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

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2007 University Coal Research

Historically Black Colleges and Universities & Other Minority Institutions

Contractors Review Conference

Pittsburgh, PA

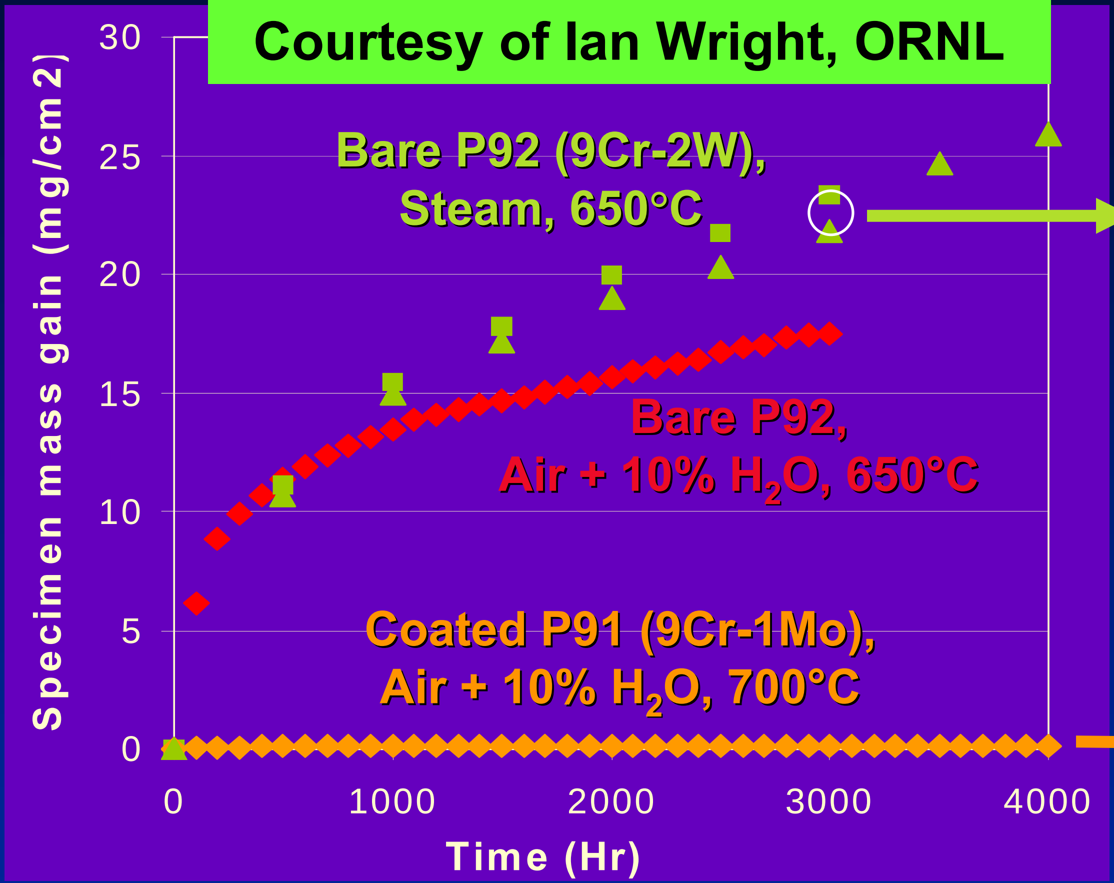
June 5-6, 2007

Why Iron Aluminide Coatings?

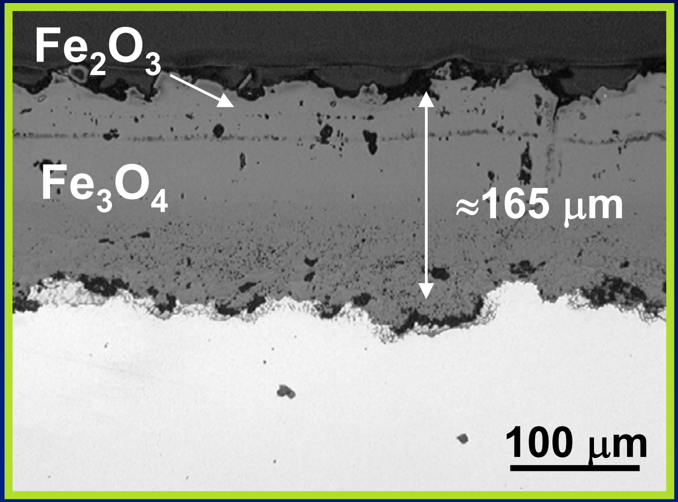
- Improvement of coal-fired power plant efficiency requires increase in steam temperature & pressure
- Advanced 9%Cr ferritic/martensitic alloys may be creep resistant up to 650°C but they will suffer extensive steam-side oxidation

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

Effect of Aluminide Coatings



Bare P92, 3000h, 650°C



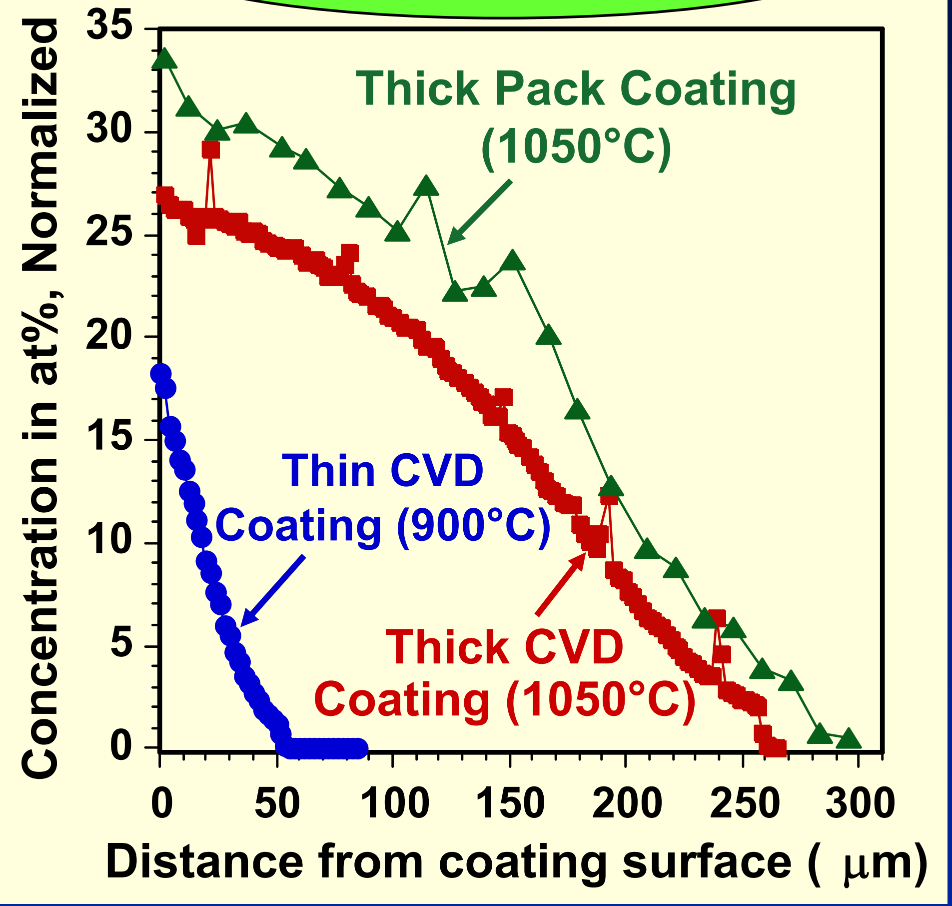
oxide scale < 2 μm thick

- Unlike in dry air, many Fe-base alloys are rapidly oxidized in steam/humid air when not coated
- 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

