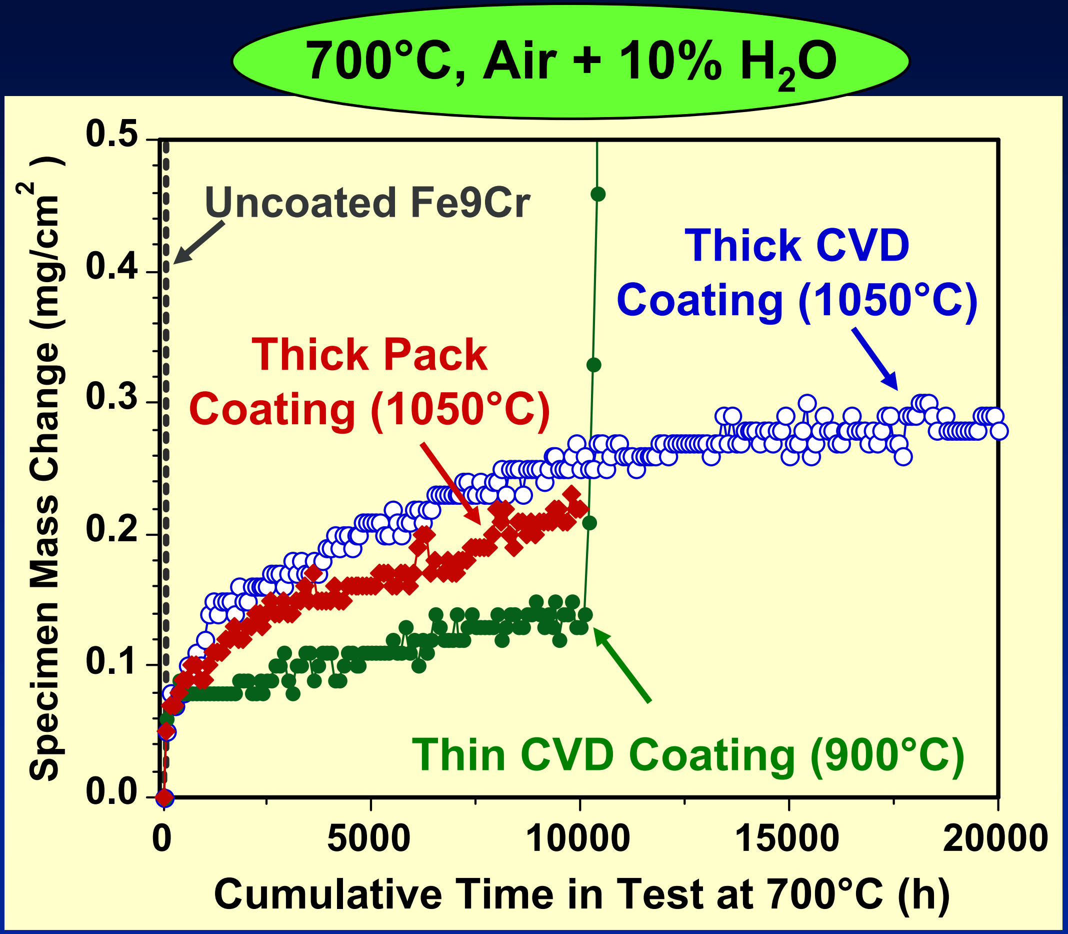
Zhang et al., *Surf. Coat. Technol.*, 2008



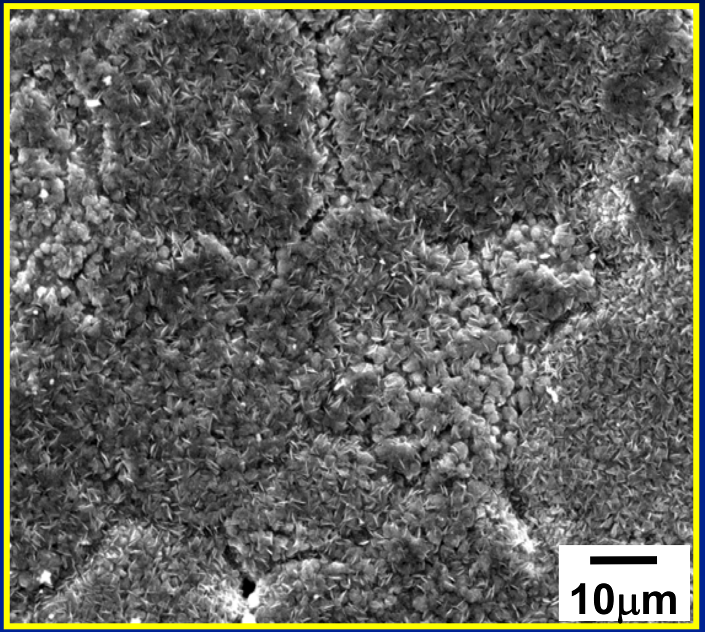


- Thick CVD or Pack Coatings: 250-300 μm (6h at 1050°C)
- Thin CVD Coatings: 50-100 μm (6h at 900°C) (Dryepondt et al., Surf. Coat. Technol., 2006)

High-temperature aluminide coatings showed good long-term oxidation protection in air + 10 vol.% H_2O

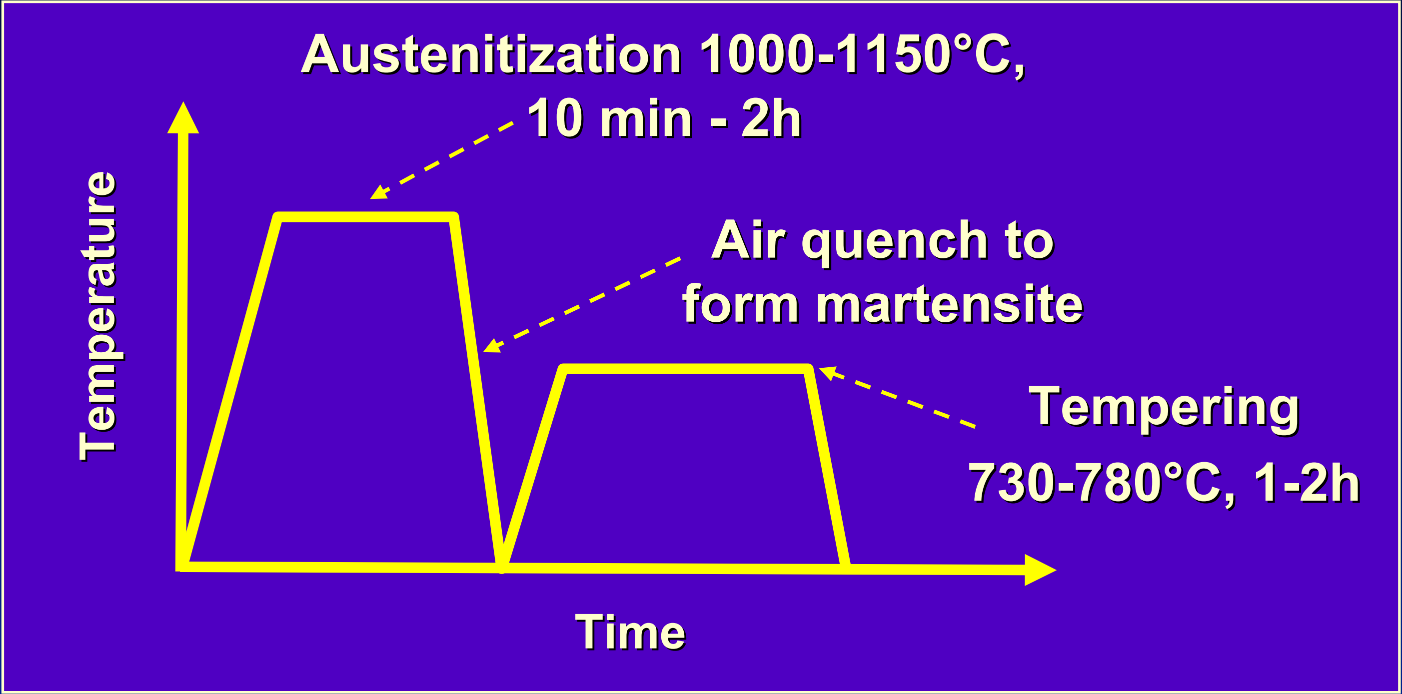


Thick CVD Coating after 20,000h



- At 700°C, thick & thin aluminide coatings have passed 20,000h & 10,000h, respectively (Pint et al., *Surf. Coat. Technol.*, 2007)
- The critical Al in the coating to form Al_2O_3 was ~3.5 at.%

