Steam Turbine Materials and Corrosion

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NETL

Office of Fossil Energy

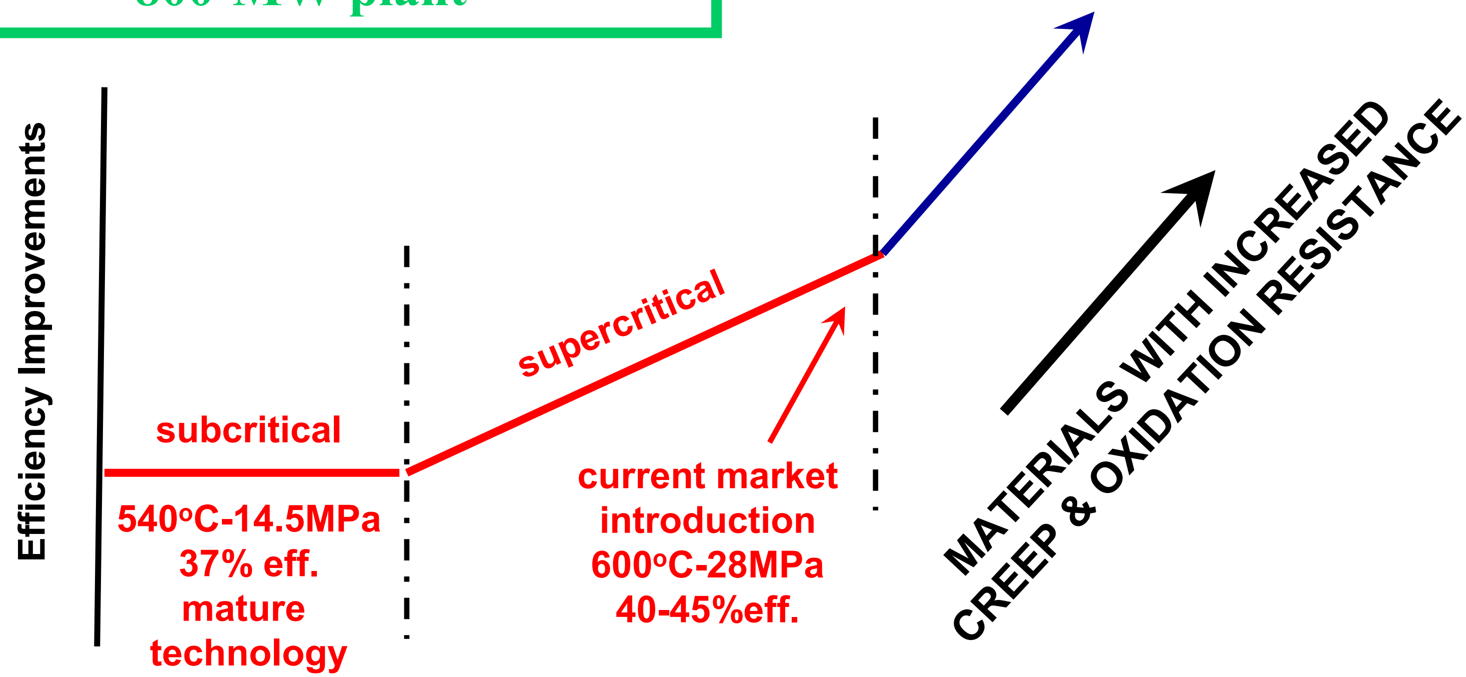
Outline

- **Introduction**
  - Overview
  - Goals
  - Background
- **Accomplishments**
  - Alloy Behavior
  - Reactive Evaporation of Chromia
- **Future plans**
- **Summary**

Increasing Efficiency

Each 1% increase in efficiency eliminates ~1,000,000 tons of CO_2 emissions over the lifetime of an 800-MW plant

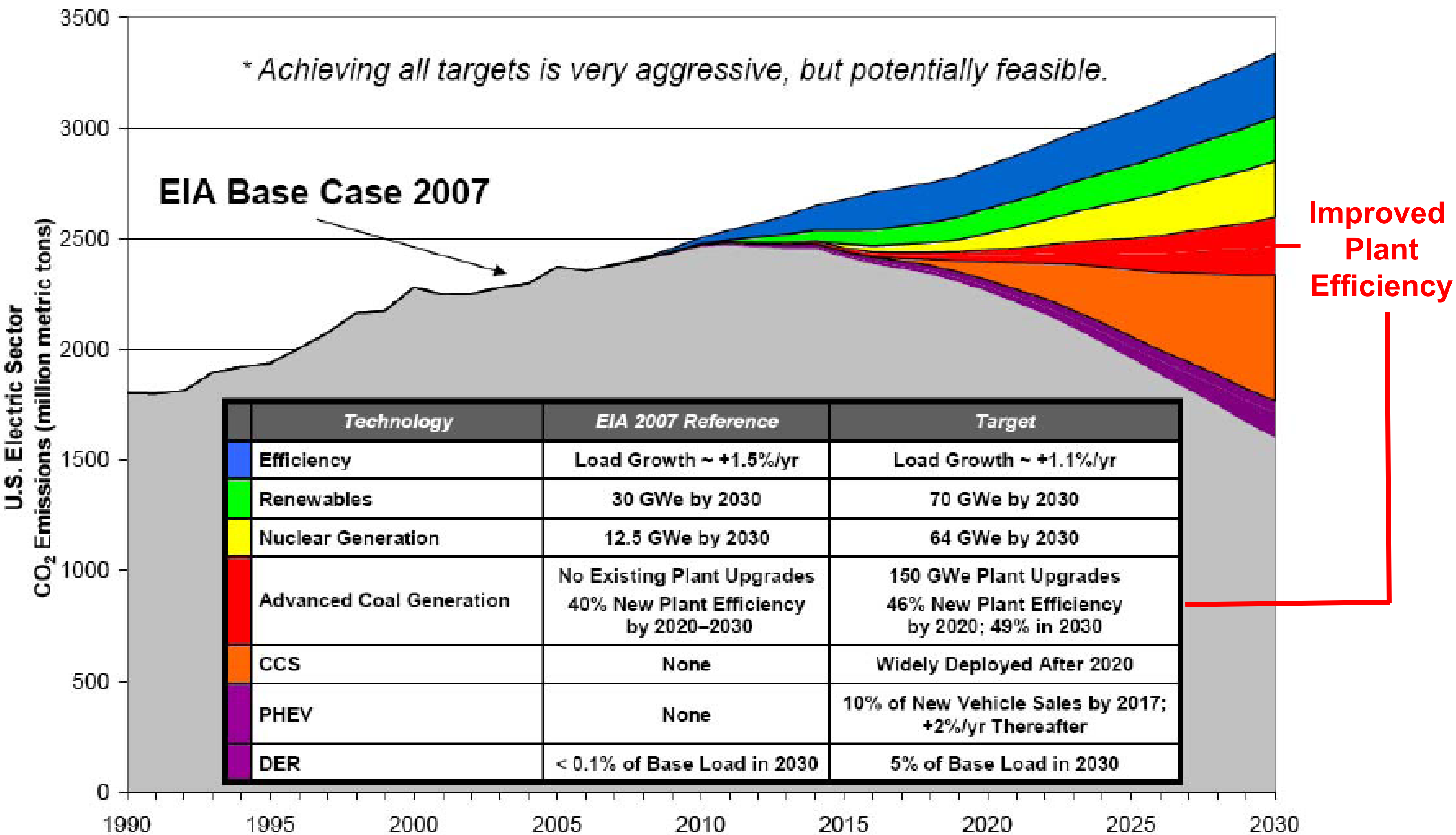
US-DOE Advanced Power System Goal
60% efficiency from coal generation
Steam condition: 760°C – 35 MPa



Plants operating above 22MPa at 538 to 565°C are "supercritical", and above 565°C are "ultra-supercritical (USC)".

Adapted from: Viswanathan, et al , 2005 and Swanekamp, 2002

Senate Hearing "The Future of Coal: Options for a Carbon-Constrained World" March 2007, Deutch & Moniz, MIT



Technology	EIA 2007 Reference	Target
Efficiency	Load Growth ~ +1.5%/yr	Load Growth ~ +1.1%/yr
Renewables	30 GWe by 2030	70 GWe by 2030
Nuclear Generation	12.5 GWe by 2030	64 GWe by 2030
Advanced Coal Generation	No Existing Plant Upgrades 40% New Plant Efficiency by 2020–2030	150 GWe Plant Upgrades 46% New Plant Efficiency by 2020; 49% in 2030
CCS	None	Widely Deployed After 2020
PHEV	None	10% of New Vehicle Sales by 2017; +2%/yr Thereafter
DER	< 0.1% of Base Load in 2030	5% of Base Load in 2030

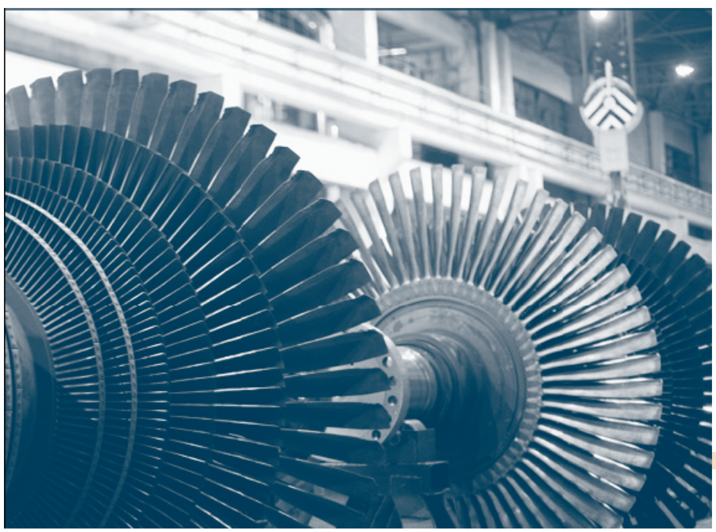
EPRI ELECTRIC POWER RESEARCH INSTITUTE

Project Goals and Objectives

- **Understand materials degradation in USC steam environments**
- **Identify or develop viable materials for use in USC steam turbines**
- **Characterize the steam oxidation resistance of candidate commercial alloys (primarily nickel-base superalloys)**
  - Compliment and not duplicate USC consortium research
- **Develop steam oxidation models for use in USC steam turbine environments**
  - Chromia evaporation
- **Project success defined as**
  - Steamside corrosion data sufficient for industry to use in USC turbines (for example in their turbine blade life models)
  - Identify and mitigate unexpected failure mechanisms

Critical Materials Properties for USC Turbines

- **Rotating Blades**
  - High temperature strength
  - Creep resistance
  - Steam oxidation resistance
  - Thermal expansion close to that of the rotors
  - Ability to be peened



- **HP and IP Rotors**
  - Creep strength
  - Low cycle fatigue strength
  - Fracture toughness
  - Steam oxidation resistance
  - Weldability