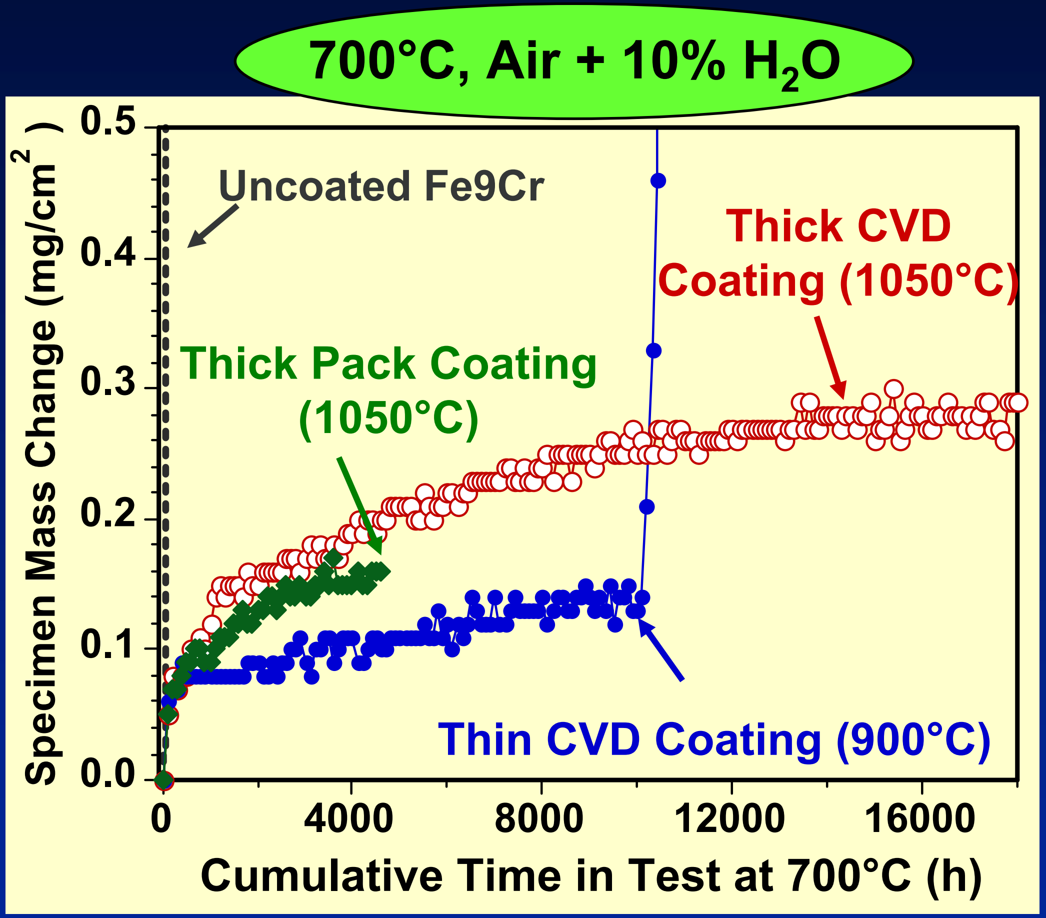
CVD, 6h @ 1050° C

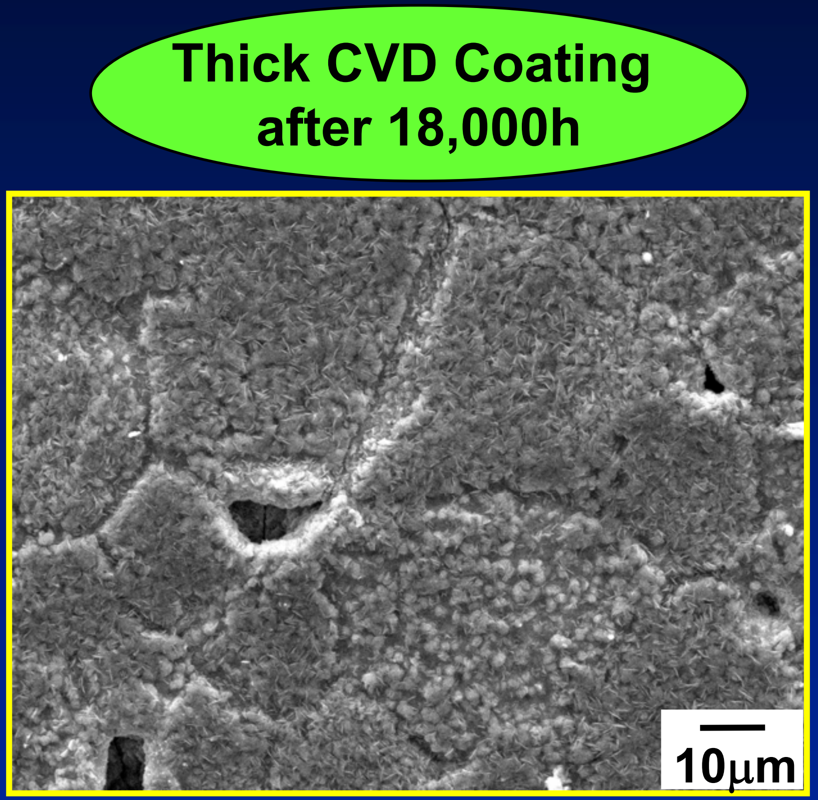
Al Profiles in the Coating



- Thick CVD or Pack Coatings: 250-300 μm (6h at 1050°C)
- Thin CVD Coatings: 50-100 μm (6h at 900°C)

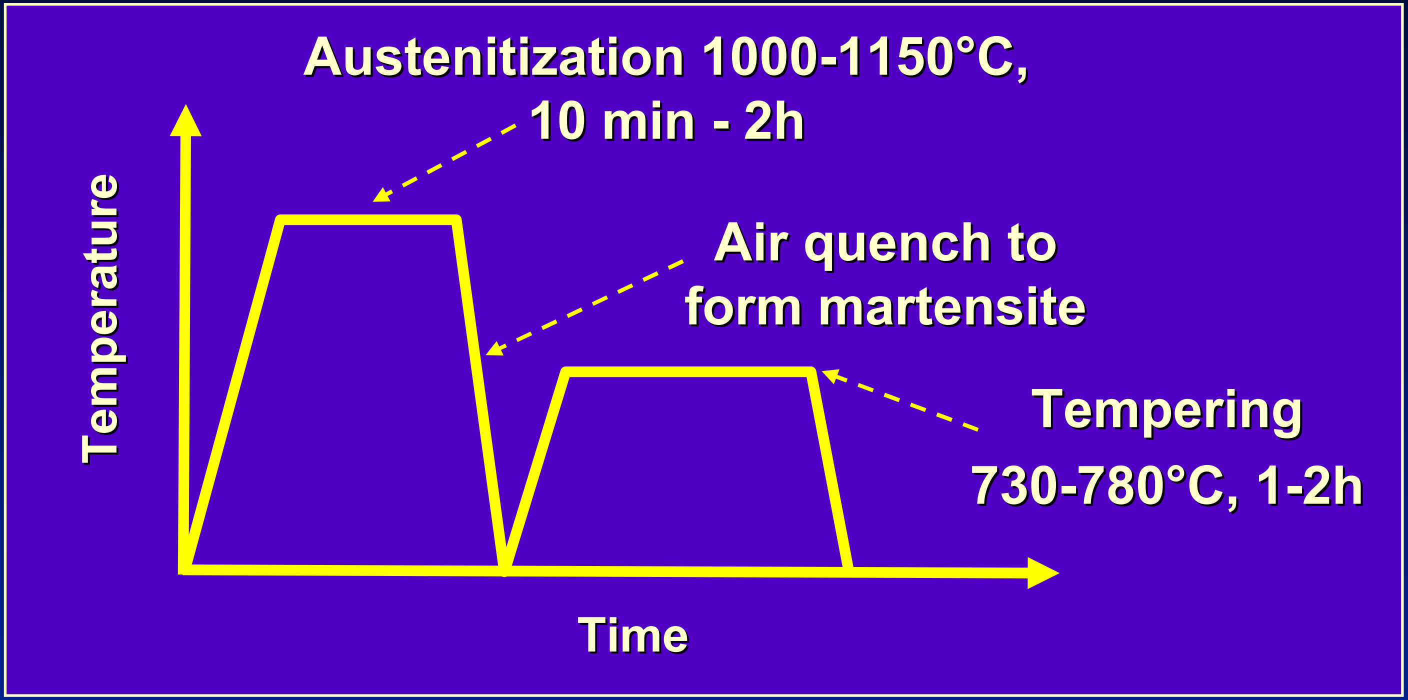
High-temperature aluminide coatings showed good long-term oxidation protection in air + 10 vol.% H_2O





- At 700°C, thick & thin aluminide coatings have passed 18,000h & 10,000h, respectively (Pint et al., submitted to *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 for 4-16h
- Thermochemical treatment of ferritic/martensitic steels at these temperatures can severely degrade their mechanical properties (creep resistance) *(Rohr et al., Mater. Corros. 2005)*

Research Focus

- Synthesize **pack aluminide coatings at low-temperatures (≤ 700°C)** on ferritic/martensitic alloys with reduced brittleness

- Low aluminizing temperature will
  - ensure no M→F phase transformation
  - prevent increase of the grain size of the substrate alloy
  - reduce manufacturing cost if combining coating process with heat-treatment cycle
- Limitations of Low Aluminizing Temperature
  - Slow coating growth due to low Al vapor pressure & slow diffusion
  - Tendency to form brittle Al-rich phases

Three Key Research Components

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

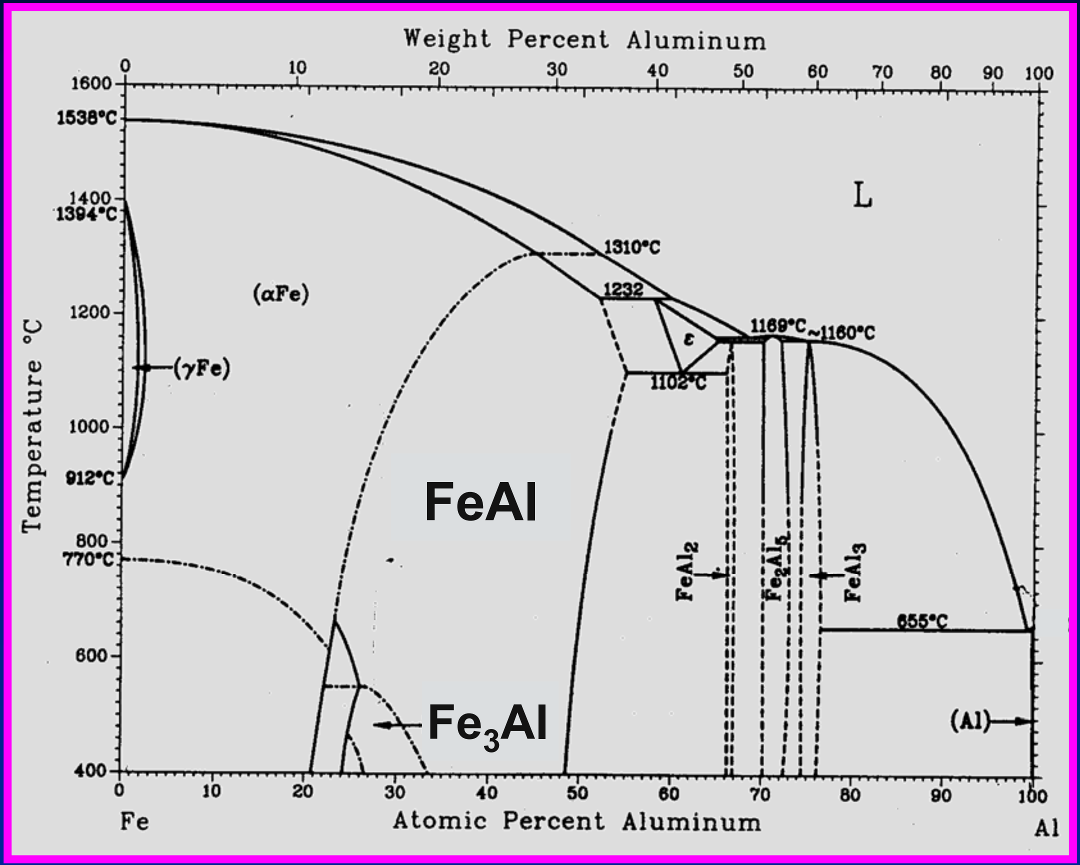
Task 2: Performance of Low-Temp. Aluminide coatings