Disadvantages of High Aluminizing Temperatures



- Nearly all aluminizing processes were carried out at 900-1150°C
- Thermochemical treatment of ferritic/martensitic steels at these temperatures can severely degrade their mechanical properties (creep resistance) *(Rohr et al., Mater. Corros. 2005)*

Low-Temperature Diffusion Aluminide Coatings

Task 1: Fabrication of Low-Temp. Aluminide Coatings

1.1 Selection of Substrate Alloys

1.2 Aluminizing Process Optimization

  1.2.1 Thermodynamic Calculations

  1.2.2 Aluminizing Process Optimization

1.3 Coating Characterization

Task 2: Performance of Low-Temp. Aluminide coatings

2.1 Oxidation Resistance in Water-Vapor Environments

2.2 Coating Compositional & Microstructural Evolution during Thermal Exposure

Task 3: Effect of Aluminide Coatings on Mechanical Properties of Substrate Alloys

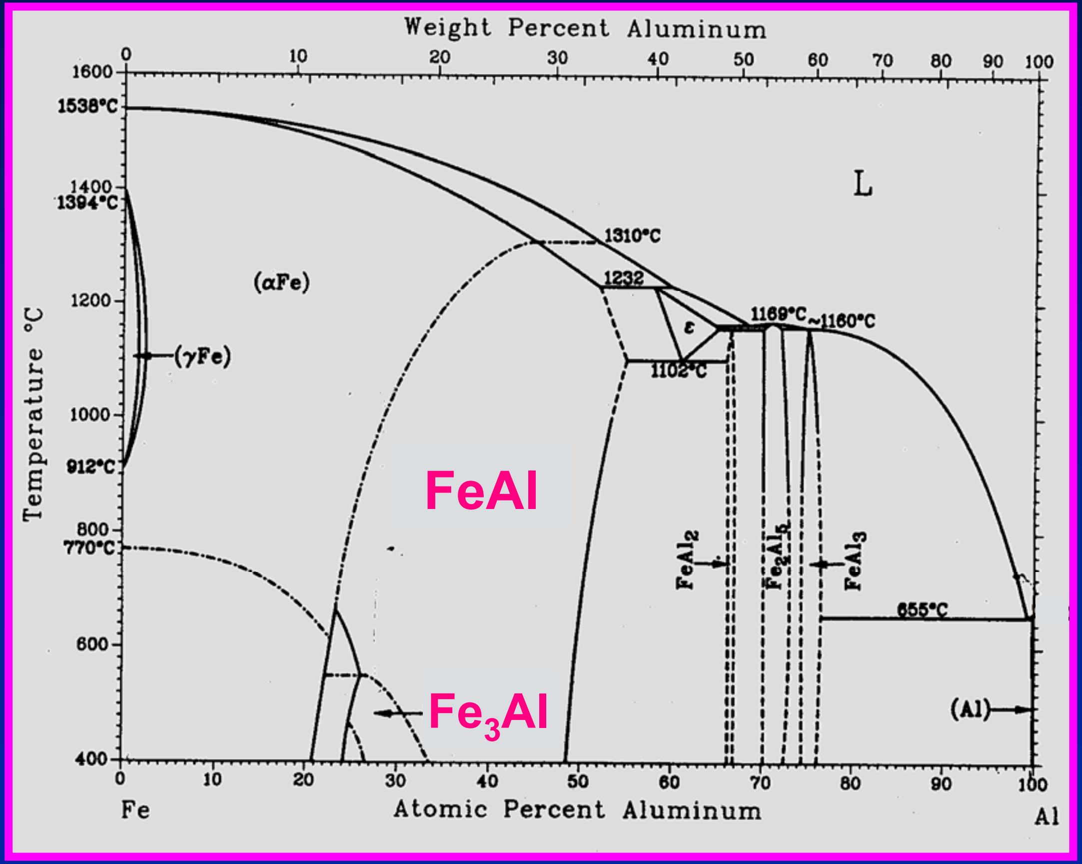
3.1 Creep Test

3.2 Cyclic Thermo-Mechanical Loading Test

Pack cementation — Commercially Viable and Cost-Effective Method for Coating Fabrication

Reaction for Al Deposition:

$$M\ (\text{masteralloy}) + AlX_x = MX_x\ (g) + Al$$



Pack

- **Masteralloy (Al donor: Al or Al-containing alloys)**
- **Activator (NH_4Cl, NaCl)**
- **Inert filler (Al_2O_3)**

Most published research used pure Al masteralloy to synthesize aluminide coatings at low temperatures

Substrate (wt%)	Aluminizing Conditions			Coating Phase
	Temp. / Time	Activator	Masteralloy	
Fe-2.25Cr-1.0Mo-0.01C	650°C / 8h	$AlCl_3$	Al	$Fe_{14}Al_{86}$
		AlF_3		FeAl
	700°C / 8h	$AlCl_3$		$Fe_{14}Al_{86}$
Fe-9Cr-1Mo	650°C / 8h	$AlCl_3$	Al	$Fe_{14}Al_{86}$
		AlF_3		Fe_2Al_5
		NH_4F		
		NH_4Cl		
		NH_4Cl	Cr_5Al_8	FeAl
	720°C / 2h	NH_4Cl	Al	Fe_2Al_5
Fe-9Cr-2W	700°C / 10h	Slurry	Al	Fe_2Al_5

(*Wang, Ph.D. Dissertation, TTU, 2006*)

- Coatings were composed of brittle Al-rich intermetallic phases that have inferior mechanical properties to FeAl, Fe_3Al, or α-Fe(Al)

Research Focus

Develop coating procedures that do not detrimentally affect the mechanical properties of ferritic/martensitic alloys

- Synthesize pack aluminide coatings at temperatures ≤ 750°C
  - ☺ Ensure no M→F phase transformation
  - ☺ Prevent detrimental effect on creep resistance of the alloy
  - ☒ Slow coating growth due to low Al vapor pressure & slow diffusion
  - ☒ Tendency to form brittle Al-rich phases
- Make the coating process compatible with the alloy's heat treatment cycle
- Evaluate coating oxidation performance in water-vapor environments