Cost vs Temperature

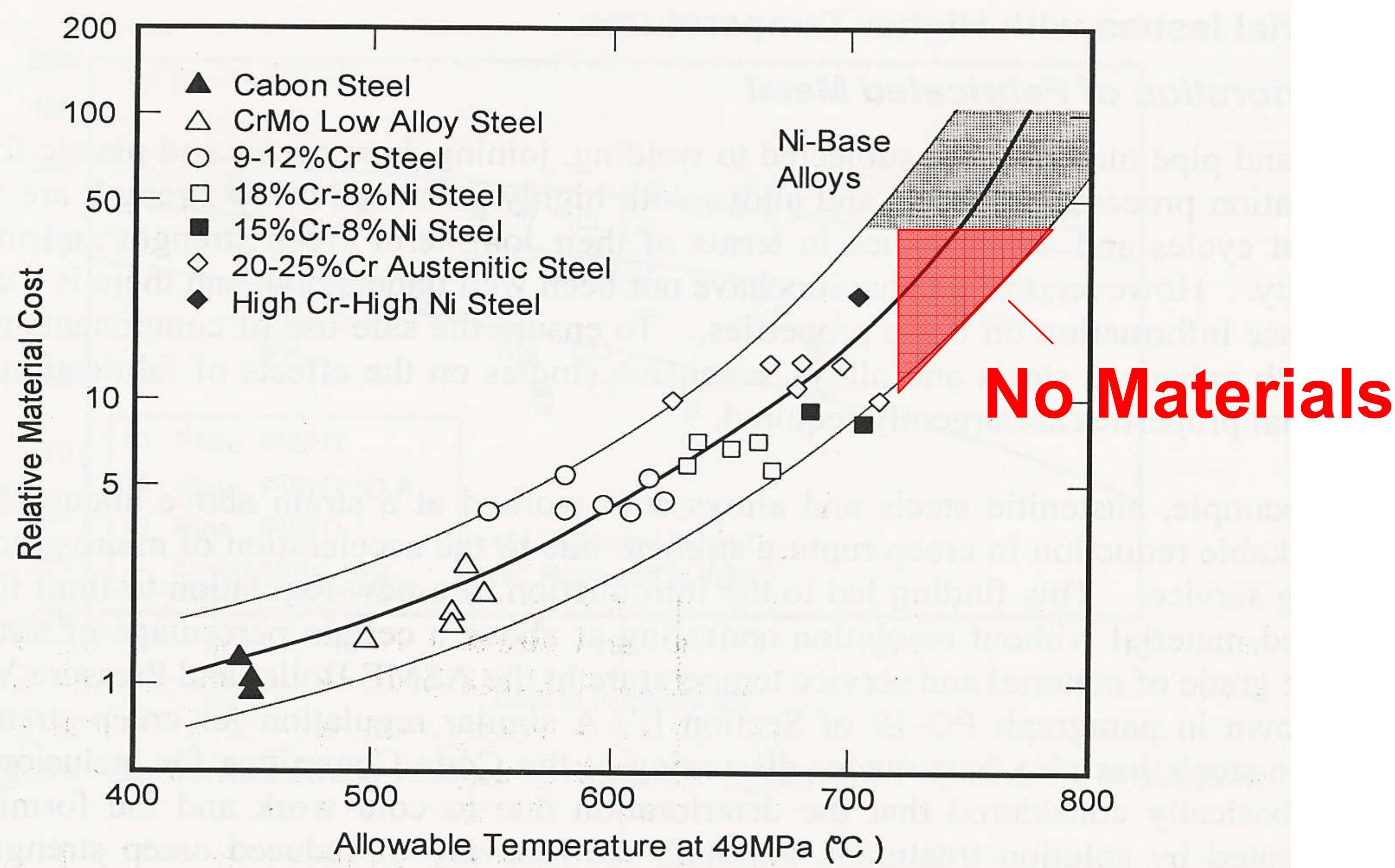
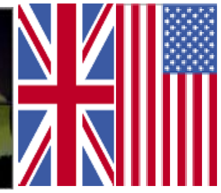


Fig. 7 Relation between allowable metal temperature at the allowable stress of 49MPa and the relative material cost

Masuyama, 2004

Commercial Alloys of Interest



Alloy	Class	USC Boiler	EPRI Turbine Candidate	Scholven Unit F Turbine	UK-US	USC Turbine
T92	Fe Ferritic	X			RR	
SAVE12 9.5Cr	Fe Ferritic	X			X	
SAVE12 10.5Cr	Fe Ferritic	X			X	
TP347HFG	Fe Austenitic	X			RR	
HR6W	High Ni & Cr	X				
Haynes 230	Ni Superalloy	X			X	
Haynes 282	Ni Superalloy					X
Inconel 617	Ni Superalloy	X		X	X	
Inconel 625	Ni Superalloy			X	X	
Inconel 718	Ni Superalloy		X		X	
Inconel 740	Ni Superalloy	X			RR	
Nimonic 90	Ni Superalloy		X		X	
Nimonic 105	Ni Superalloy					X
Udimet 720Li	Ni Superalloy					X

Environment and Conditions

Condition	Current Advanced Supercritical	Target Ultra Supercritical	Current Tests	Future Tests
Temperature	560-620°C	760°C	650-800°C	650-800°C
Pressure	280-310 bar	350-385 bar	1 bar	Up to 350 bar
Atmosphere	Steam	Steam	Moist Air	Steam
Gas Velocity	Boiler 10-25 m/s Turbine 300 m/s	Boiler 10-25 m/s Turbine 300 m/s	~$2\text{-}8\times10^{-3}$ m/s	Up to 40 m/s

Best practices in corrosion testing involves

- **Duplication of the environment**
- **Use conditions that give the same corrosion mechanisms**

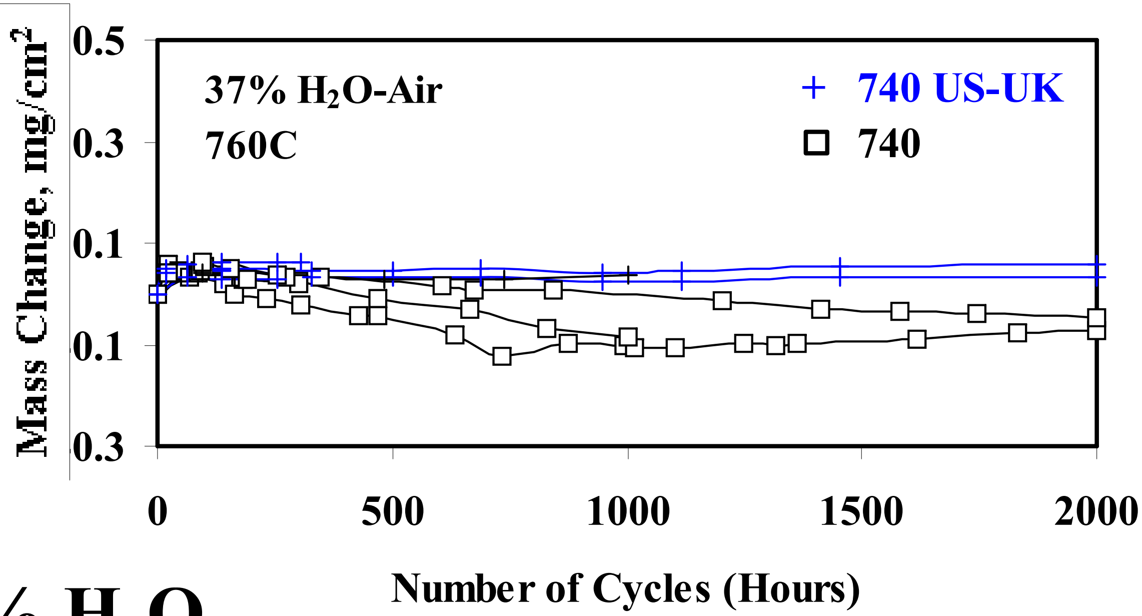
Commercial Alloy Behavior
Result Comparison

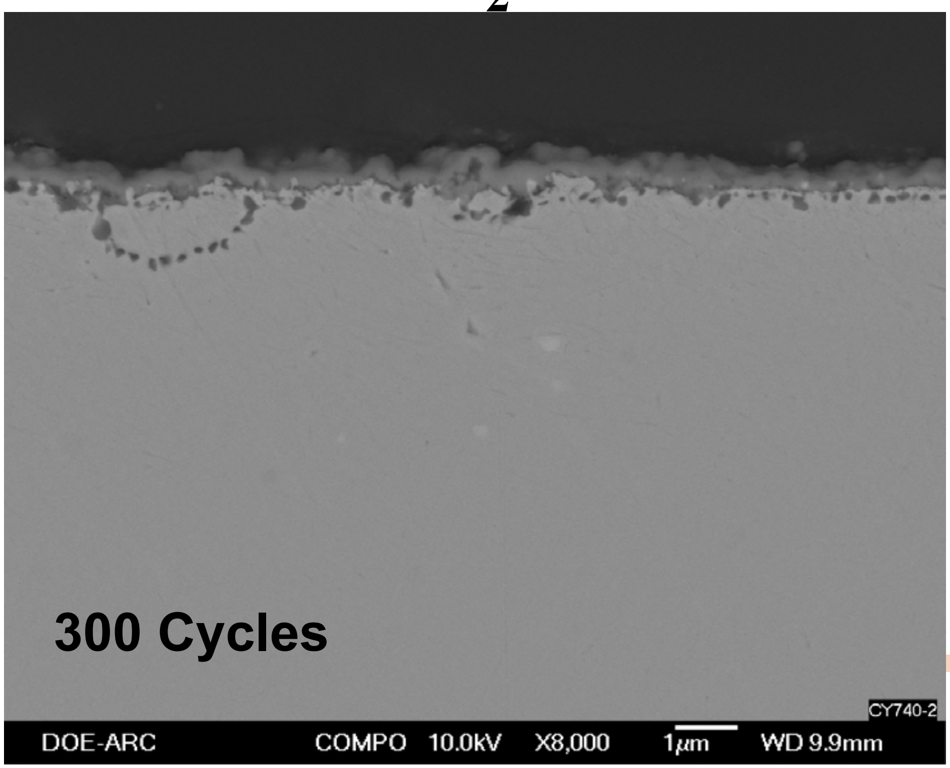
760°C after 2000 cycles or hours

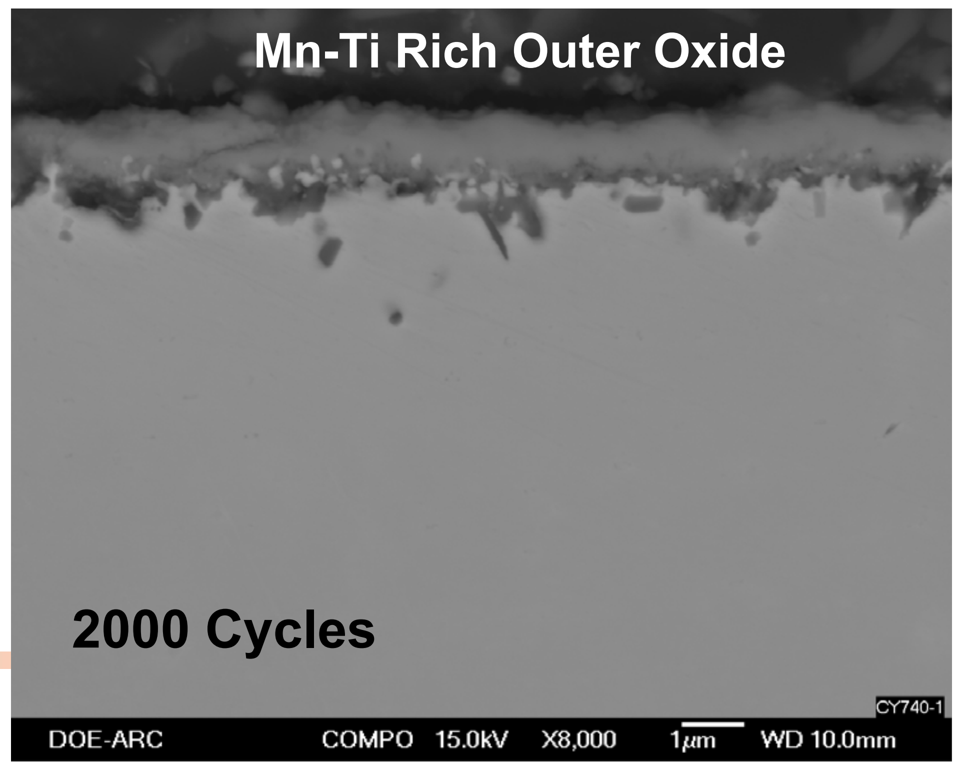
Alloy	Cyclic with Air+40%H_2O			Furnace with Air+3%H_2O		
	Max Internal Oxidation, μm	Max Scale Thickness, μm	Mass Change, mg/cm^2	Max Internal Oxidation, μm	Max Scale Thickness, μm	Mass Change, mg/cm^2
Haynes 230	12.7	3.1	-0.217	5.1	3.6	0.097
Inconel 617	11.8	4.4	0.008	3.8	2.7	0.118
Inconel 718	6.7	2.9	-0.031	4.0	3.1	0.183
Inconel 740	10.2	2.7	-0.059	5.1	1.8	0.180
Nimonic 90	18.2	6.7	0.363	8.7	3.1	0.818