- 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

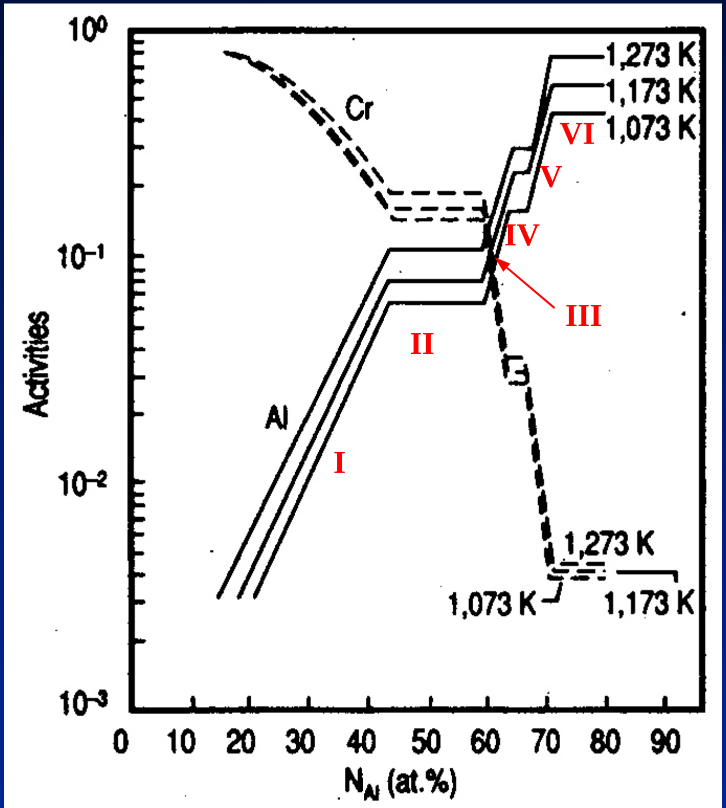


Pack
- Masteralloy (Al donor: Al or Al-containing alloys)
- Activator (NH_4Cl, NaCl)
- Inert filler (Al_2O_3)

Reaction for Al Deposition: M (masteralloy) + AlX_x = MX_x (g) +Al

- **Binary masteralloys can be used to lower the Al activity & reduce tendency of forming brittle Al-rich phases (Fe_2Al_5, $FeAl_3$)**

Thermodynamic Considerations



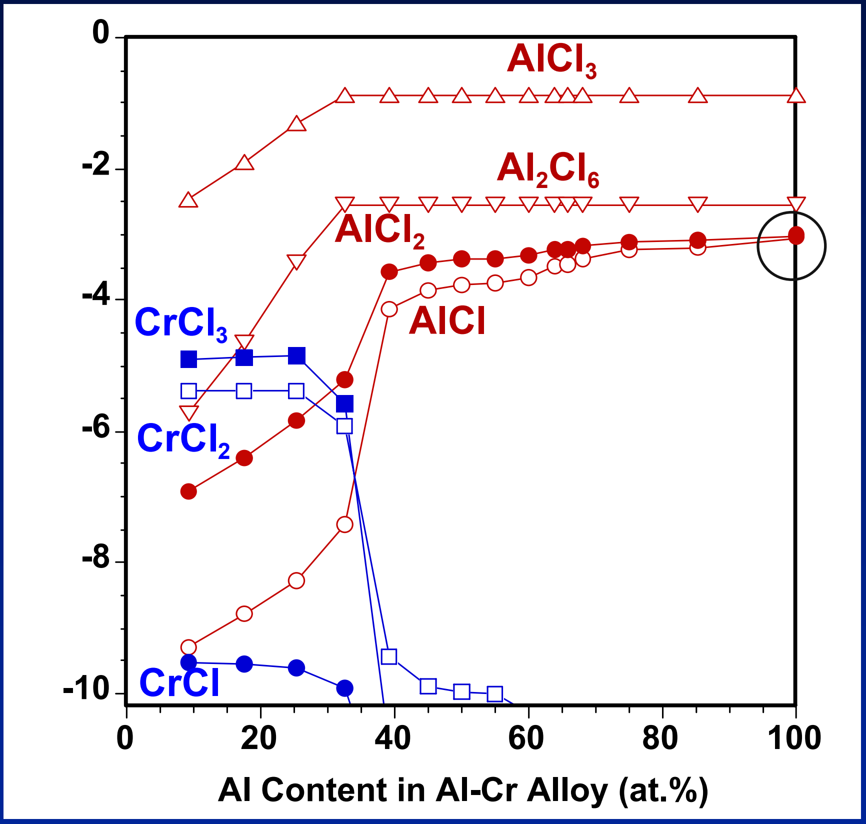
Nciri & Vandenbulcke, in *Proc. 4th European Conference on Chemical Vapor Deposition*, 1983

- For the Al-Cr binary alloy, the activities of both Al and Cr are a function of the Al content
- Vapor pressures of Al halides were calculated for packs containing Al-Cr masteralloys with various Al at 700°C

The Al activity in the pack process can be tailored by adjusting the Al content in the masteralloy

$6NH_4Cl$-20(Al-Cr)-$74Al_2O_3$ (in wt.%), 700°C

HSC 5.0 Thermodynamic Software



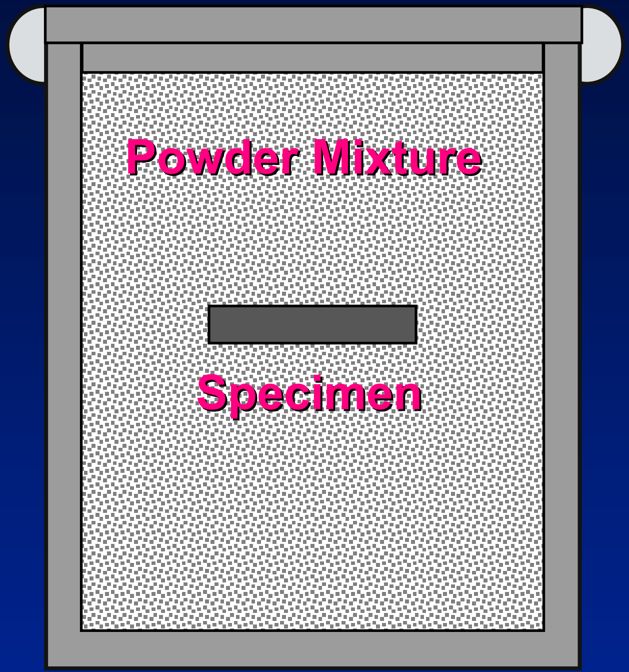
- **AlCl and $AlCl_2$ are the species directly responsible for Al deposition** (Xiang and Datta, *J. Mater. Sci.*, 2005)
- **When Al > 40 at.% in the Al-Cr masteralloys, Al deposition becomes dominant**