Routes in Coating Fabrication

Baseline Coating
Pure Al
Masteralloy

→

Binary Masteralloy
Cr-25 wt.% Al
Cr-15 wt.% Al

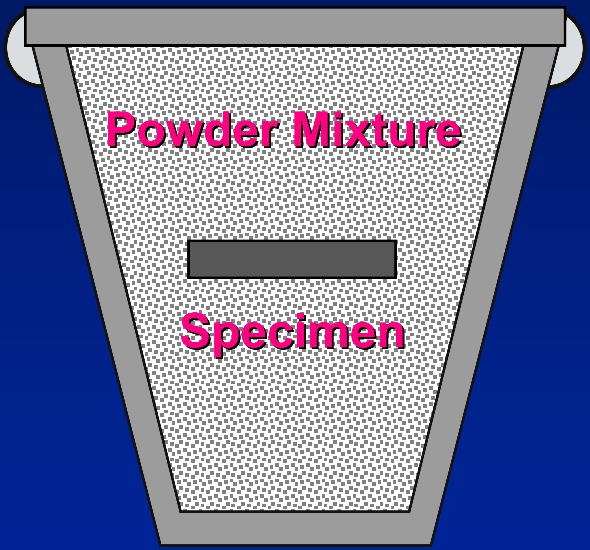
- 700°C
- 750°C

Surface Mechanical Treatment
(Xiang & Datta, *Scipta Mater.*, 2006)

Combined Heat Treatment Cycle

Experimental Approaches

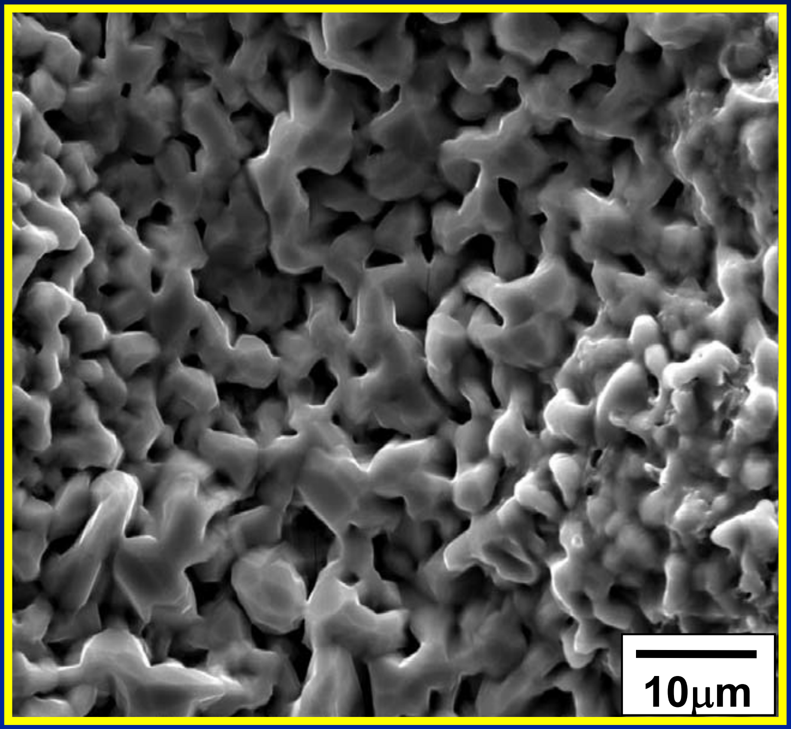
- **Substrates: Commercial Ferritic/Martensitic Alloy P91**
  – Fe-9Cr-1Mo steel (wt.%) (Fe-9.8Cr-0.5Mo, at.%)
- **Pack cementation**
  – Power mixture
    - 10-20 wt.% masteralloy
    - 2 wt.% NH_4Cl activator
    - Balance Al_2O_3 filler
  – Aluminizing time/temperature
    - 6-12 h at 650 ~ 750°C
    - 2h at 1050°C + 2h at 750°C

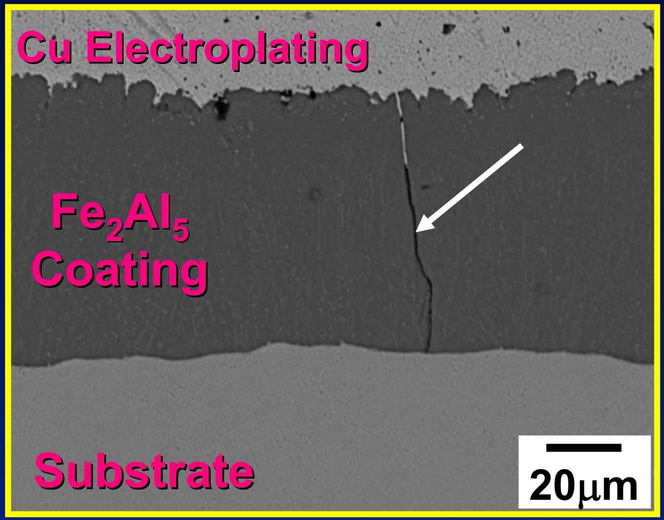


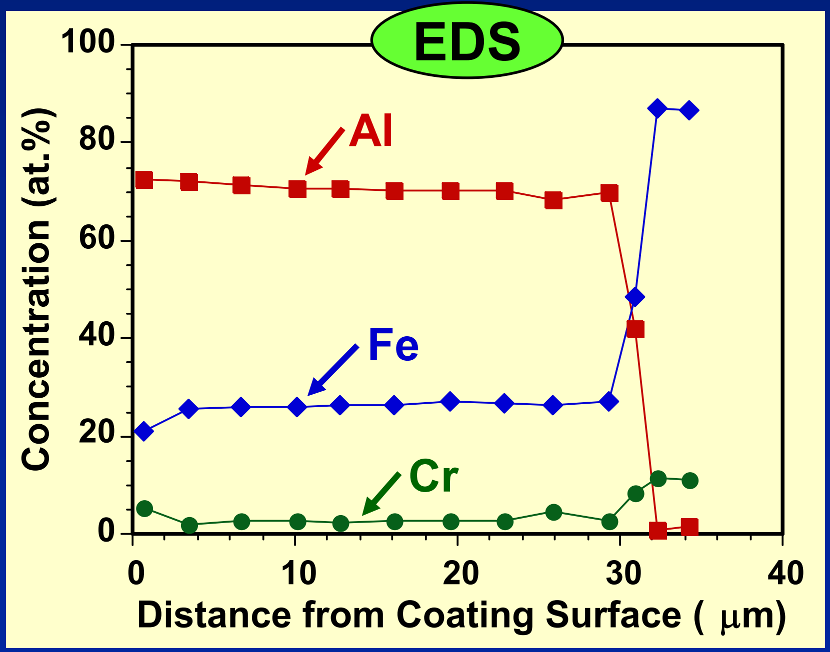
- **Oxidation Testing**
  – 650°C, 100-h cycles, air + 10 vol.% H_2O