Inconel 740

760°C Air + 37% H_2O



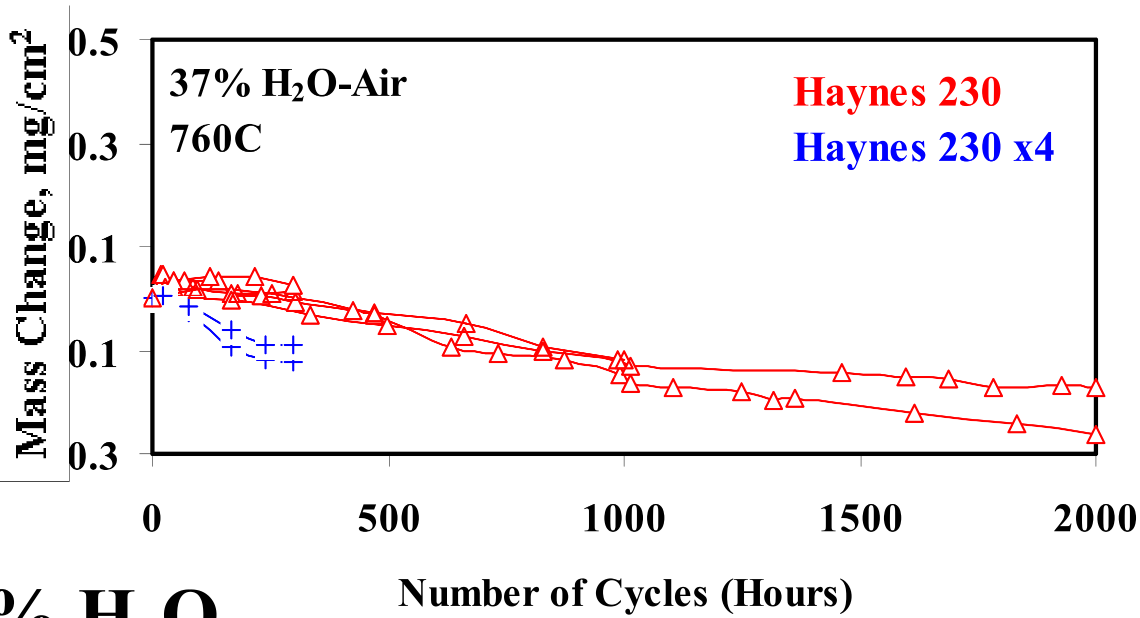


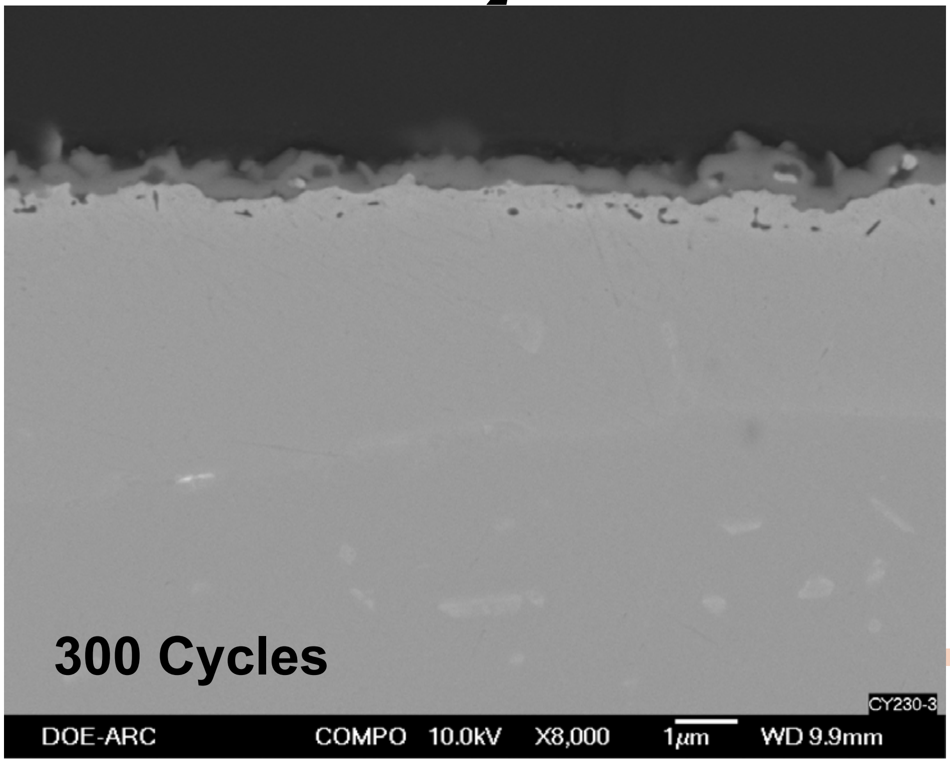


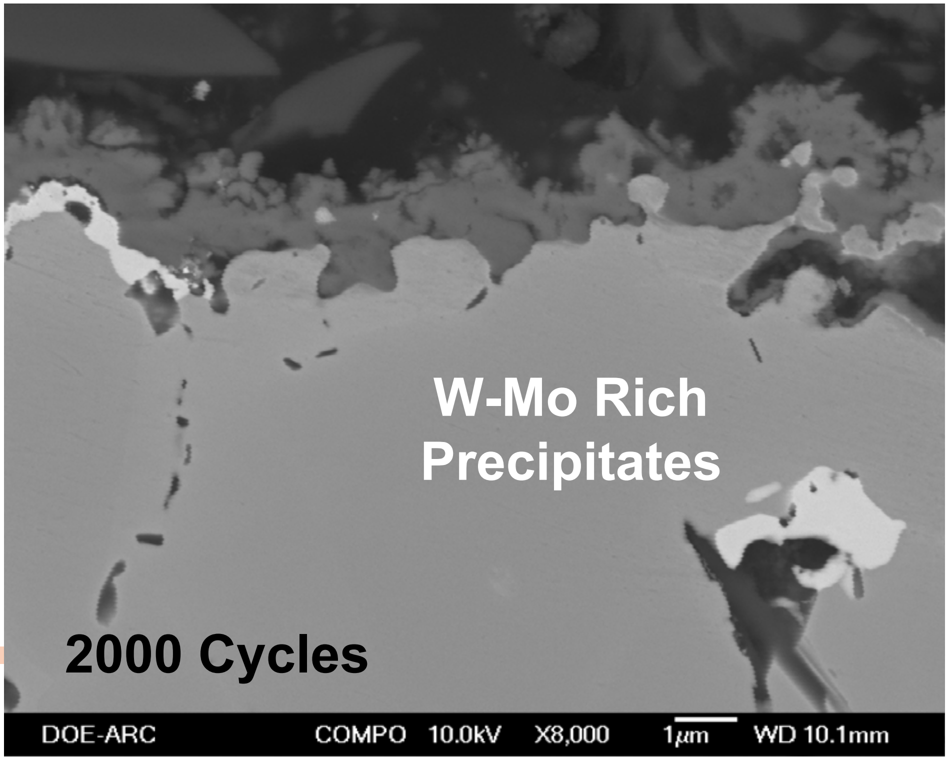
Haynes 230

760°C

Air + 37% H_2O



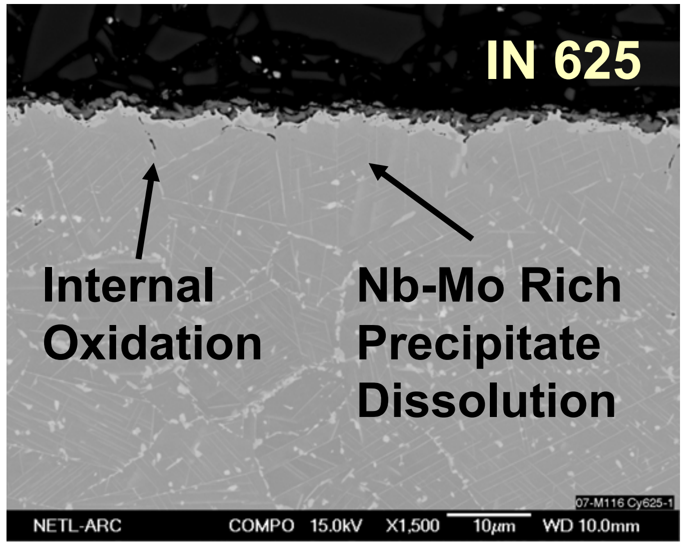




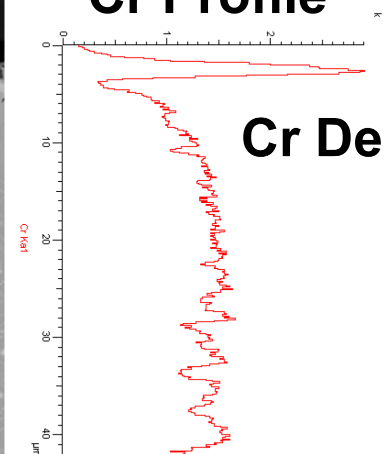
Result Comparison

Cyclic Oxidation
2000 Cycles
760°C
Air + 37% H_2O
Low Gas Flow
Boldly Exposed

Cr Evaporation



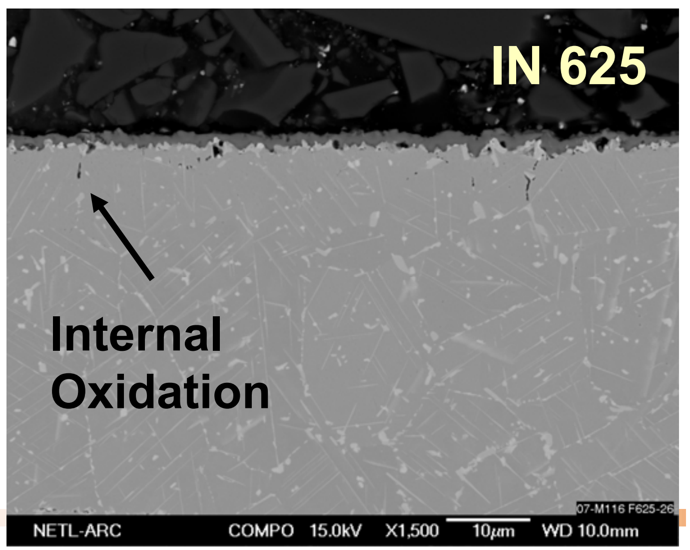
Cr Profile



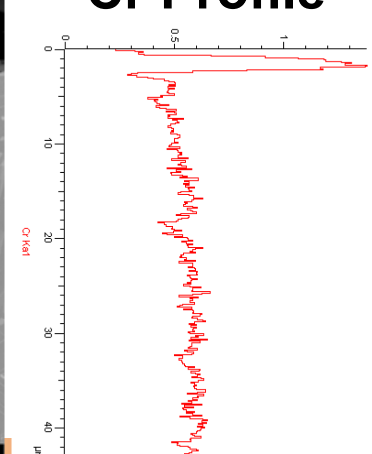
Cr Depletion

Furnace Exposure
2000 Hours
800°C
Air + 3% H_2O
Low Gas Flow
Sheltered Exposure

Suppressed Cr Evaporation



Cr Profile



Evaporation of Chromia

- Very small effect in dry oxidation until > 900°C

$$0.5Cr_2O_3(s) + 0.75O_2(g) \rightarrow CrO_3(g)$$

- Water allows another reaction important at lower temperatures

$$0.5Cr_2O_3(s) + H_2O(g) + 0.75O_2(g) \rightarrow CrO_2(OH)_2(g)$$

Evaporation

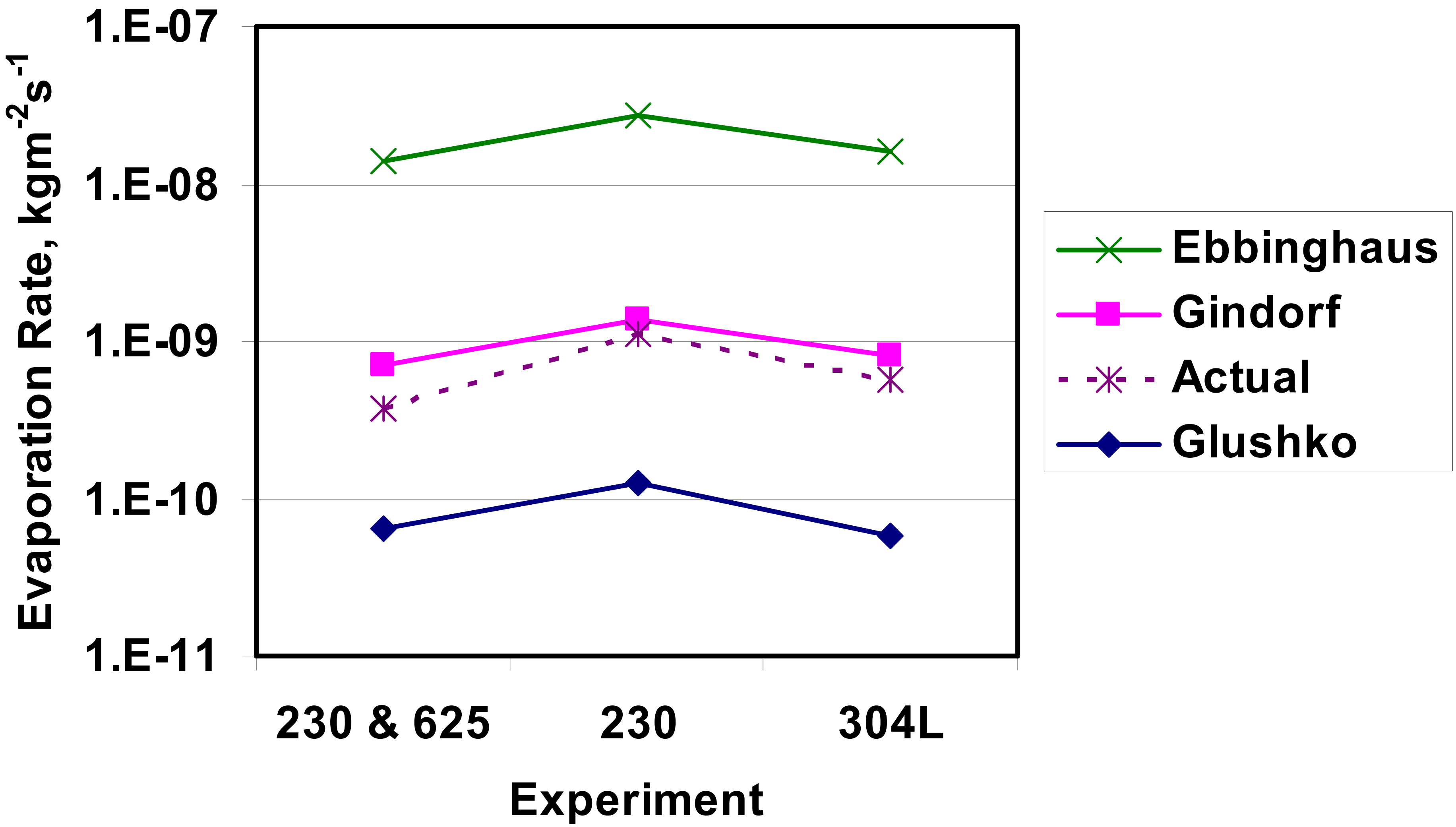
Kinetics

Saturation

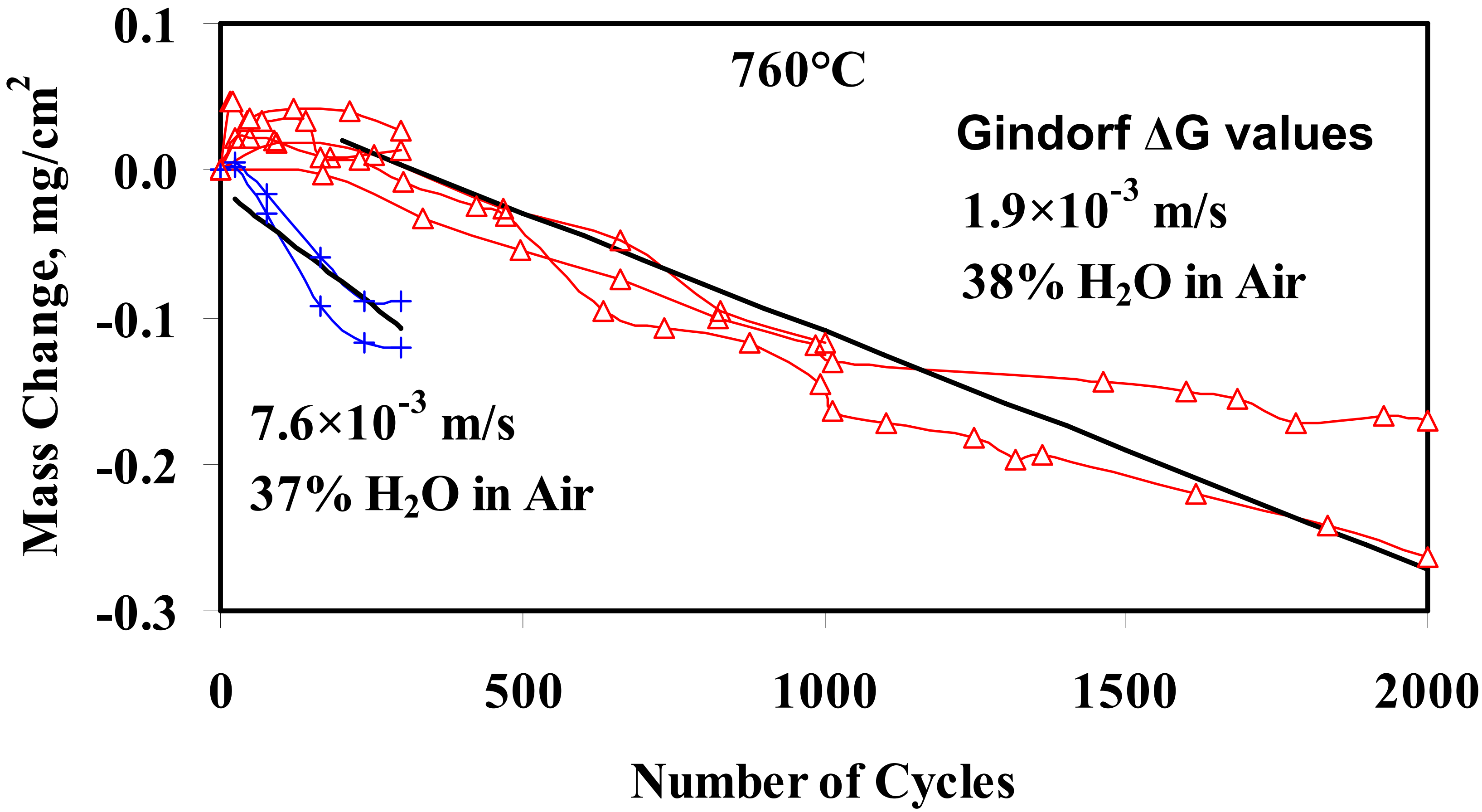
$$k_e\left(\frac{kg}{m^2 s}\right) = Sh_{Ave}\,\frac{D_{AB} M_{CrO_2(OH)_2}}{LRT}\left(P_{CrO_2(OH)_2} - P^{\circ}_{CrO_2(OH)_2}\right)$$