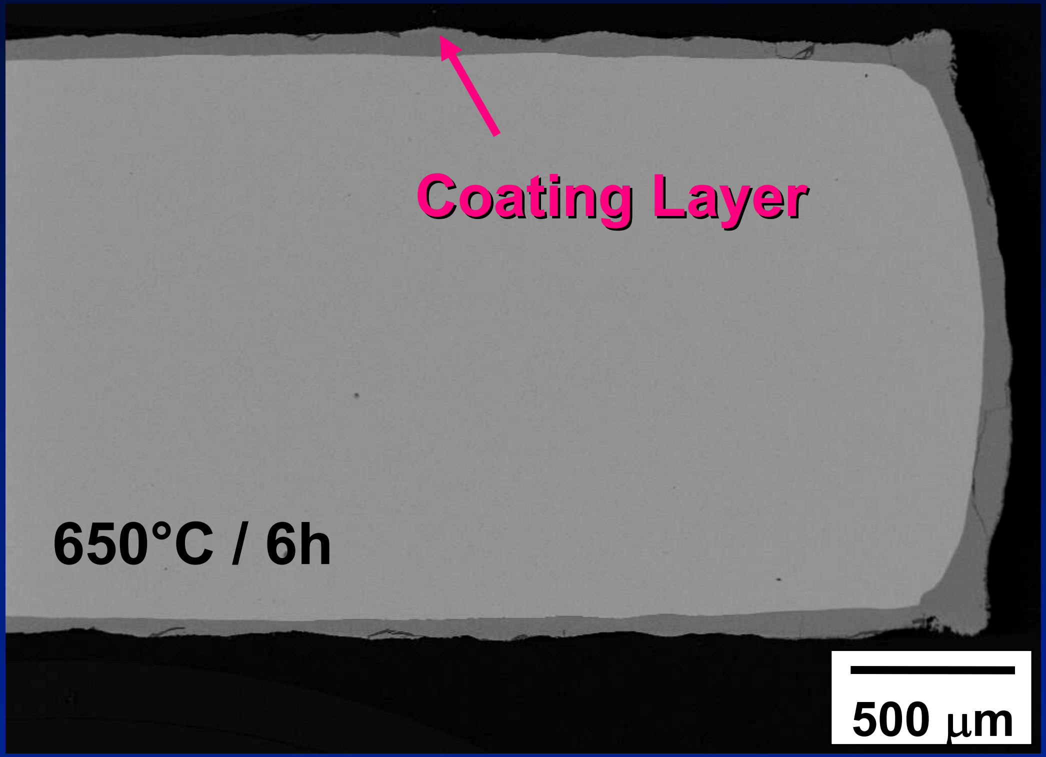
Experimental Approaches

- Substrates: Commercial Ferritic/Martensitic Alloy P91
  - Fe-9Cr-1Mo steel (wt.%)
- Pack Cementation: 6-12 h at 650°C and 700°C
- Pack Powder Mixture
  - 1-2 wt.% NH_4Cl activator
  - 10-20% masteralloy
  - Balance Al_2O_3 filler
- Oxidation Testing:
  - 650°C
  - 100-h cycles

Elements	wt.%	at.%
Fe	88.46	87.75
Cr	9.26	9.87
Mo	0.96	0.55
Mn	0.47	0.47
V	0.23	0.25
Si	0.19	0.37
Ni	0.16	0.15
Cu	0.07	0.06
Nb	0.05	0.03
C	516 ppm	0.238
N	480 ppm	0.190
O	26 ppm	0.009
S	8 ppm	0.001

Pure Al was used as the masteralloy to obtain the baseline coatings at 650°C

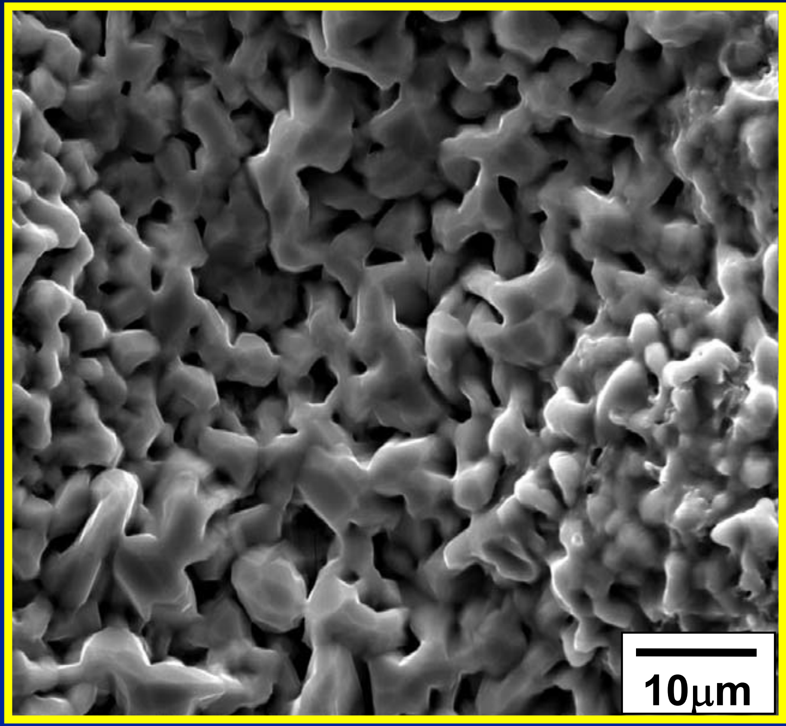


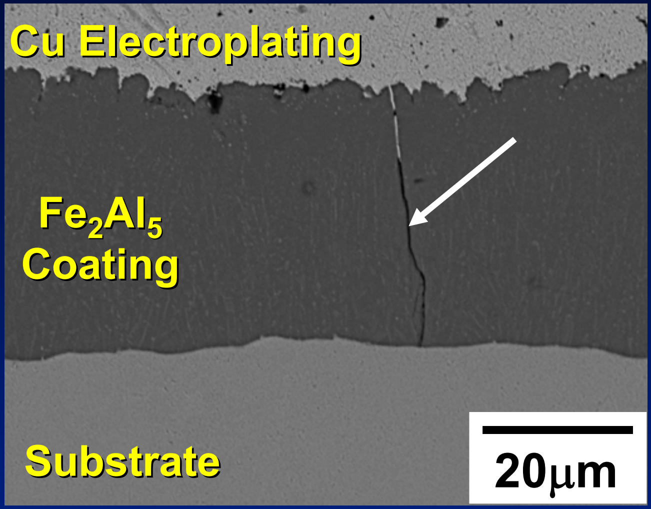


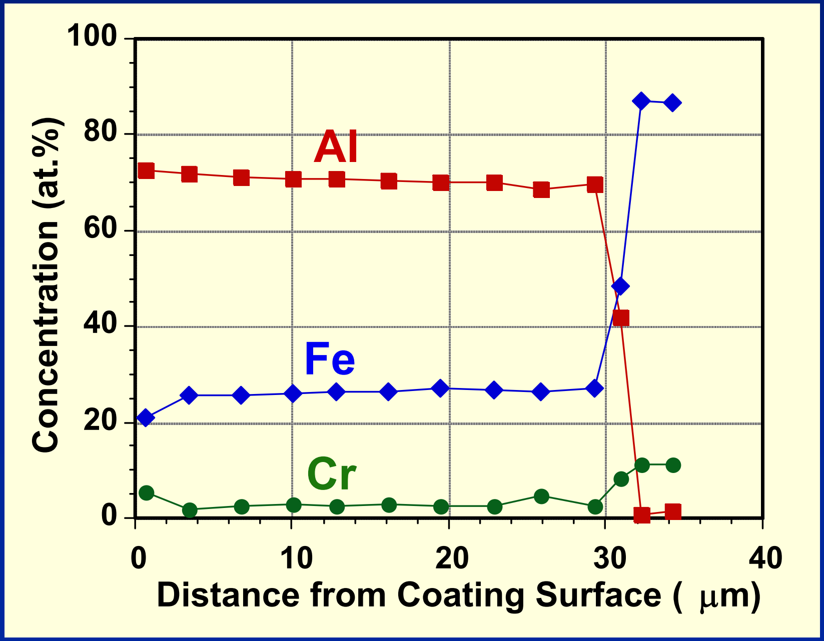
Pack Composition (wt.%)	Average Coating Thickness (μm)	
	Surface	Around Corner
$1NH_4Cl$-10Al-$89Al_2O_3$	7-47	60
$2NH_4Cl$-20Al-$78Al_2O_3$	32-79	190

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

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







Modifications in the Pack Aluminizing Process

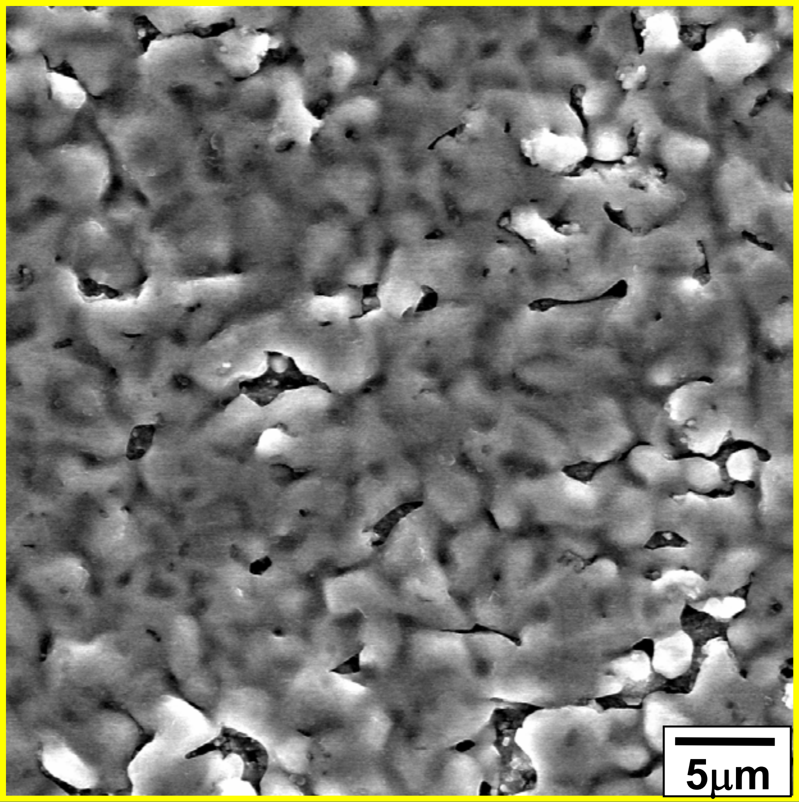
Baseline Coating:
650°C/6h with pure Al masteralloy
2NH_4Cl-20Al-78Al_2O_3 (wt.%)
non-uniform Fe_2Al_5