Brittle Fe_2Al_5 coating was formed when pure Al was used as masteralloy

$2NH_4Cl$-20Al-$78Al_2O_3$ (wt.%)
650°C / 6h

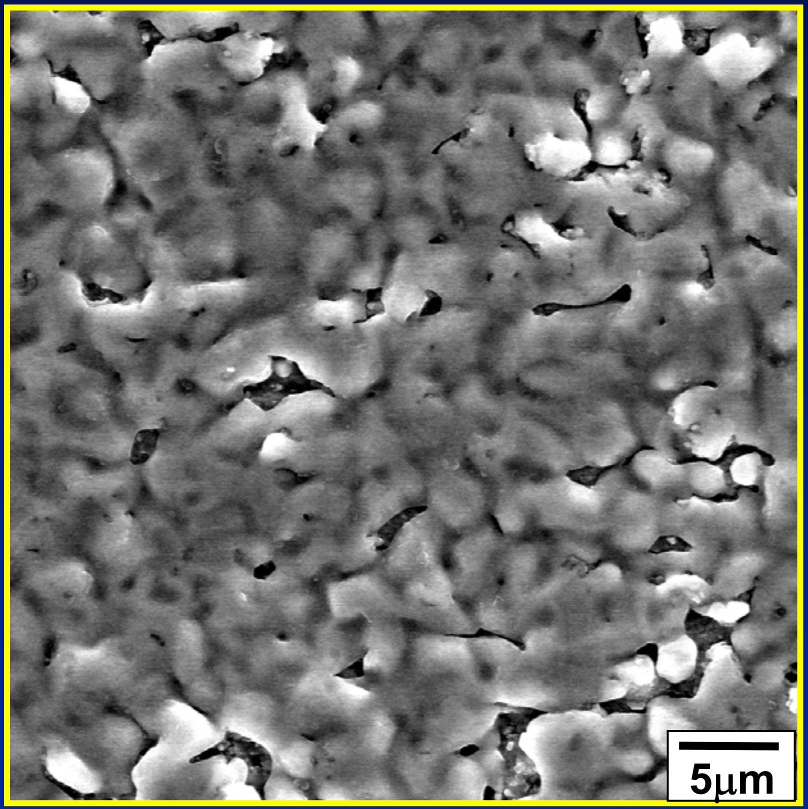


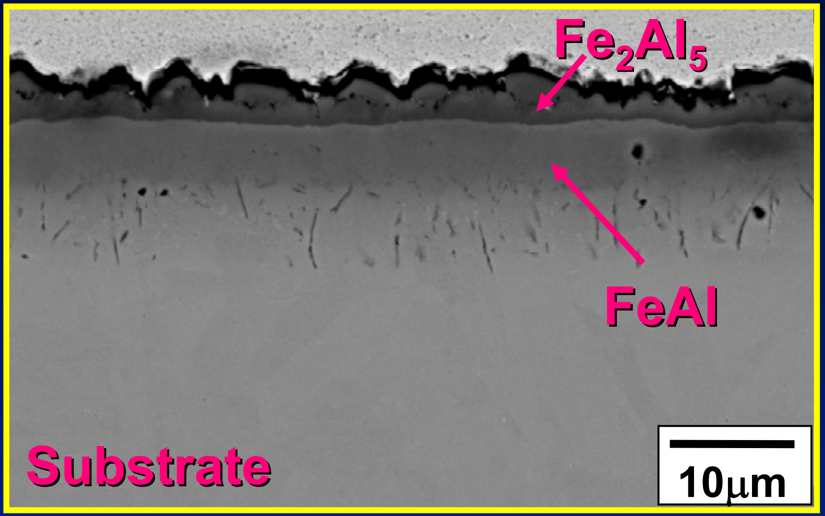


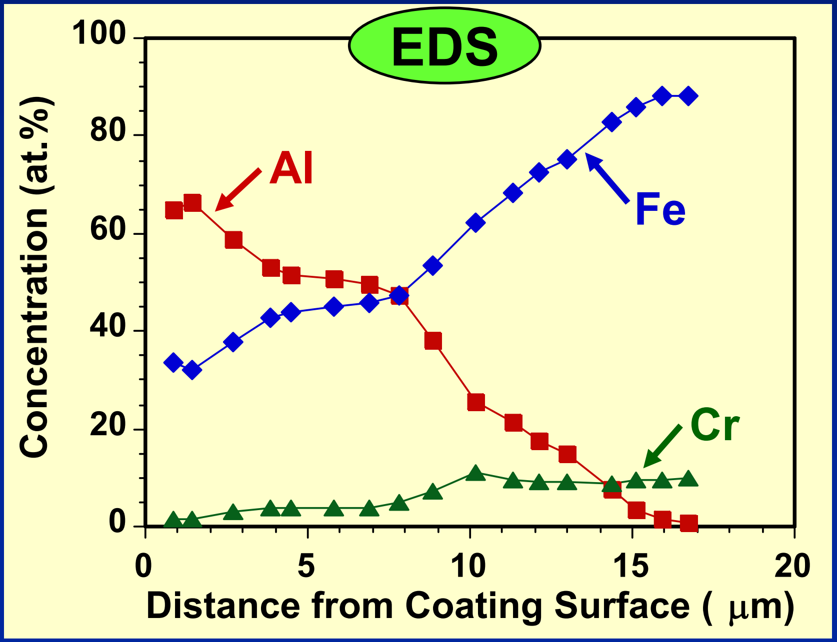


Fe_2Al_5/FeAl two-layer coating was formed using Cr-25wt.%Al masterallloy at 700°C