Thermodynamics

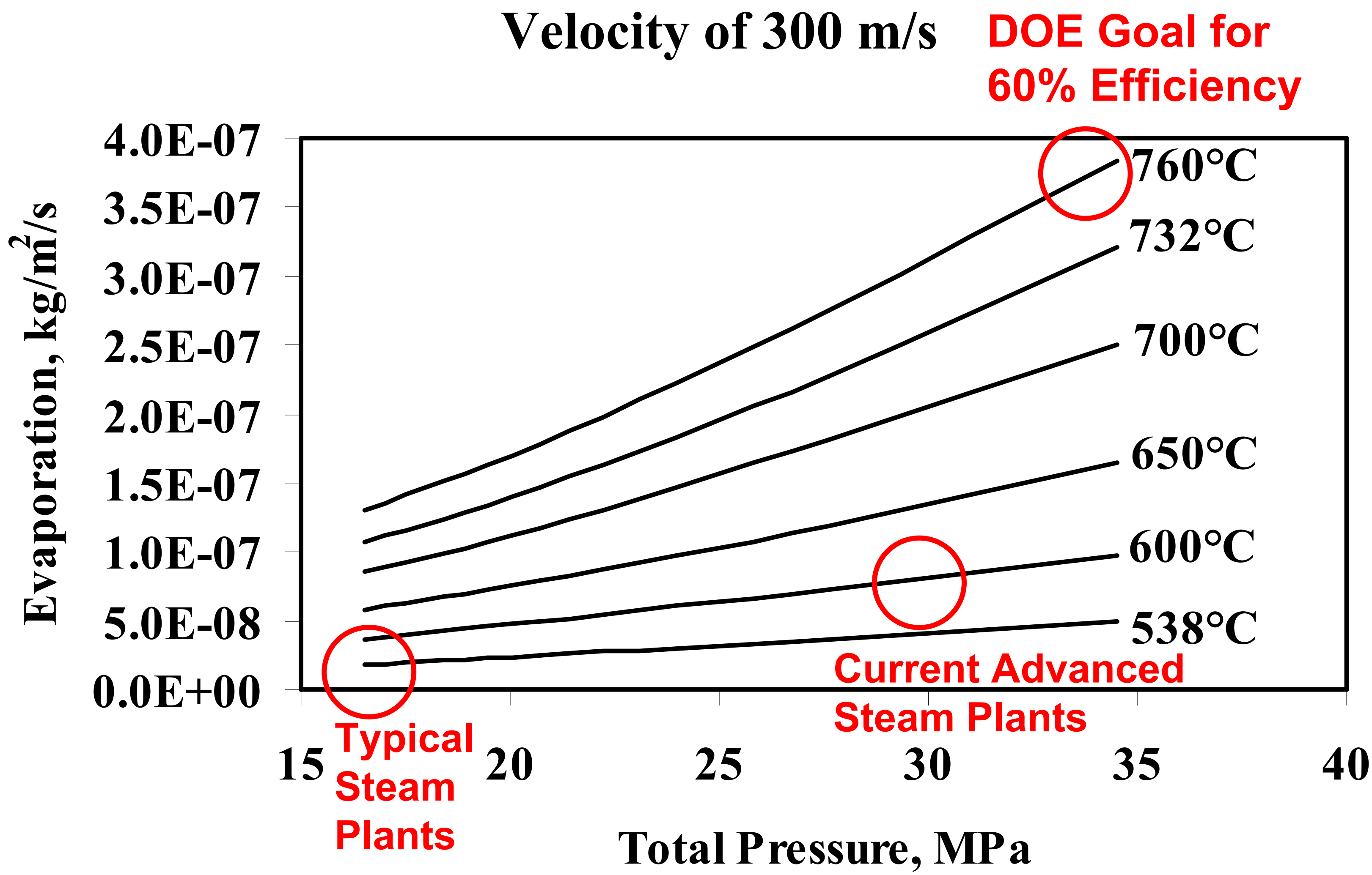
Thermodynamics of $CrO_2(OH)_2(g)$



Evaporation Model – Some Verification
Haynes 230



Advanced Steam Turbine Environments



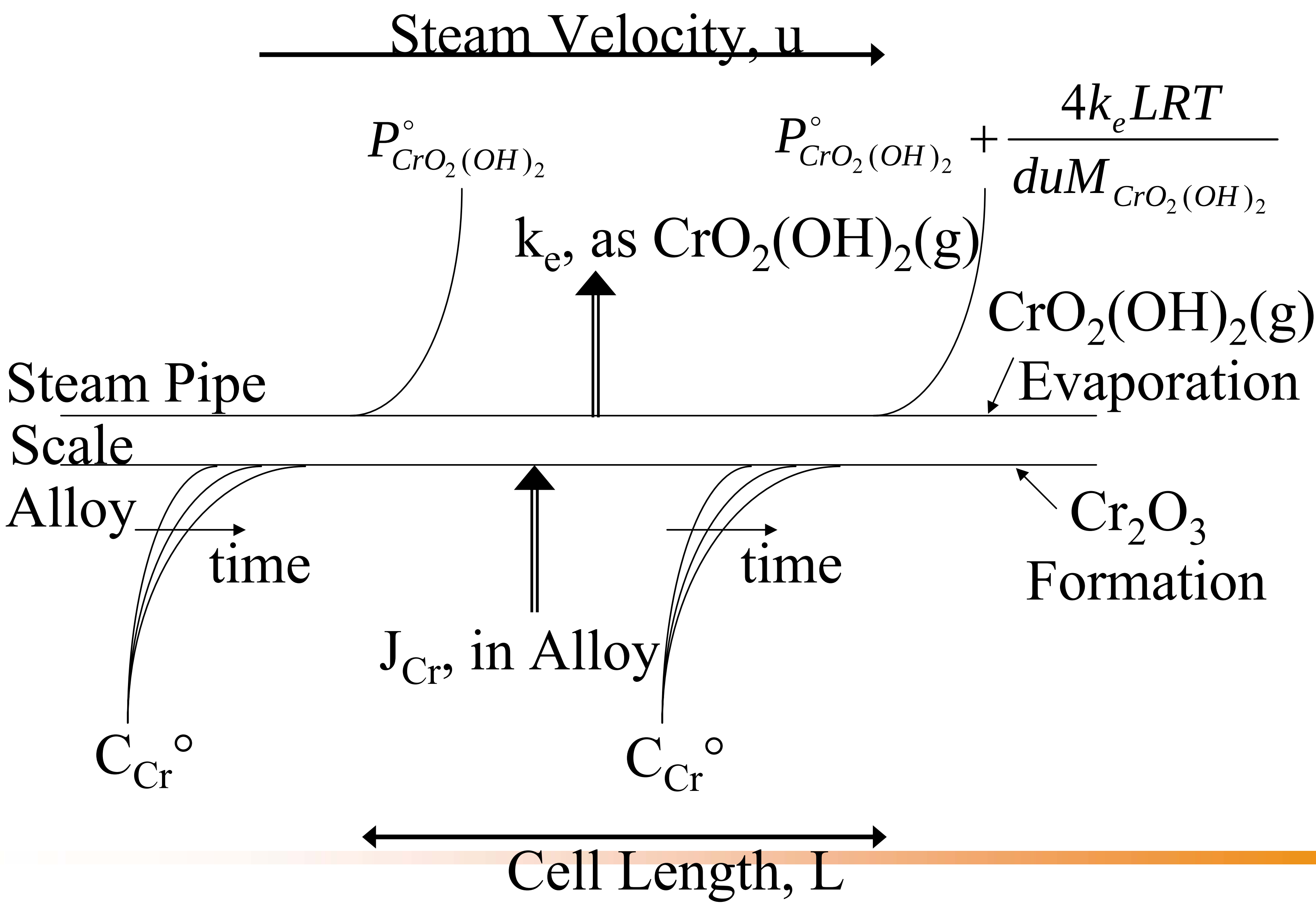
Additional Model Development

- **Aim is to answer the question:**

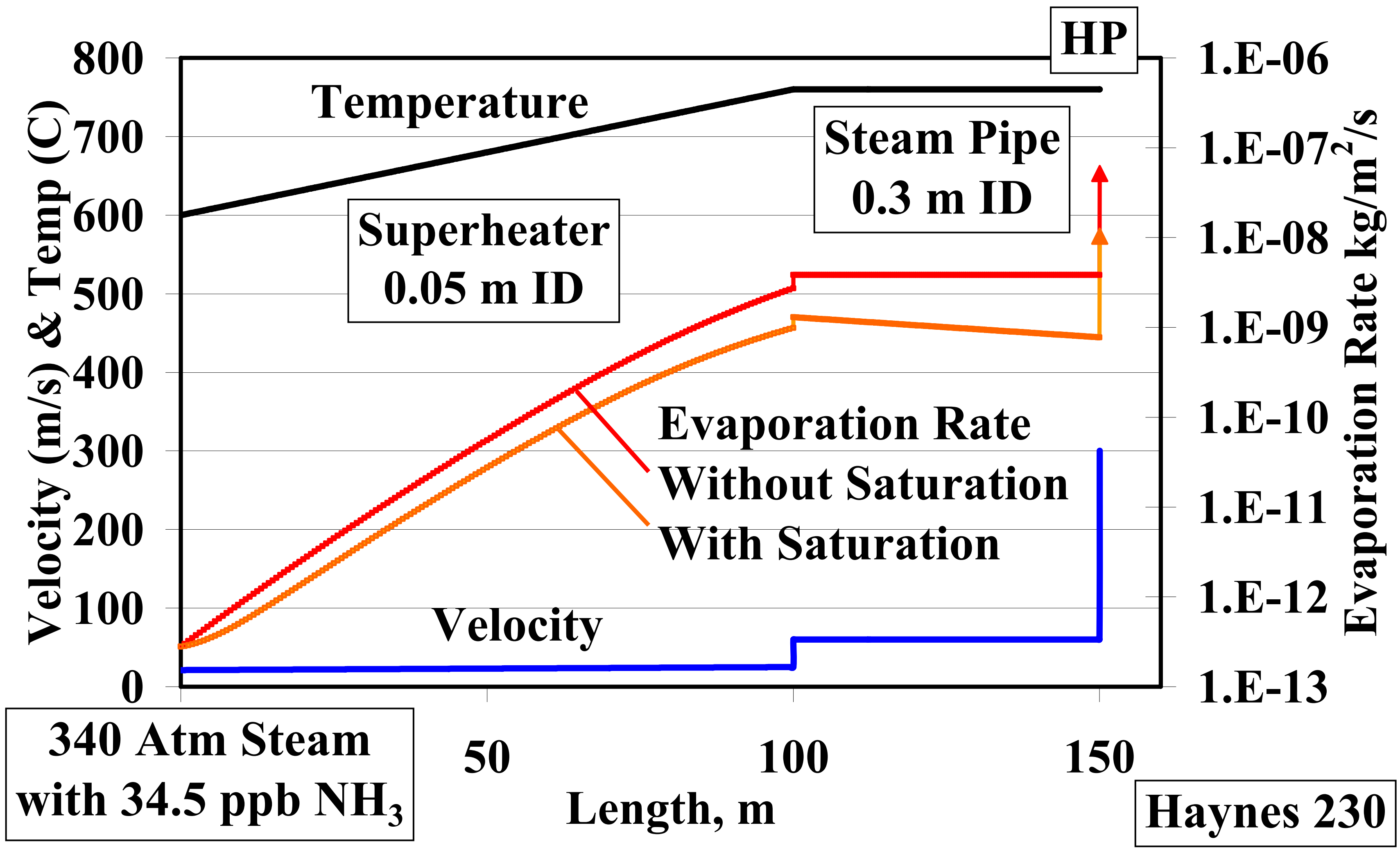
  Should evaporation of chromia be a concern in USC boilers and turbines?

- **Saturation of steam with $CrO_2(OH)_2(g)$**
- **Translation of evaporation rates to breakaway oxidation times**