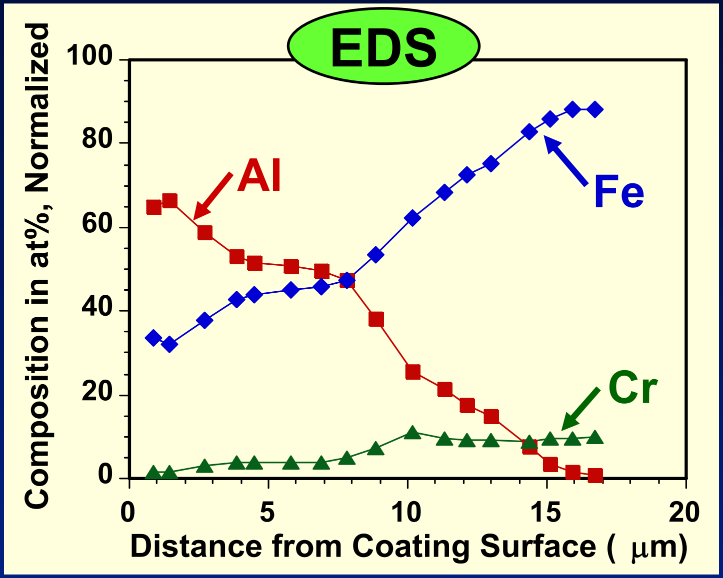
Binary Cr-Al masteralloy
Cr-25 wt.% Al
Cr-15 wt.% Al

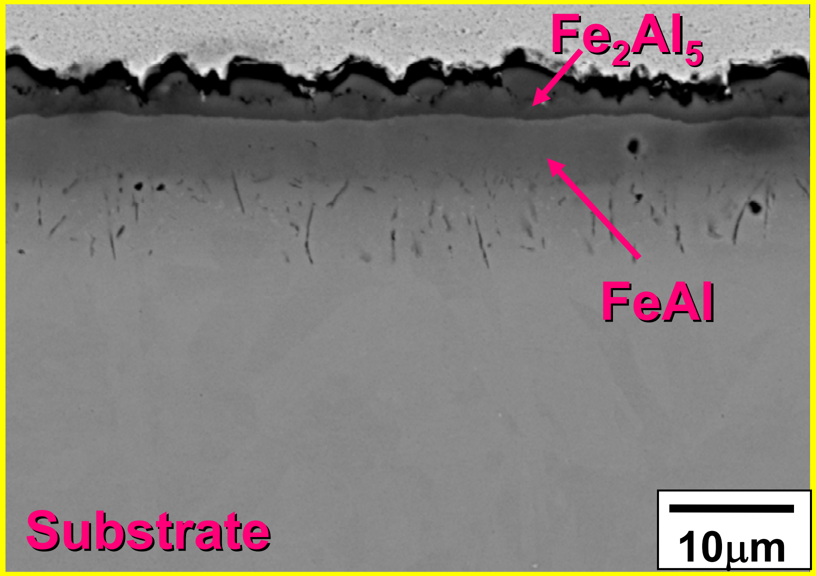
Increase aluminizing temperature and time
700°C/12h

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

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



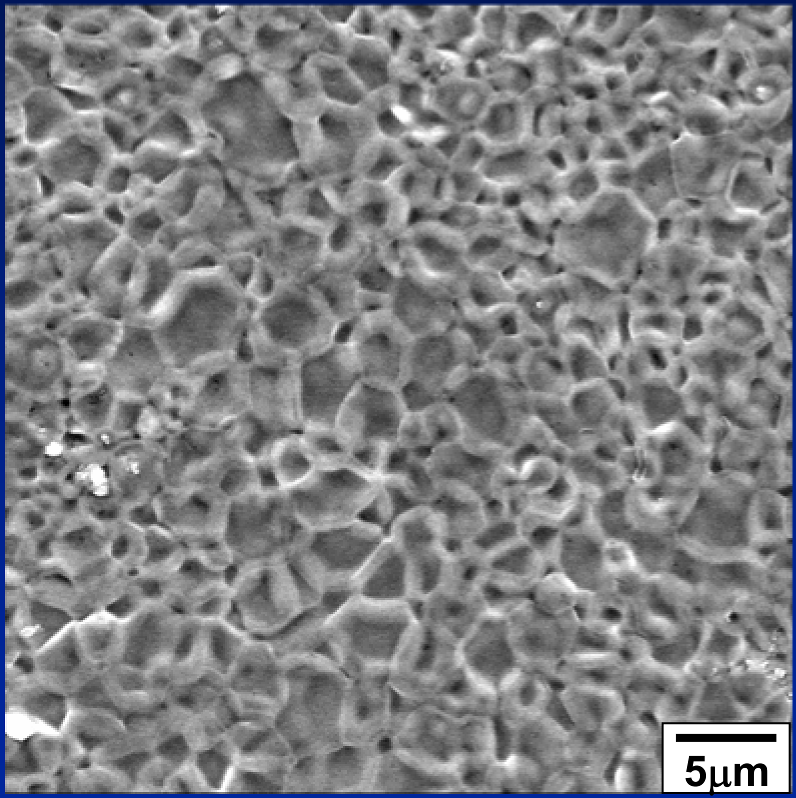


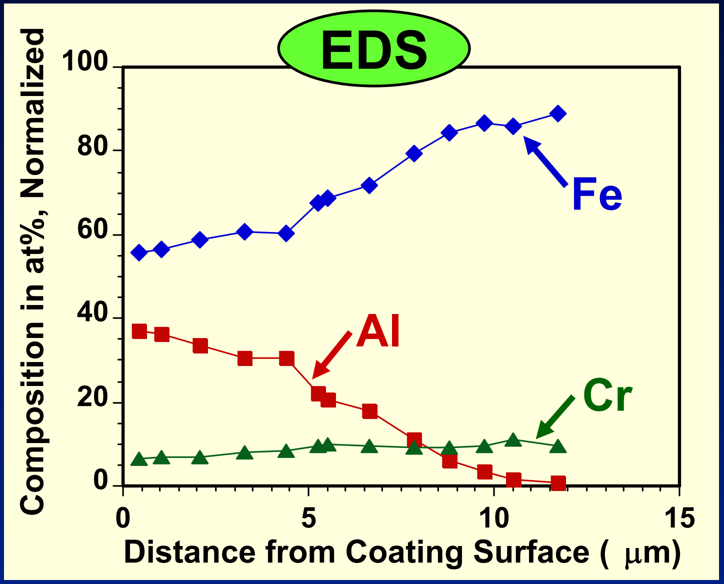


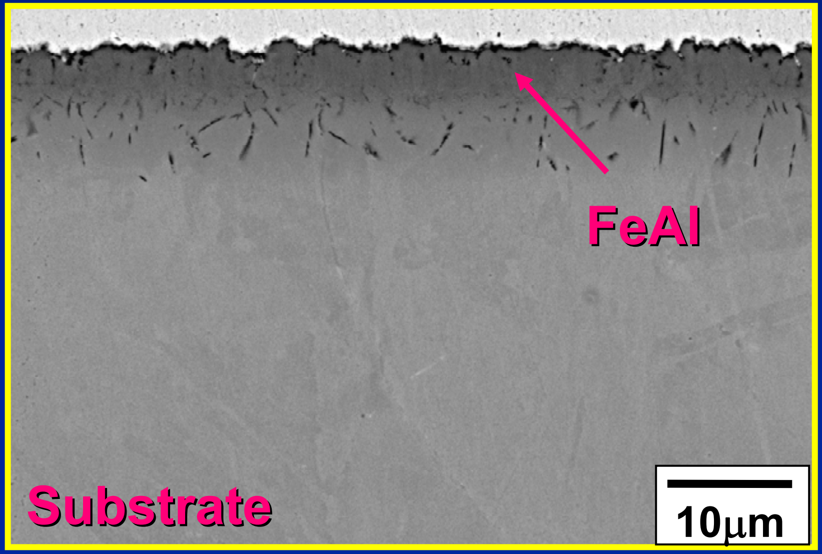
- A layer of 4 µm Fe_2Al_5 on top of 12 µm FeAl

FeAl coating (~10μm) was obtained with reduced Al activity using Cr-15wt.%Al masteralloy