$2NH_4Cl$-15(Cr-25Al)-$83Al_2O_3$
12h at 700°C



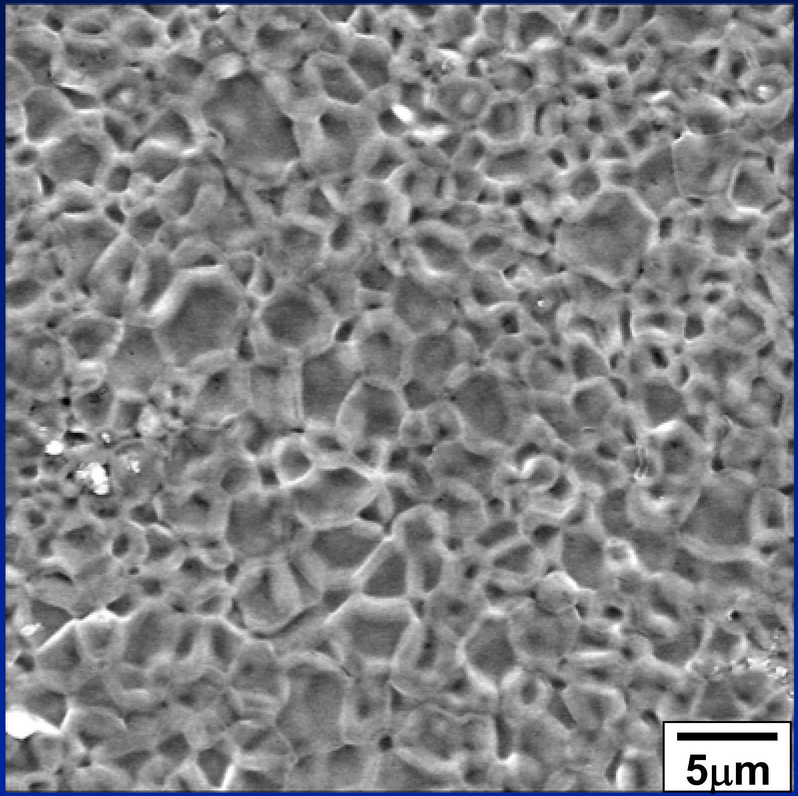


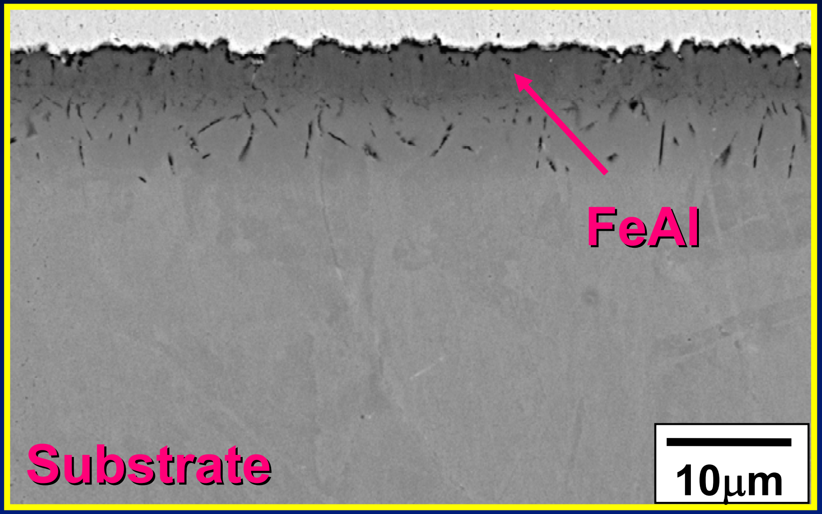


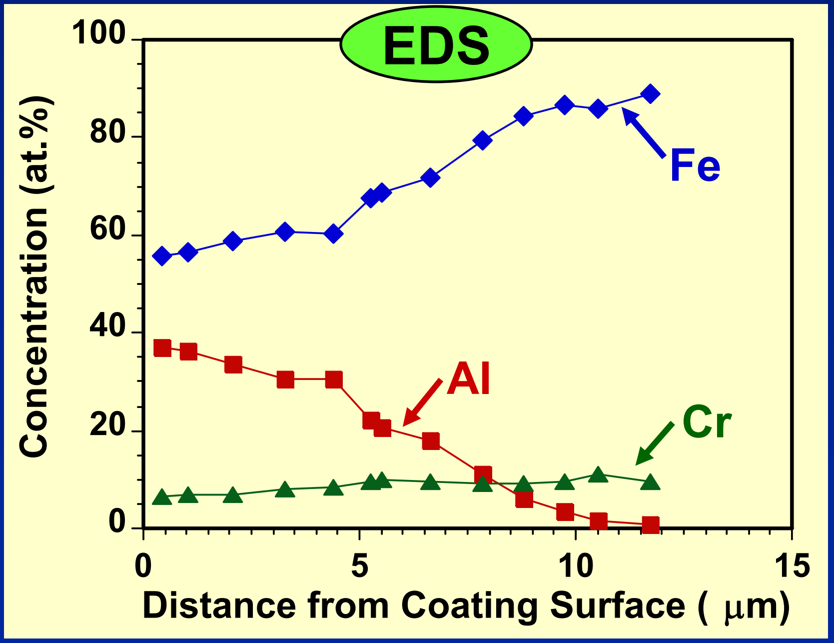
- A layer of 4 μm Fe_2Al_5 on top of 12 μm FeAl

FeAl coating was obtained with reduced Al activity using Cr-15wt.%Al masteralloy

$2NH_4Cl$-20(Cr-15Al)-$78Al_2O_3$
12h at 700°C





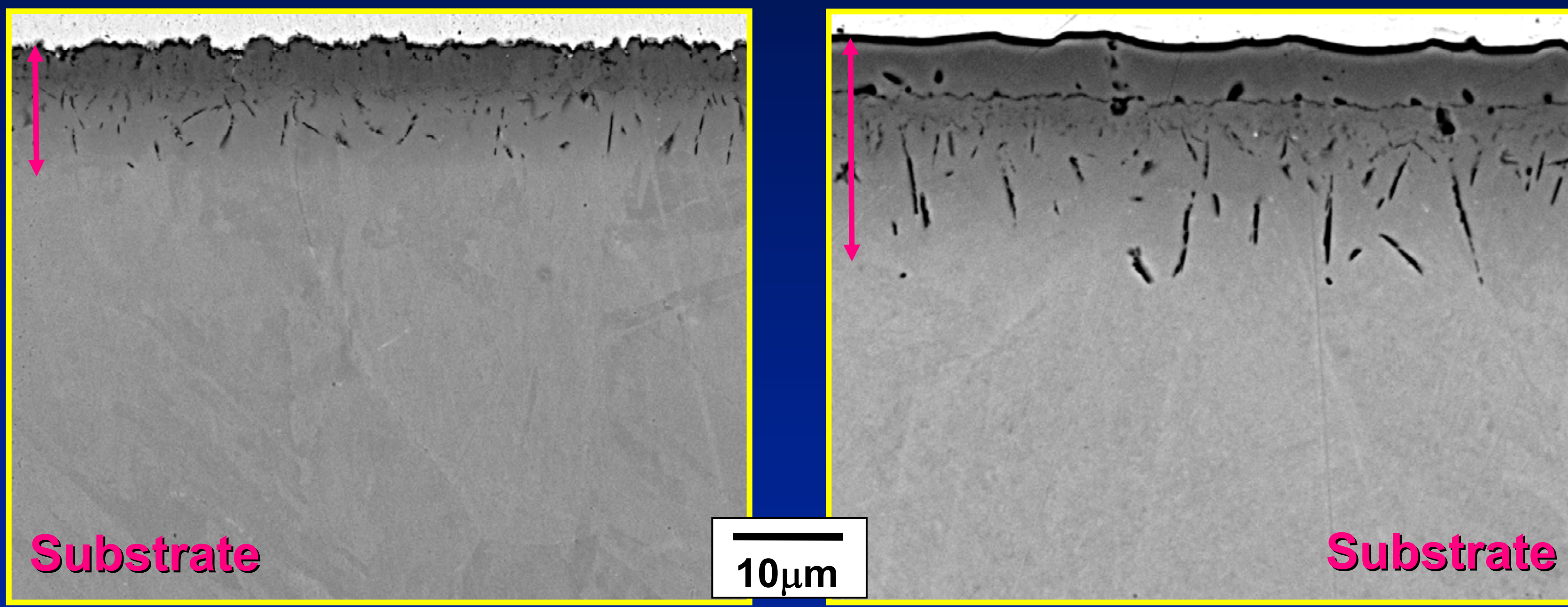


- FeAl coating, 12 µm
- Surface Al: ~40 at.%

Increasing coating temperature from 700 to 750°C resulted in ~70% increase in coating thickness

$2NH_4Cl$-20(Cr-15Al)-$78Al_2O_3$

12h at 700°C | 12h at 750°C



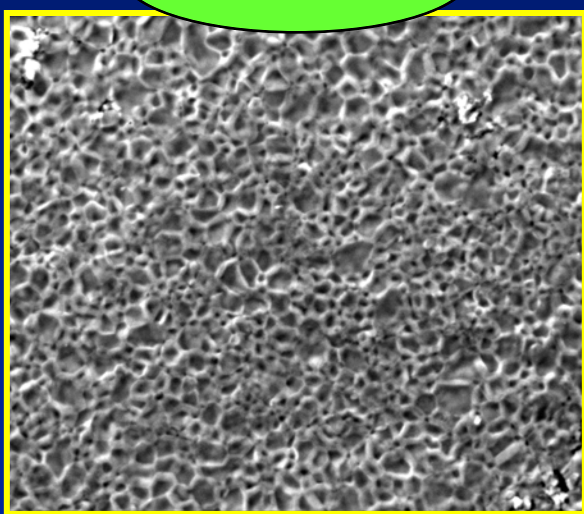
- The coating thickness increased from ~12 to 20 μm
- The Al content at the surface remained ~ 35-40 at.%