- **Inclusion of Opila thermodynamic measurements**

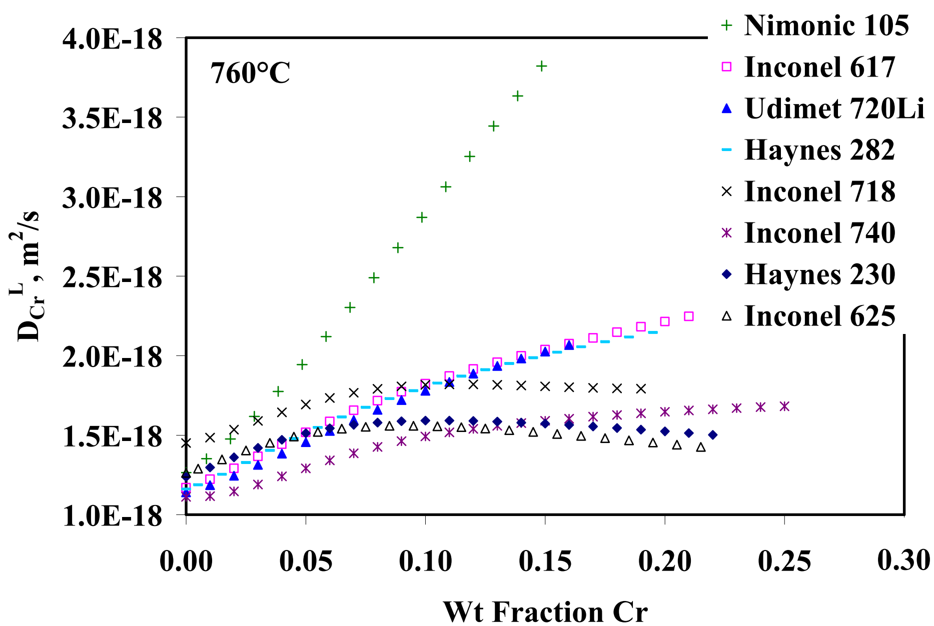
Saturation from Upstream Evaporation



Saturation from Upstream Evaporation



Translation of Evaporation Loss to Breakaway Oxidation

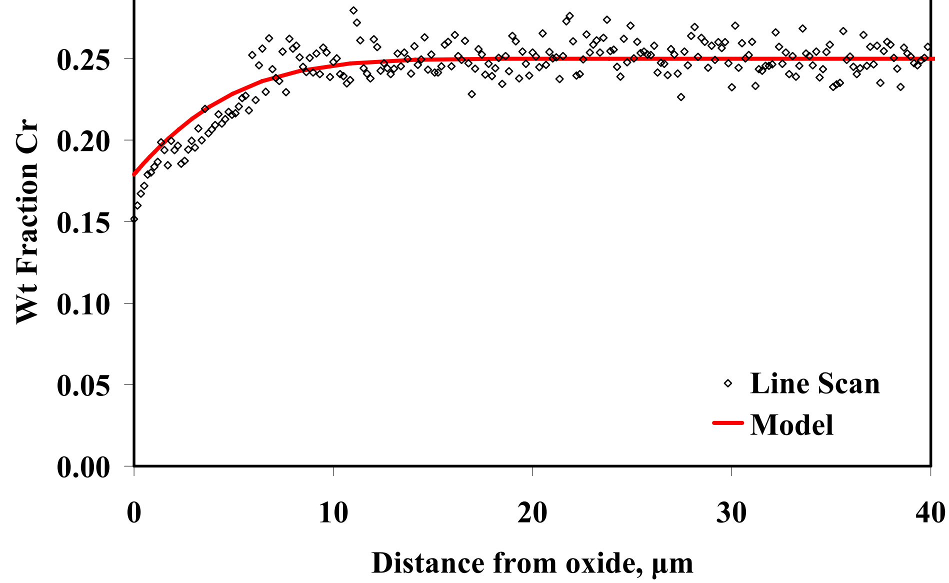


$$D_{Cr} \cong D_{Cr}^{L} + \frac{2\delta}{\lambda} D_{Cr}^{gb}$$

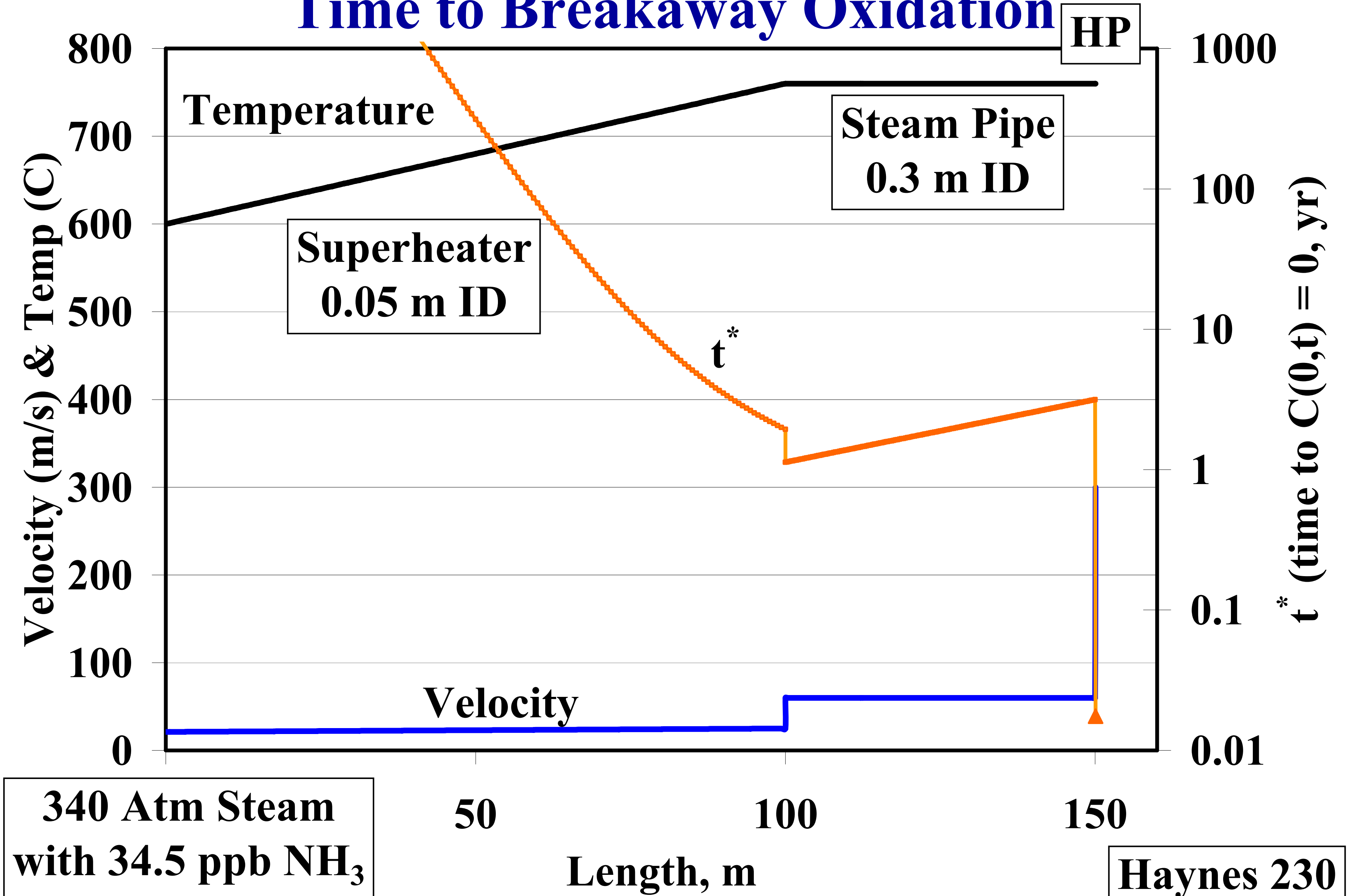
D_{Cr}^{L} from Dictra for the FCC phase
D_{Cr}^{gb} from ratio for IN800 (Paul, 1994)