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

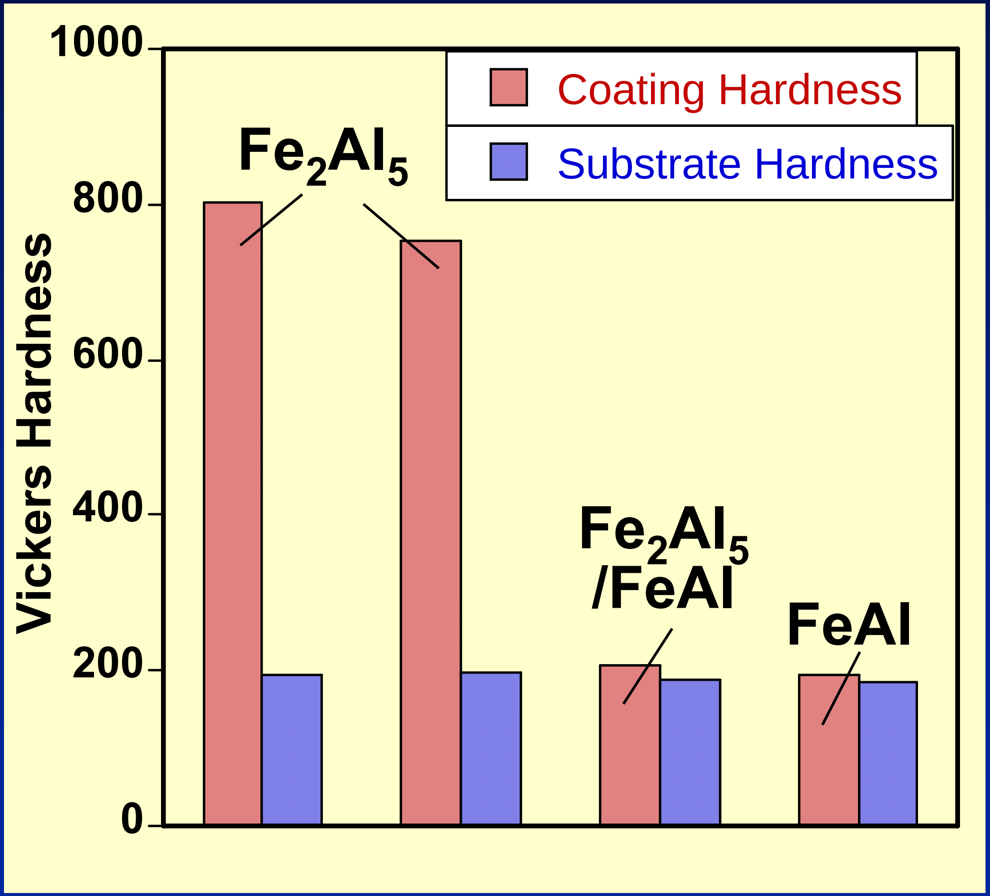


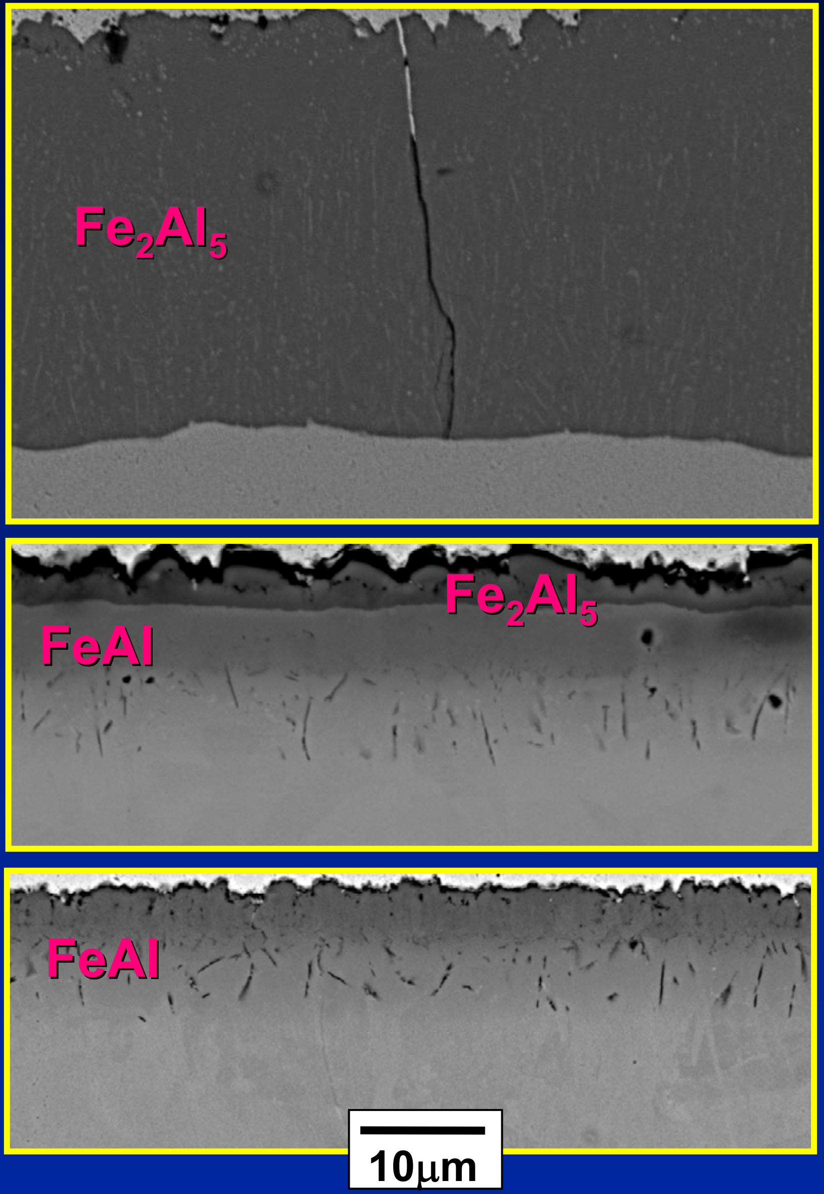




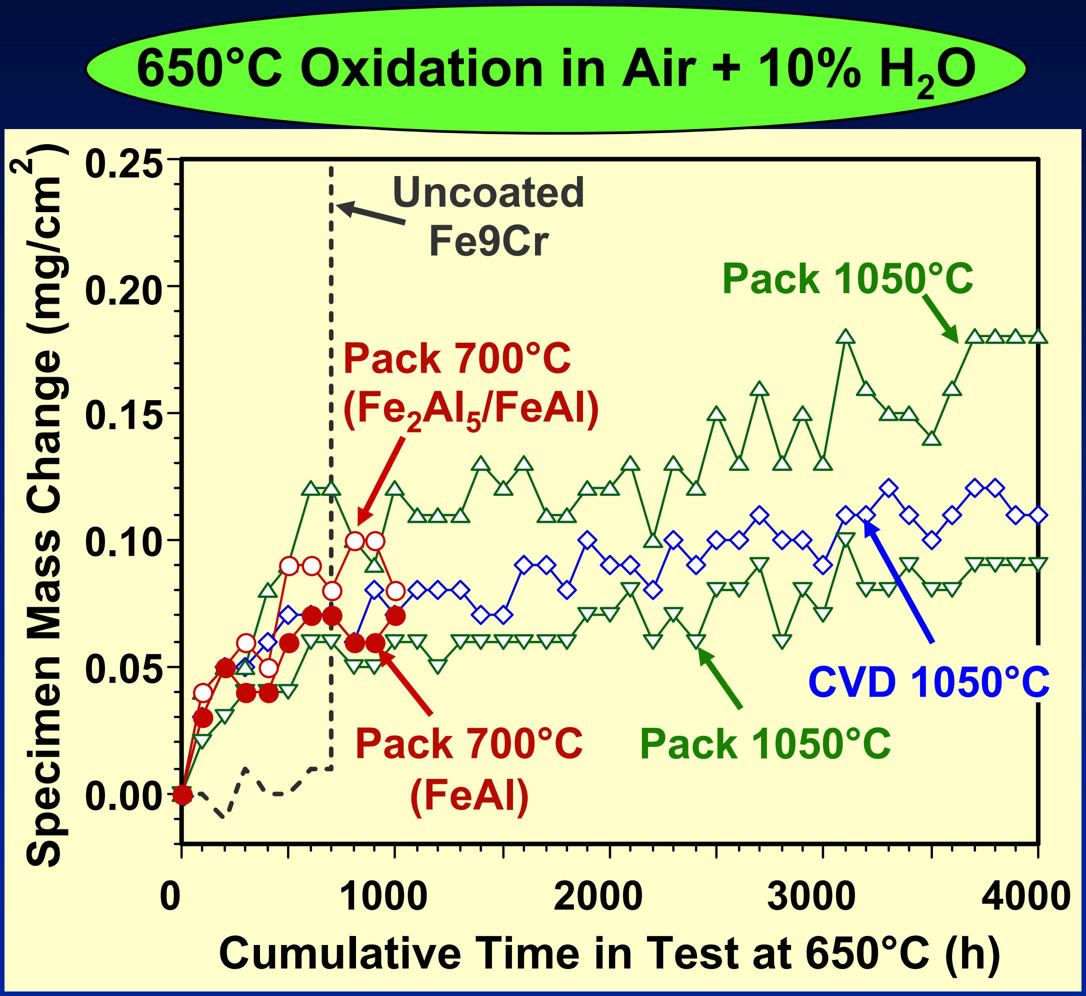
Hardness of Fe_2Al_5, Fe_2Al_5/FeAl and FeAl Coatings