Effect of Surface Treatment Prior to Aluminizing

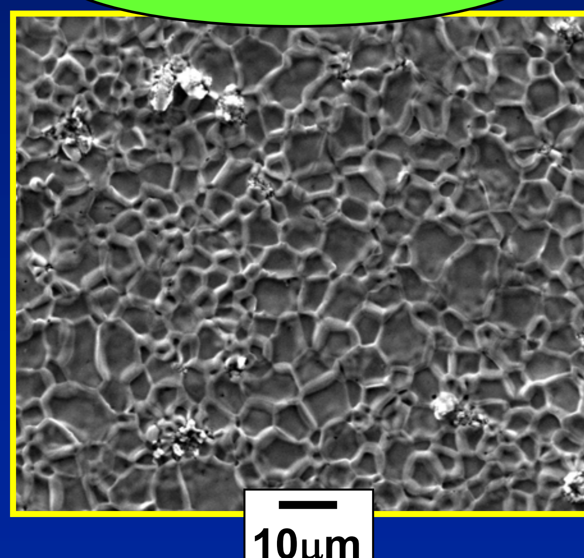
$2NH_4Cl$-20(Cr-15Al)-$78Al_2O_3$
12h at 700°C

Laboratory Ball Milling
- 1/4” steel balls
- 22 Hz frequency

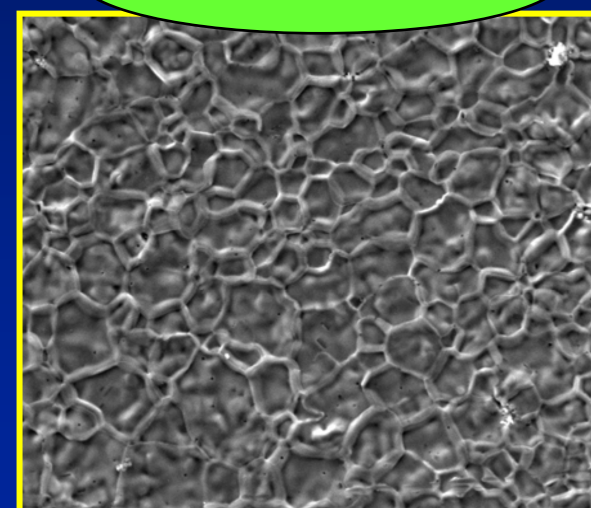
#600 Grit



15min Treatment

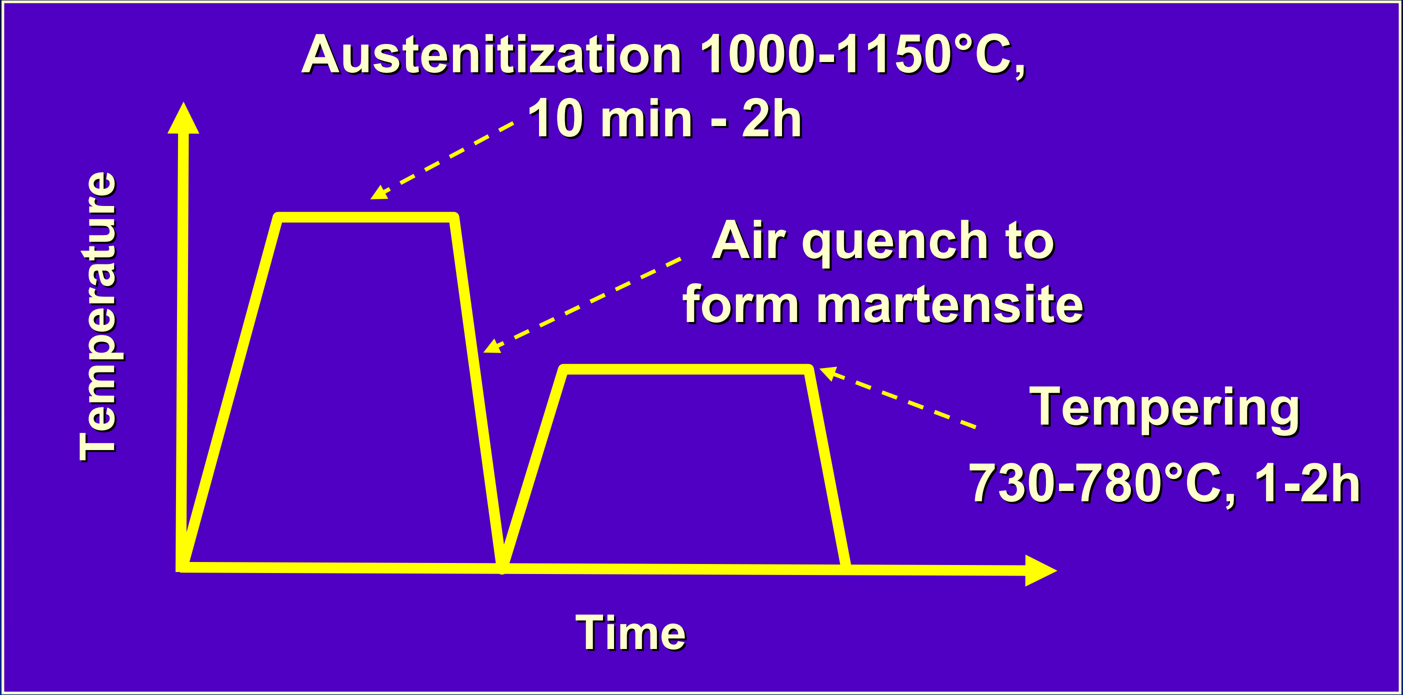


30min Treatment



- An increase in coating grain size was observed with surface mechanical treatment prior to aluminizing

Combined Heat Treatment Cycle

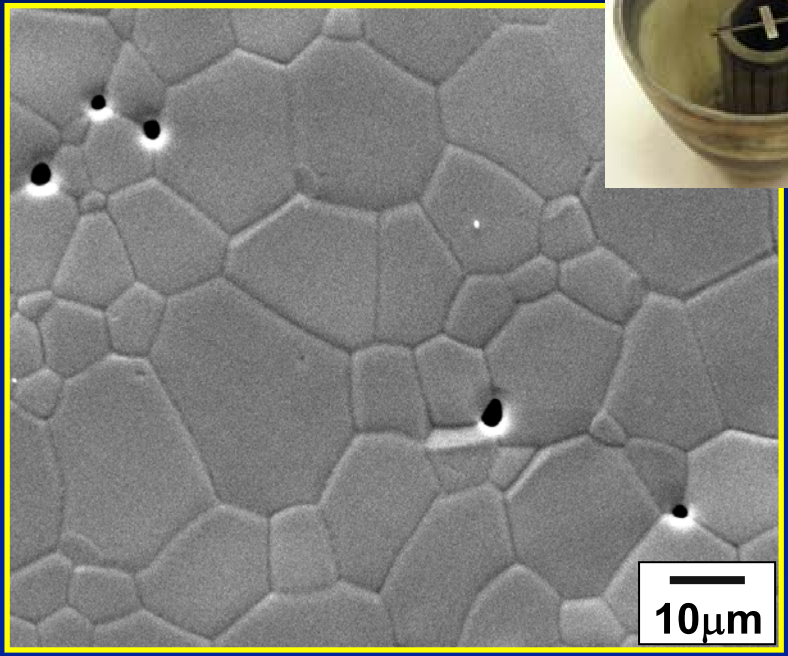


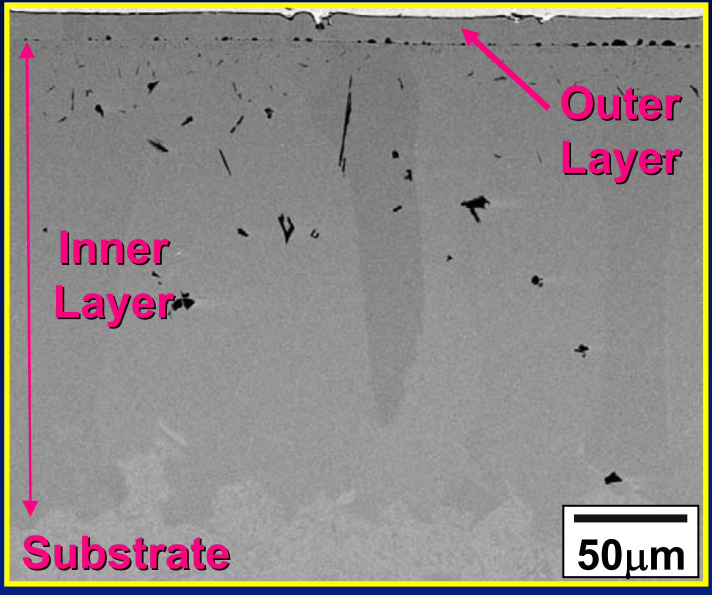
- Pack aluminizing
  - 1050˚C x 2h + 750˚C x 2h
- Air quench is difficult to achieve in pack aluminizing; however, other aluminizing processes such as slurry aluminizing may be able to accomplish it