Transient diffusion of Cr given a constant evaporative loss
t^* is the time at which Cr becomes zero at the surface

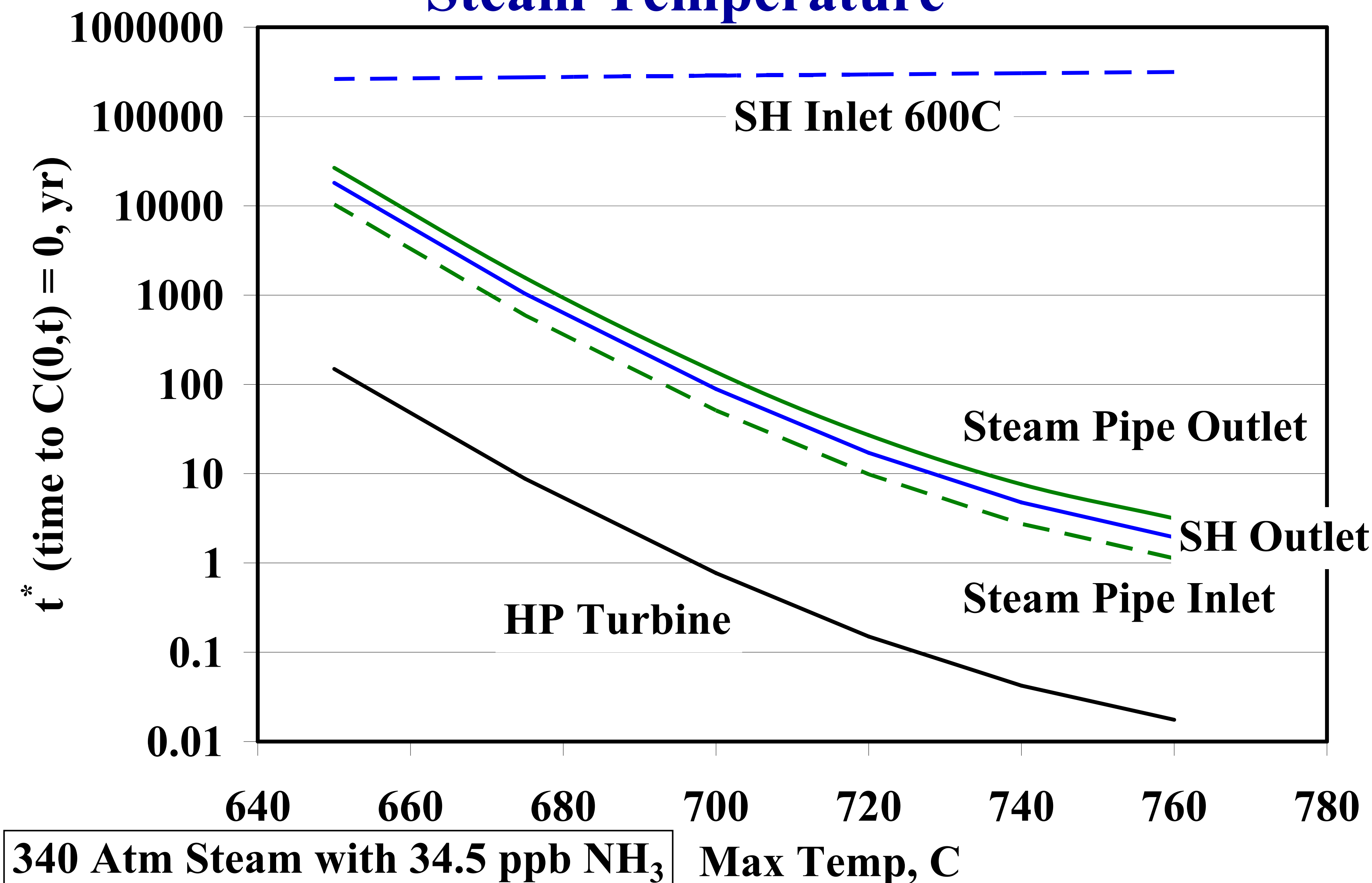
$$t^* = \frac{\pi D_{Cr}}{4}\left(\frac{M_{CrO_2(OH)_2} C_{Cr}^{\circ}}{k_e}\right)^2$$