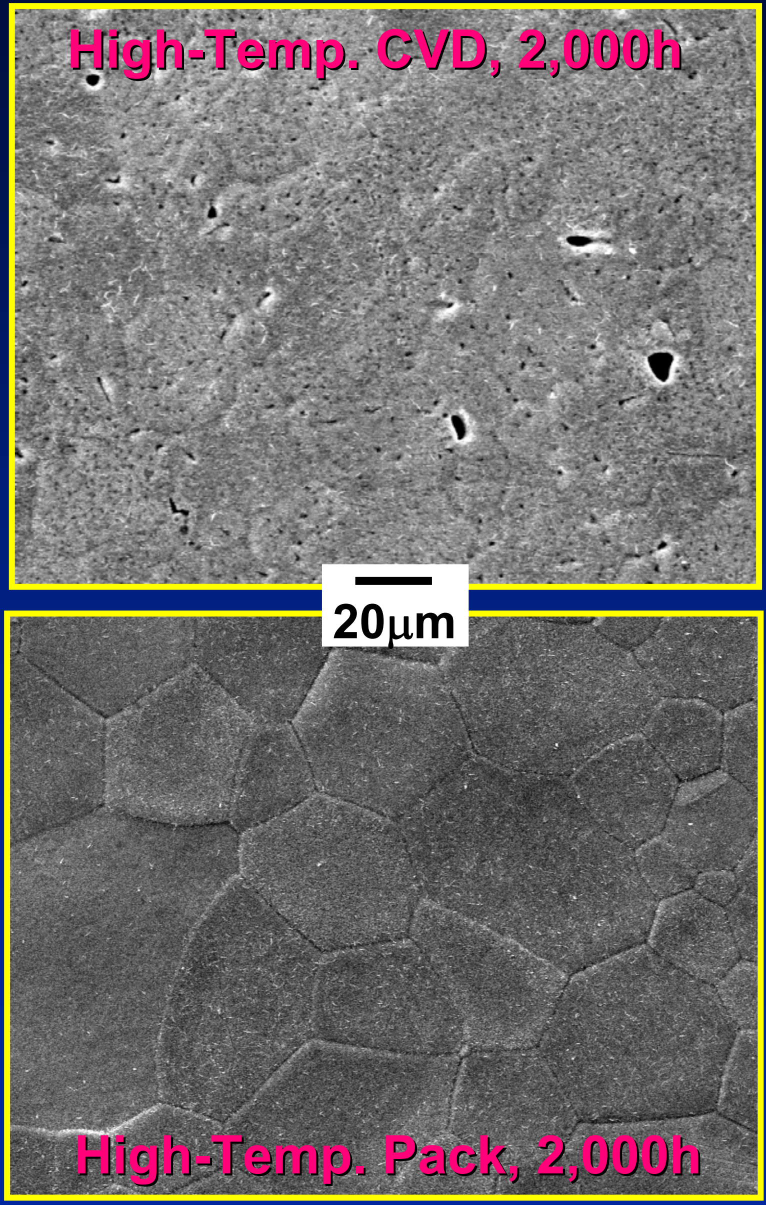
Vickers Hardness Load: 50 g





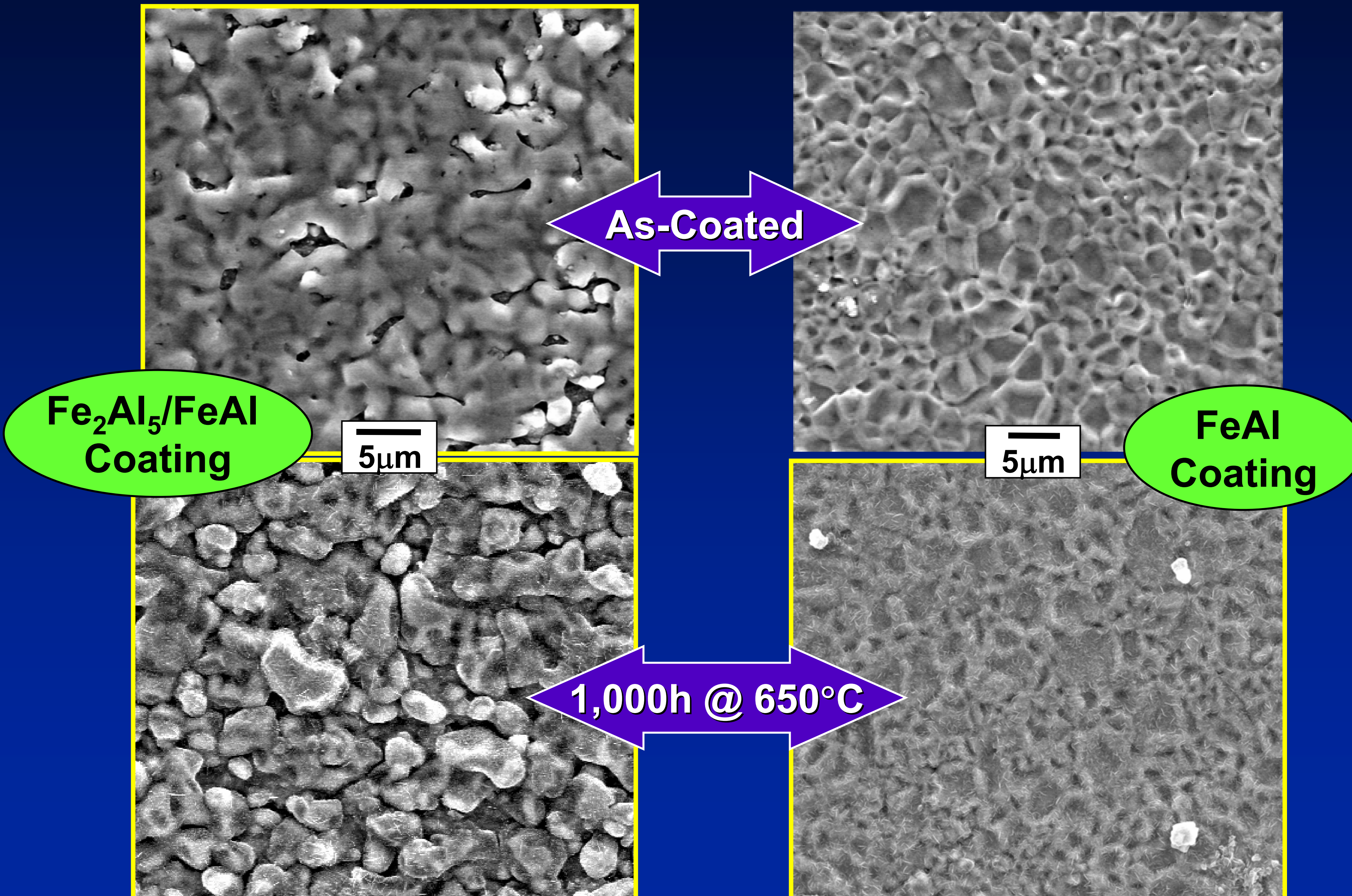
Initial Oxidation Results of Low-Temperature Pack Coatings in Air + 10 vol.% H_2O at 650°C





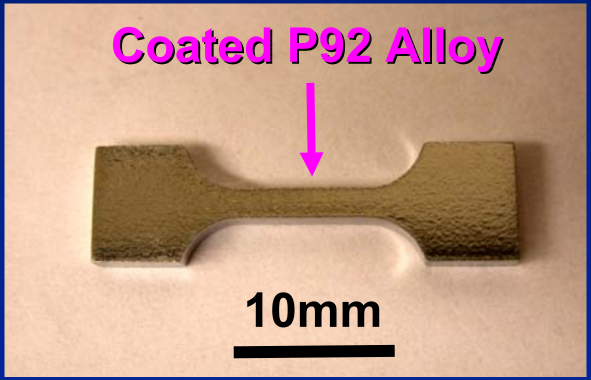
- Pack coatings (LT and HT) registered similar mass gains to CVD coatings

Low-temperature pack coatings mimic the as-coated morphology after 1,000h air + 10% H_2O at 650°C

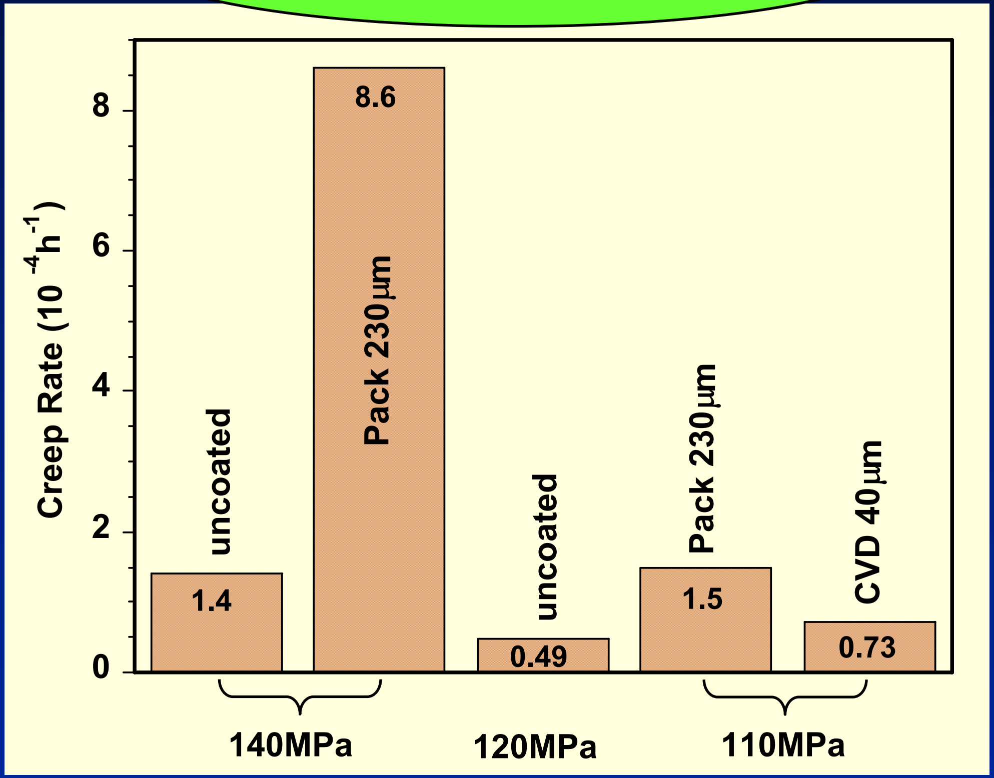


Thin coatings (50-100μm) are preferred for concerns of CTE mismatch and creep resistance