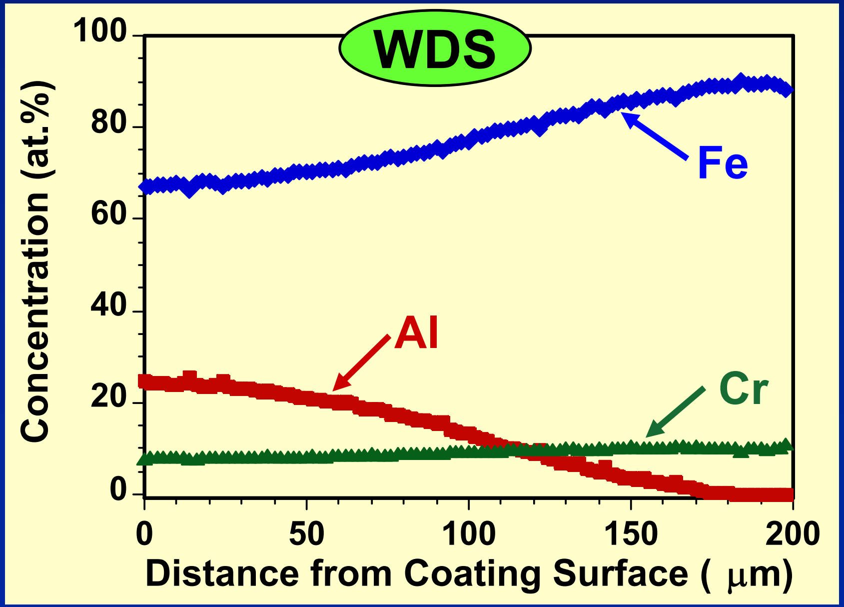
The heat treatment cycle produced a coating of ~170μm thick with 25 at.%Al at the surface