Time to Breakaway Oxidation

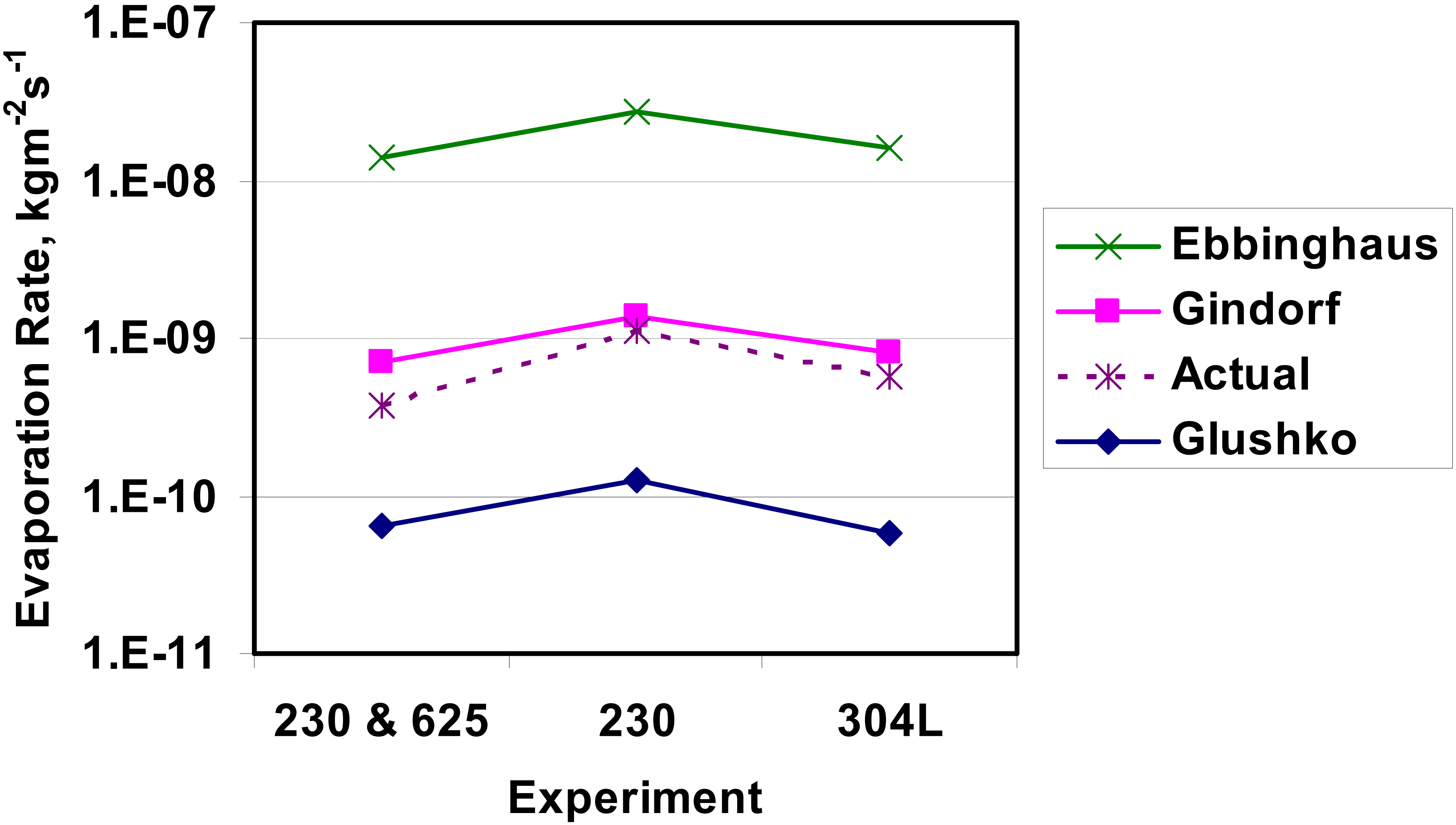


Steam Temperature



340 Atm Steam with 34.5 ppb NH_3

Thermodynamics of $CrO_2(OH)_2(g)$



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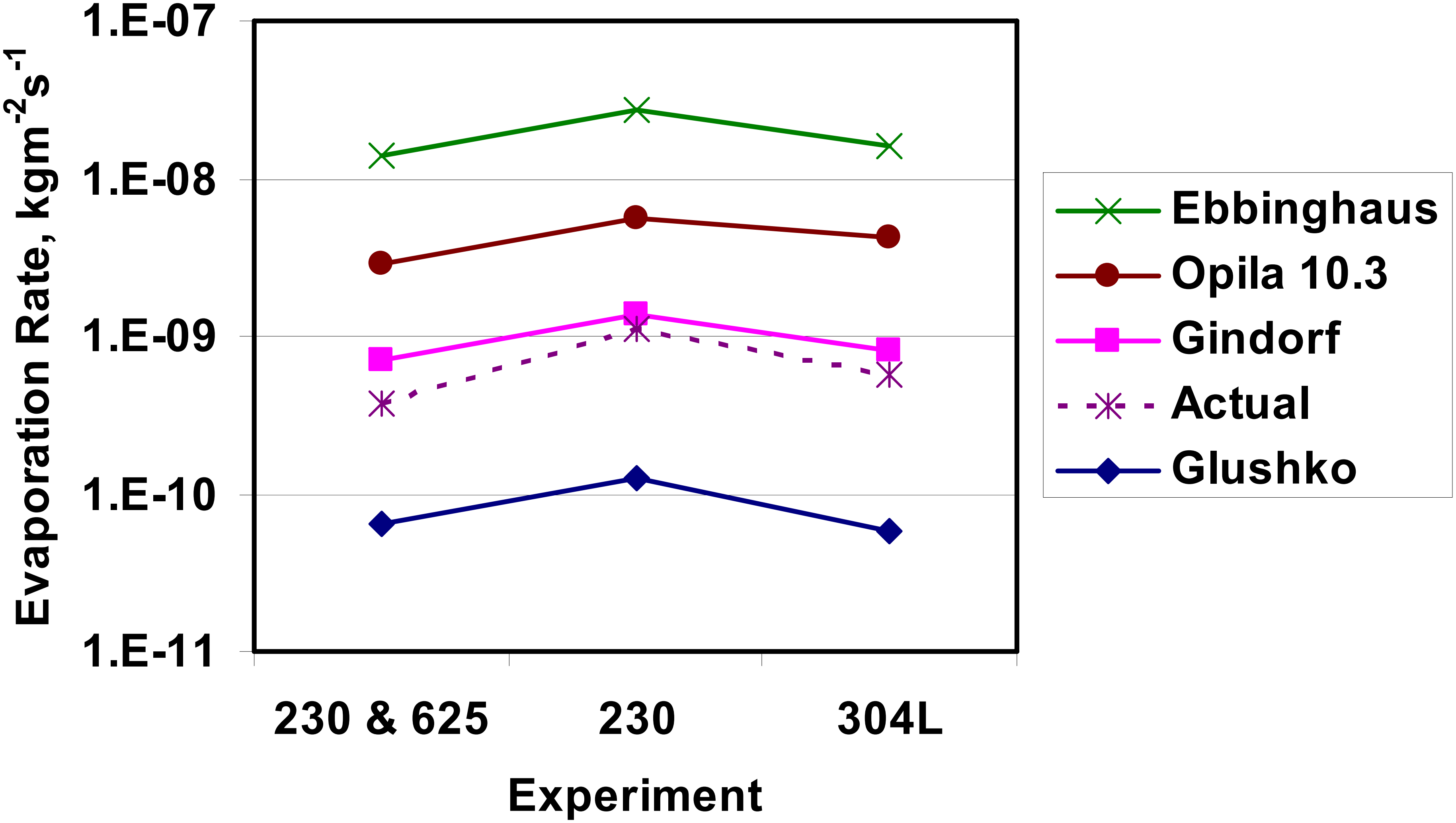
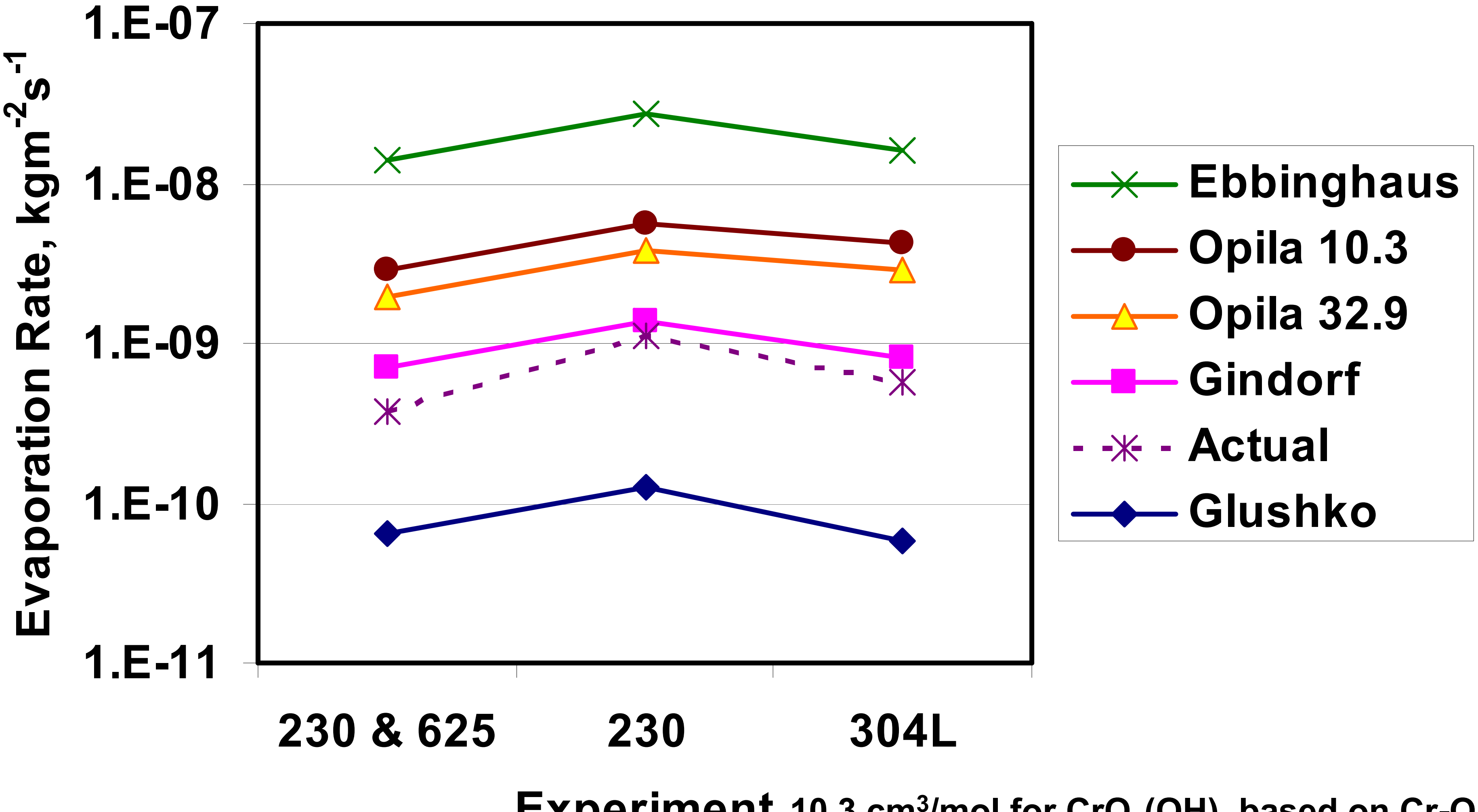


Thermodynamics of $CrO_2(OH)_2(g)$

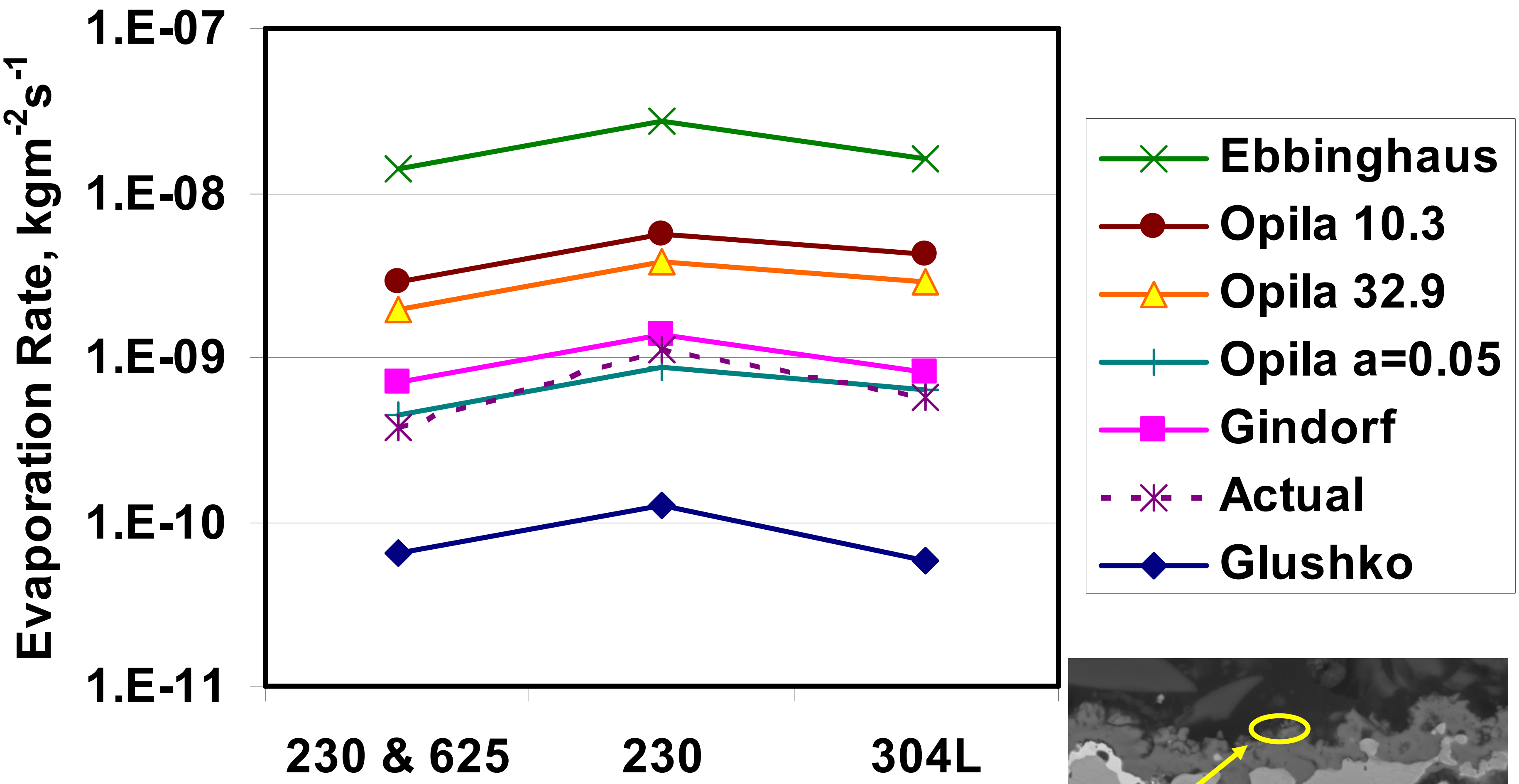


$$D_{AB} = \frac{(3.203\times10^{-4})T^{1.75}}{P_T(v_A^{1/3}+v_B^{1/3})^2}\sqrt{\frac{1}{M_A}+\frac{1}{M_B}}$$

10.3 cm^3/mol for $CrO_2(OH)_2$ based on Cr-O bond in CrO

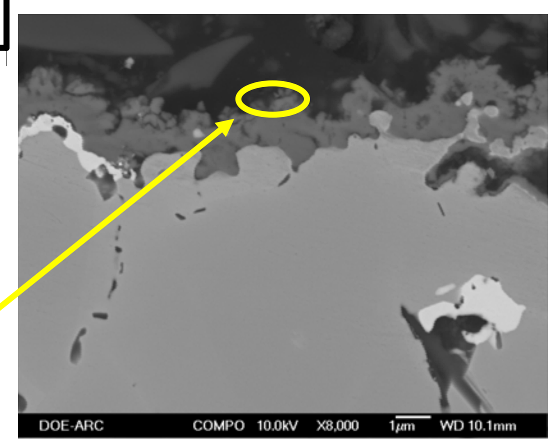
Opila model of $CrO_2(OH)_2$ => 32.9 cm^3/mol based on Cr-H bond

Thermodynamics of $CrO_2(OH)_2(g)$



In comparison, $MnCr_2O_4$ has an activity of Cr_2O_3 of about 0.0006 (Holcomb & Alman 2006)

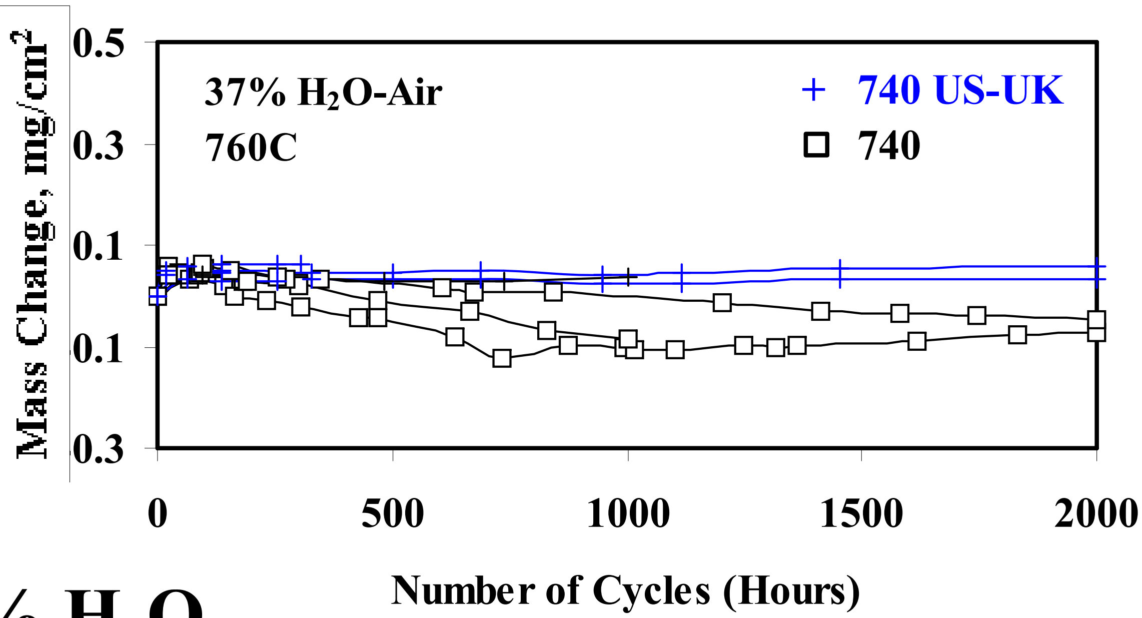
Decreased Chromia Activity at the Scale-gas interface