25 mm long with
gauge section of 2 x 2 (mm^2)



Dryepondt et al., *Surf. Coat. Technol.*, 201 (2006) 3880

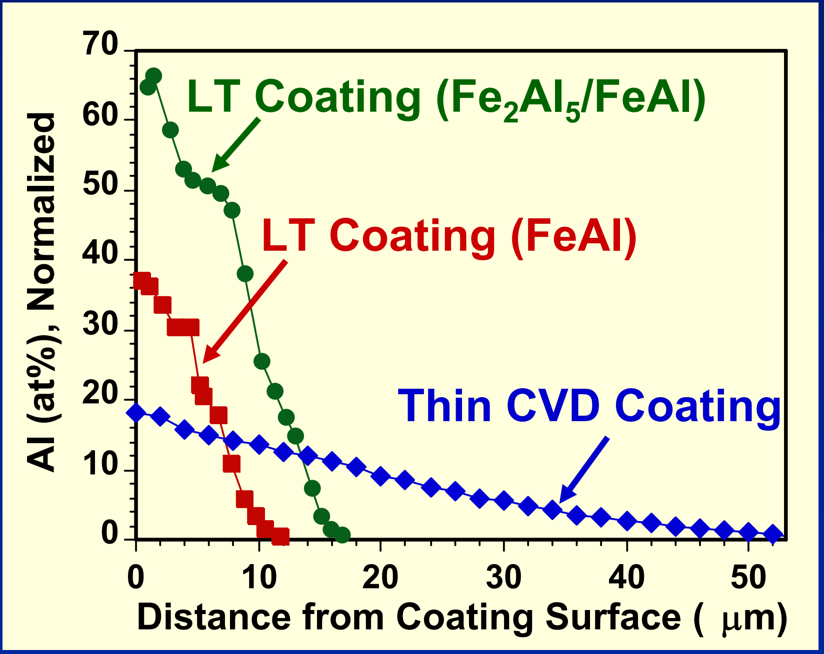


- The main degradation of mechanical strength of the coated alloy was due to the decrease in the load-bearing section because of the weak creep properties of Fe-Al compared to the P92

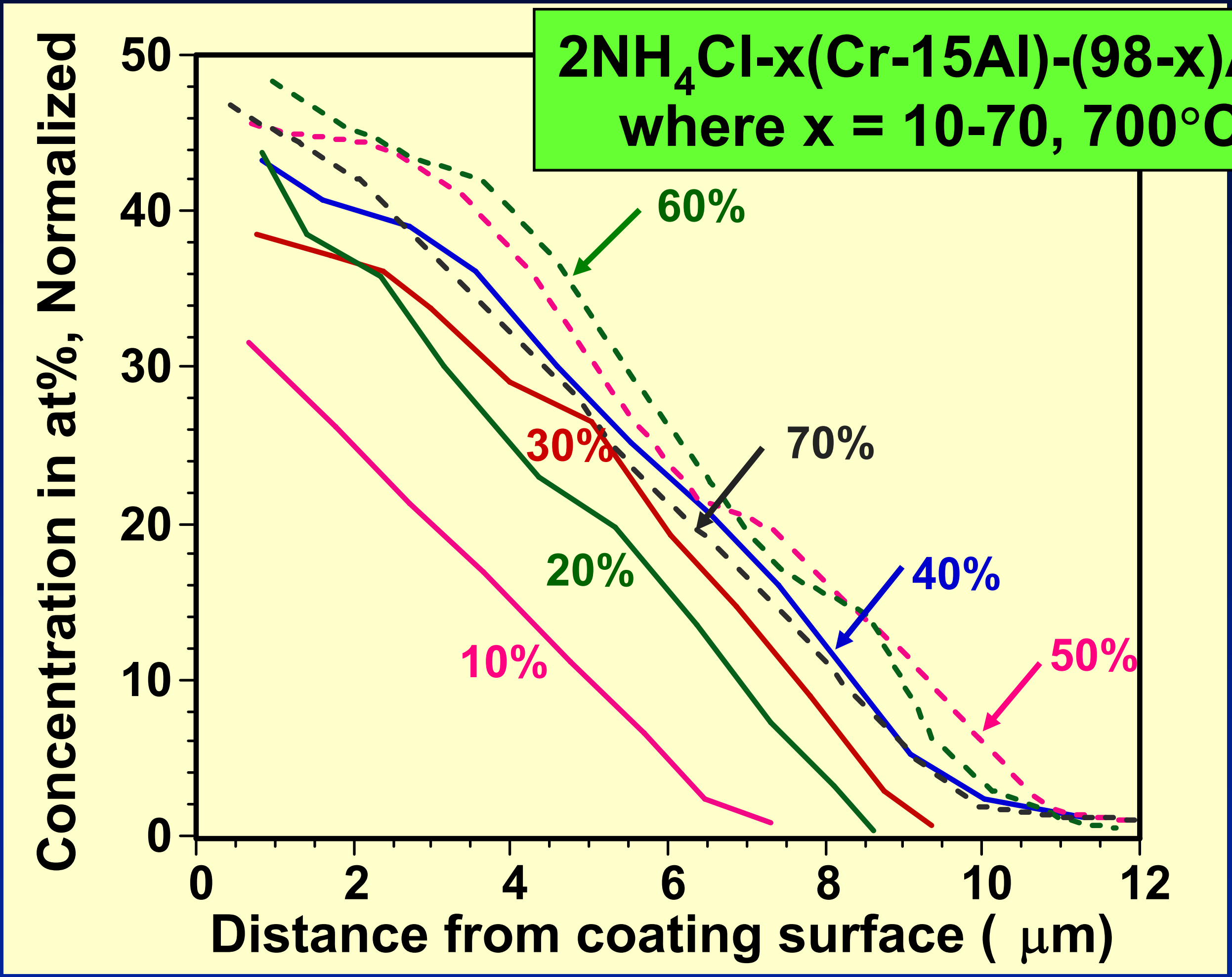
Comparison of Al Reservoir in Aluminide Coatings

Coating	Thickness (μm)	Surface / Interface Al (at.%)	Al Reservoir
Thin CVD Coating	50	18	450
LT Fe_2Al_5 / FeAl coating	4 + 12	65 + 50	560
LT FeAl coating	10	40	200

- 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, in press)
- Low-temp. pack coatings with Fe_2Al_5/FeAl should have a lifetime comparable to CVD thin coatings
- Brittle Fe_2Al_5 could lead to cracking



Effect of the Amount of Masteralloy



- The Al reservoir increased with the amount of materalloy
- When > 50 wt.% of masteralloy was used, the change of the Al profiles became insignificant

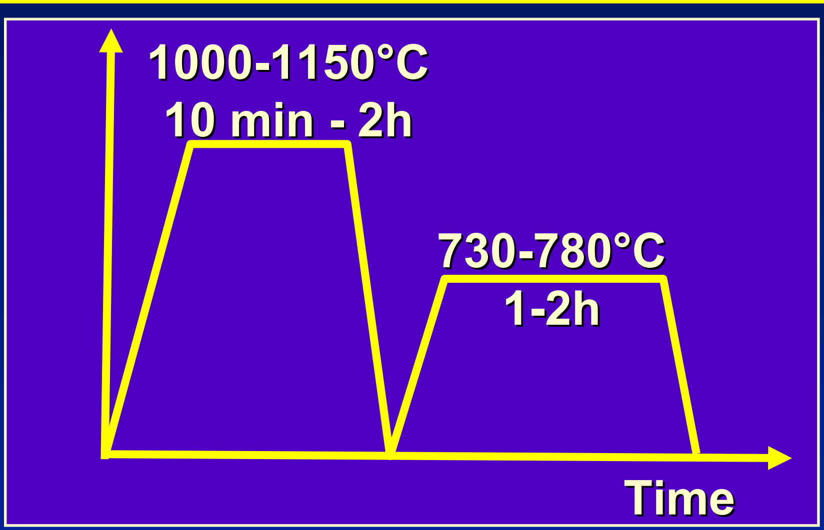
Summary

- Non-uniform Fe_2Al_5 coating was formed when pure Al was used as the masteralloy at 650°C
- The Al activity in the pack cementation process was reduced by using Al-containing binary masteralloys
  - With Cr-25Al masteralloy, a coating of Fe_2Al_5/FeAl was formed at 700°C
  - Cr-15Al masteralloy led to formation of a thin (10-12 μm) FeAl coating
  - The Al reservoir increased with the amount (< 50%) of Cr-15Al materalloy at 700°C
- The aluminide coatings synthesized at 700°C showed good initial oxidation behavior at 650°C in air + 10% H_2O

Future Work

1. Fabrication of Low-Temp. Aluminide Coatings
2. Performance of Low-Temp. Aluminide coatings
3. Effect of Aluminide Coatings on Mechanical Properties of Substrate Alloys: **Creep Test in Steam Environment**

Increase the thickness of the FeAl coating



- Increase the pack aluminizing temperature to 750°C
- Combine the coating process with standard heat treatment
- Apply surface mechanical treatment (shot peening) prior to coating processing (Xiang and Datta, *Scipta Mater.*, 2006)

Acknowledgments

- J. L. Moser, K. M. Cooley, S. Dryepondt, and L. R. Walker, ORNL
- DOE Advanced Coal Research at U.S. Colleges and Universities, under grant No. DE-FG26-06NT42674
- DOE Fossil Energy Advanced Research and Technology Development Materials Program, under contract DE-AC05-00OR22725 with UT-Battelle, LLC and subcontract 4000032193 with Tennessee Tech