$2NH_4Cl$-20(Cr-15Al)-78Al_2O_3

1050˚C x 2h + 750˚C x 2h

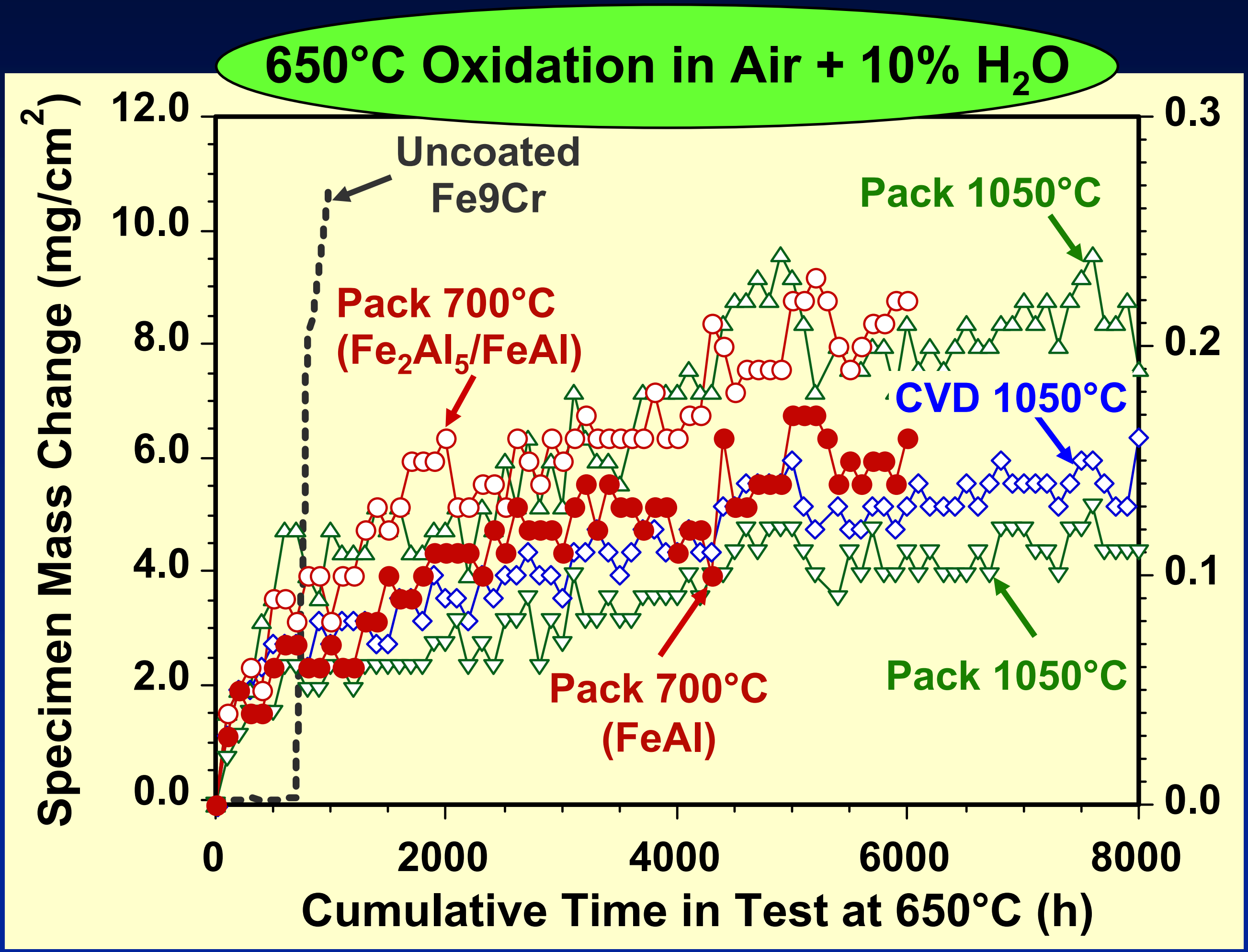






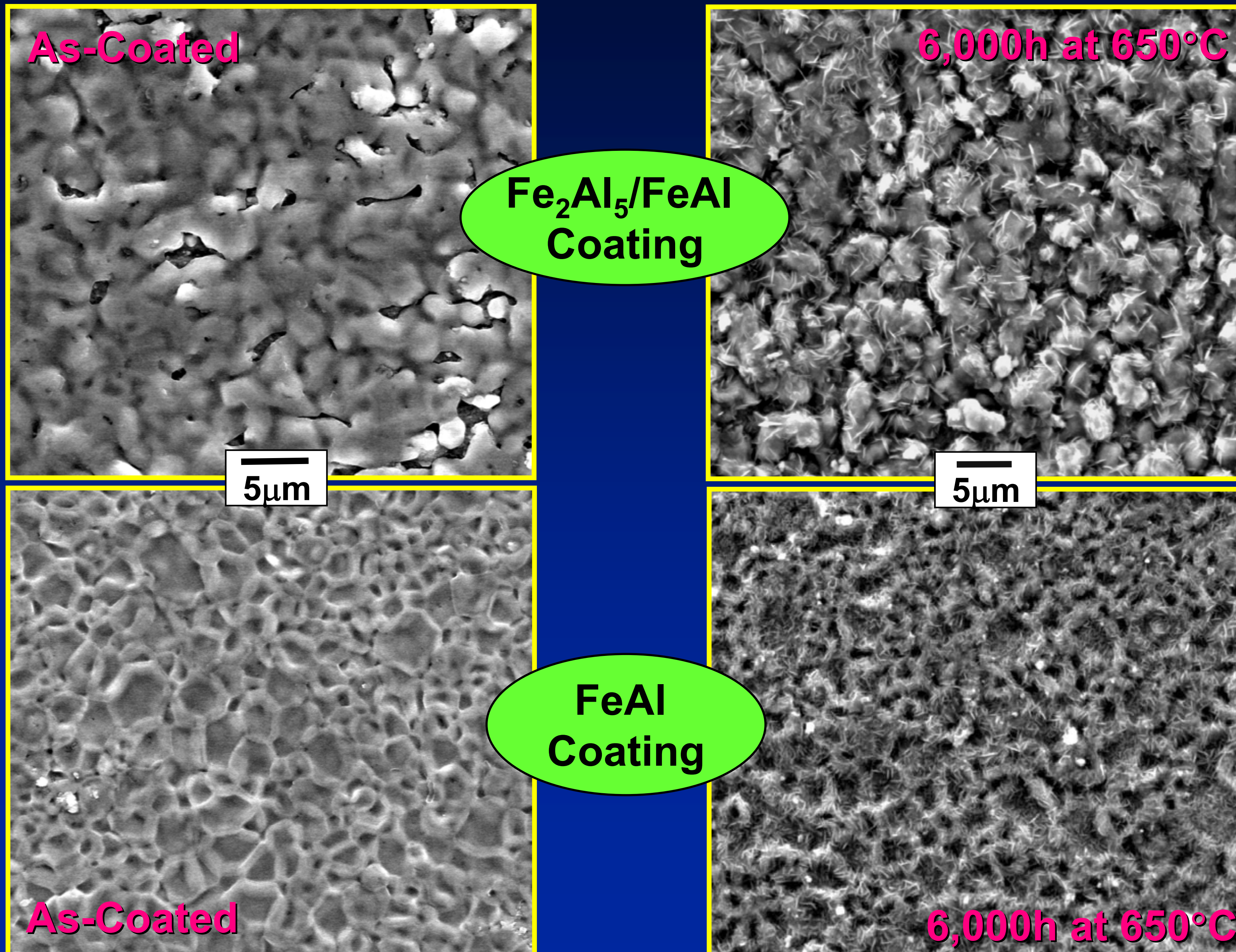
- FeAl coating: ~ 170 μm

Low-temperature pack coatings have passed 6,000h oxidation testing in air + 10 vol.% H_2O at 650°C



- Pack coatings made at 700°C registered similar mass gains to CVD and pack coatings fabricated at 1050°C

Thin & adherent oxide was formed on low-temperature pack coatings after 6,000h in air + 10% H_2O at 650°C



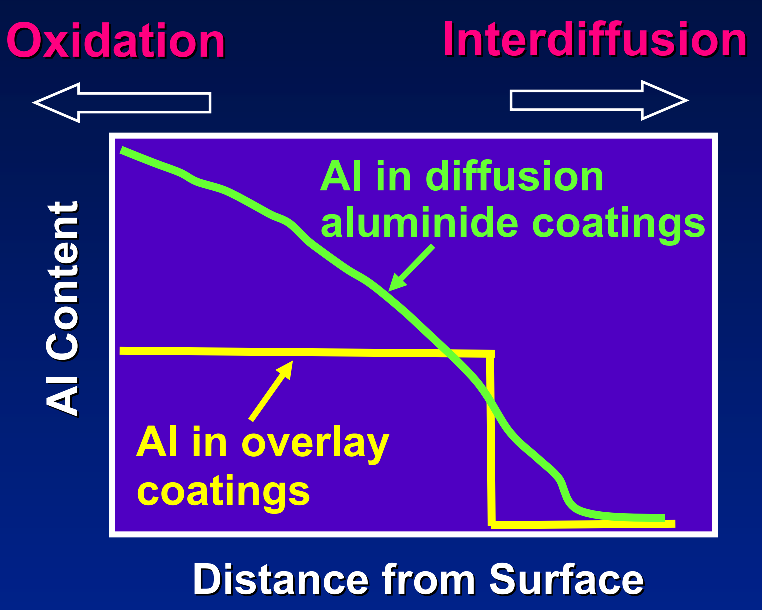
Comparison of Al Reservoir in Aluminide Coatings

Coating	Thickness (μm)	Surface Al (at.%)	Al Reservoir (at.% x μm)	Oxidation Test
Thin CVD (900°C)	50	18	450	10kh / 700°C
Thick CVD (1050°C)	260	26	3380	20kh / 700°C
Fe_2Al_5 / FeAl (700°C)	4 / 12	65 / 50	560	6kh / 650°C
FeAl (700°C)	10	40	200	6kh / 650°C
FeAl (750°C)	20	40	400	—
FeAl (1050 / 750°C)	25	170	2125	—

- The thin CVD coating passed 10,000h at 700°C before failure
- Minimal interdiffusion is expected at 650°C (Zhang et al., *Mater. Corros.*, 2007)
- Low-temp. pack coatings should have a lifetime comparable to CVD thin coatings

A model is needed to predict coating lifetime

- Al is consumed via oxidation at the coating surface and interdiffusion between the coating & the substrate



- COSIM (*Coating Oxidation & Substrate Interdiffusion Model*) was developed to predict concentration profiles in MCrAlY overlay coatings (J.A. Nesbitt, NASA/TM, 2000-209271)
- In contrast to overlay coatings with a constant Al profile, diffusion aluminide coatings exhibit a composition gradient
- COSIM will be modified to model Al loss and to predict coating lifetime (Zhang et al., *Mater. Corros.*, 2007)

Initial Work to Coat Mechanical Testing Samples

As-machined

10mm

As-coated

$2NH_4Cl$-20(Cr-15Al)-$78Al_2O_3$
12h at 700°C

- **Uniform coating was obtained on the dog-bone specimens using a non-contact pack-specimen arrangement**

Summary

- Routes were explored to coat ferritic/martensitic alloys that do not detrimentally affect their mechanical properties
  - Brittle Fe_2Al_5 coating was formed when pure Al was used as the masteralloy
  - With Cr-25Al masteralloy, a coating of Fe_2Al_5/FeAl was formed at 700°C
  - Use of Cr-15Al masteralloy led to formation of a thin (10-12 μm) FeAl coating; increasing aluminizing temperature to 750°C nearly doubled coating thickness
  - Surface mechanical treatment affected coating nucleation
  - Combination of alloys' heat treatment with coating fabrication resulted in a significant increase in coating thickness

Summary (Cont'd)

- The aluminide coatings synthesized at 700°C showed excellent oxidation resistance behavior for 6,000h (> 8 months) at 650°C in air + 10% H_2O
- Initial effort shows that uniform coatings could be achieved on the dog-bone specimens using a non-contact pack-specimen arrangement

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