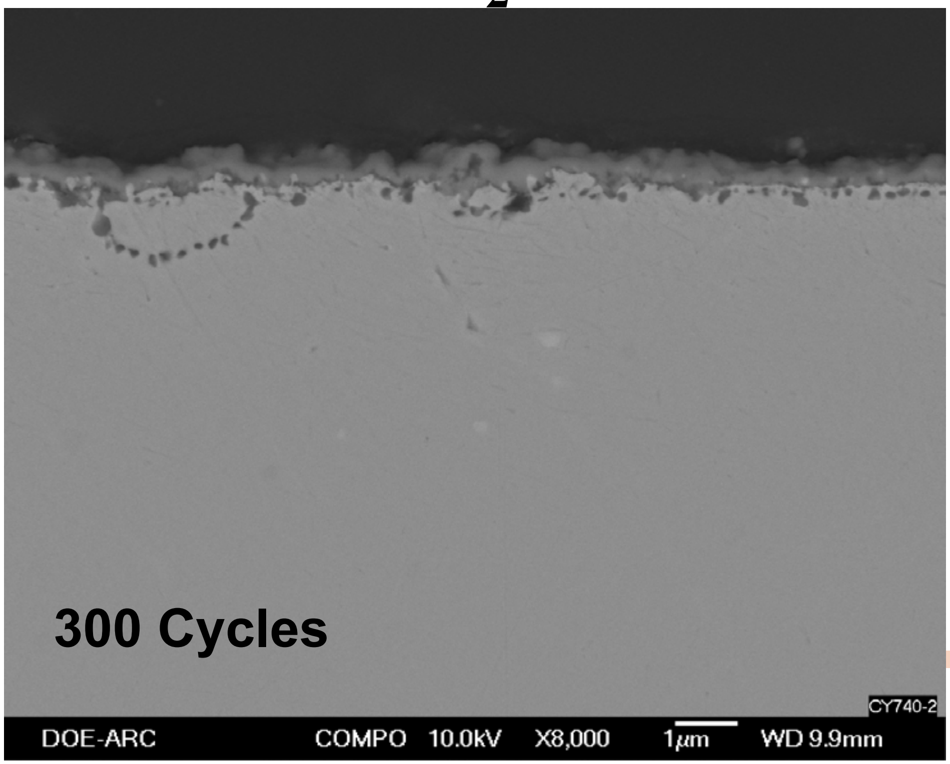


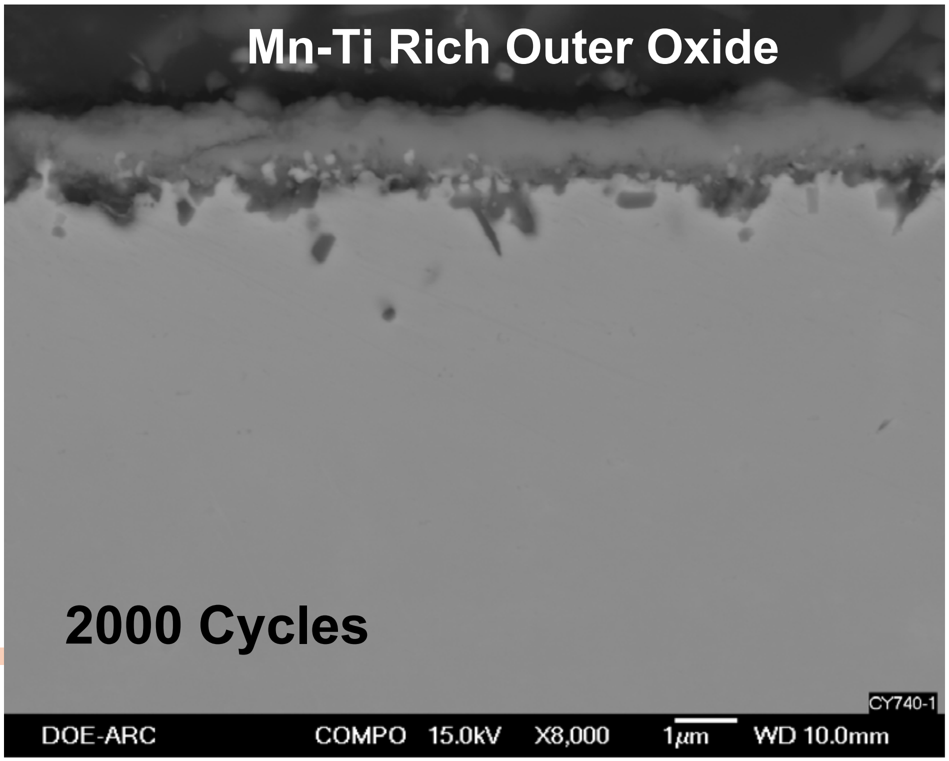
Inconel 740

760°C

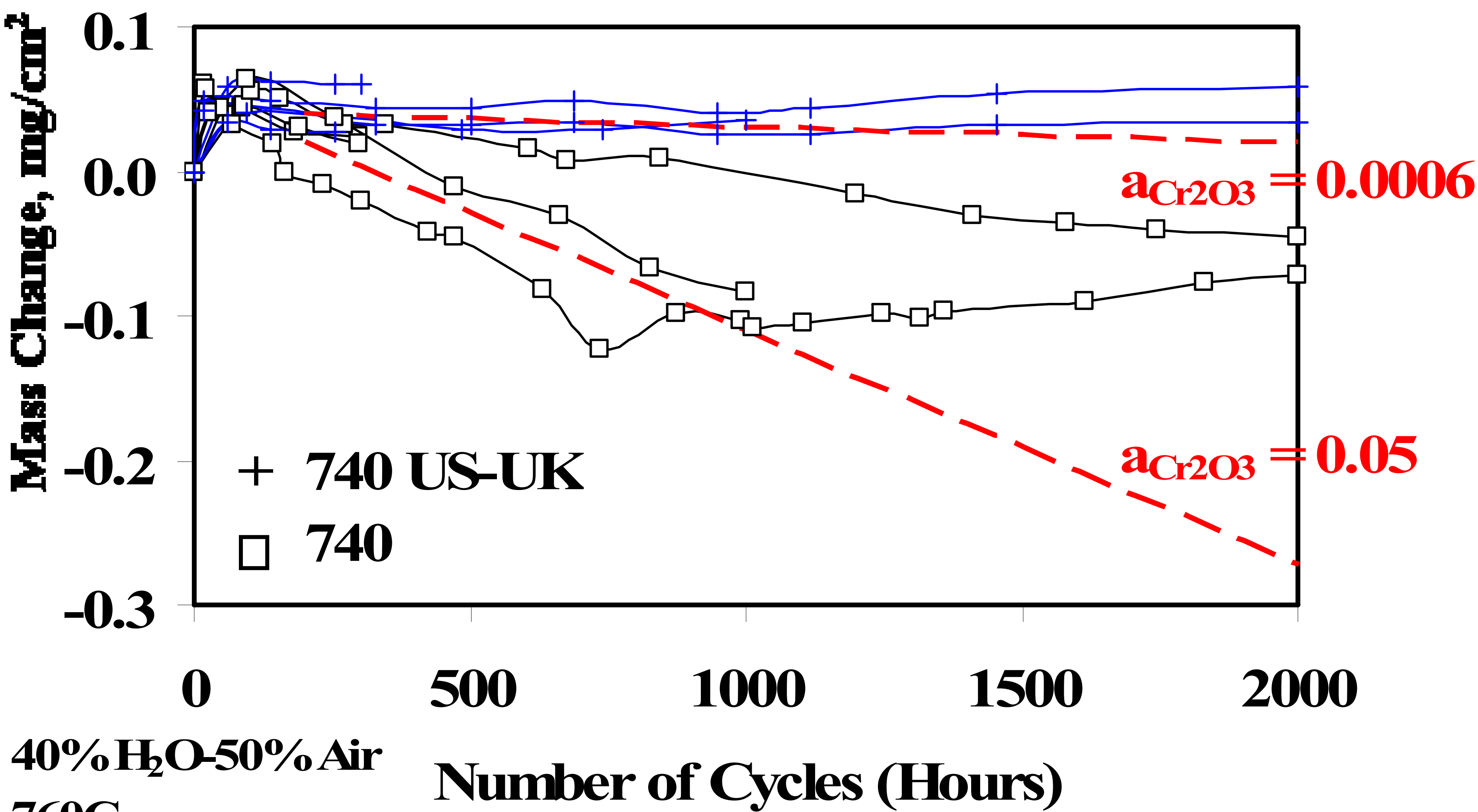
Air + 37% H_2O







Inconel 740



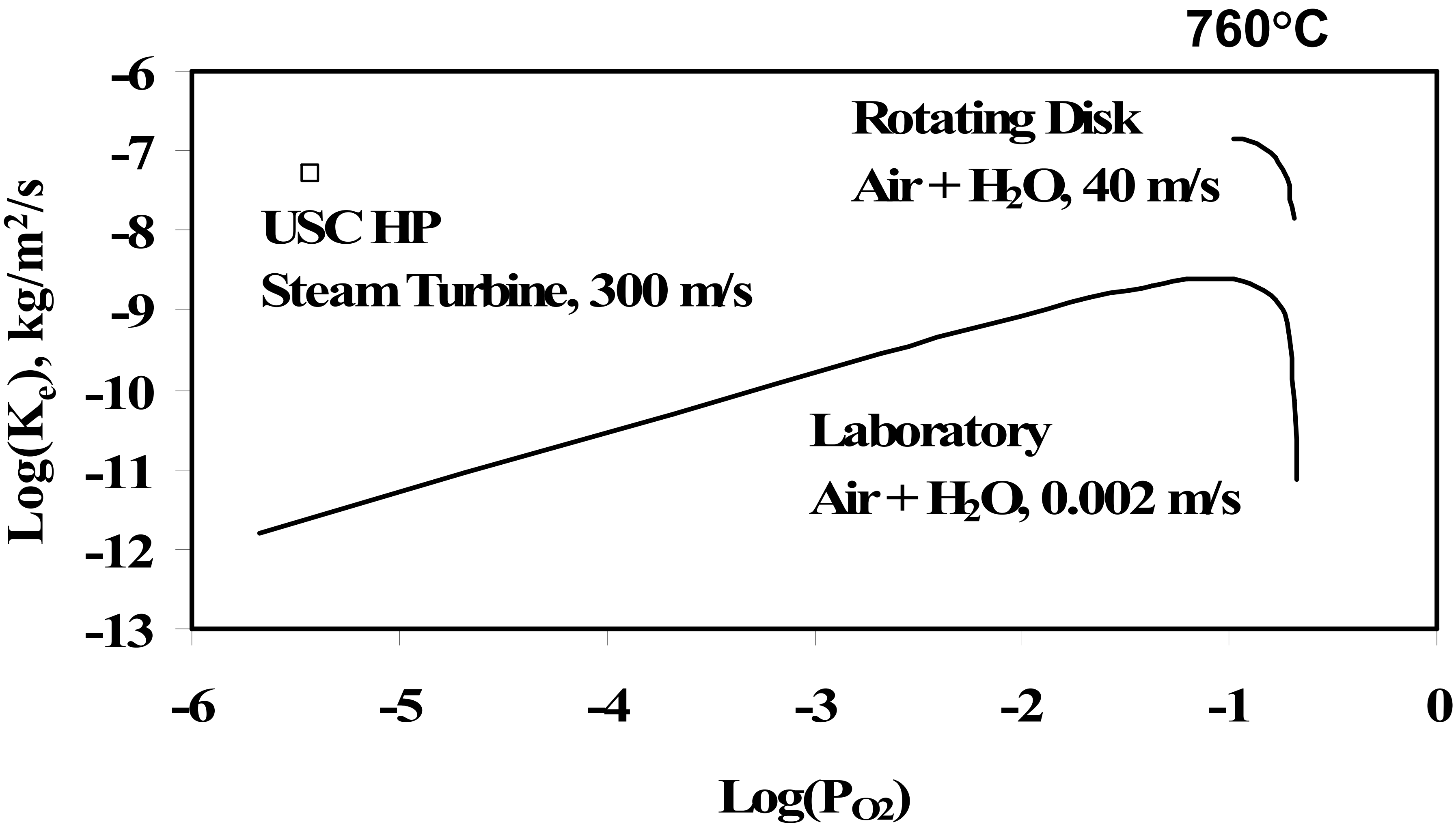
40% H_2O-50% Air
760C

Alloy	Mn	Ti	Apparent Cr_2O_3 Activity
230	0.5	--	0.05
617	0.1	0.3	0.05
740	0.3	1.6	Initially 0.05 Then ~0.0006
740 US/UK	0.3	1.8	~0.0006

Future Work

- **Additional Model Verification**
  - Exposures in up to 40 m/s moist air
  - ESCA analysis of oxide scale surface for composition and oxidation state
- **Examine Oxidation Behavior of Cast Alloys Compared with Wrought Alloys**
  - Haynes 230, 263, 282
  - Inconel 617, 625, 740
  - Nimonic 105
  - Scaling and internal oxidation in steam, both at atmospheric pressure and at up to 5000 psi
  - Evaporation in moist air
- **Compare results with that from the Niles steam loops (Babcock & Wilcox)**

Advanced Steam Turbines vs Laboratory Exposures

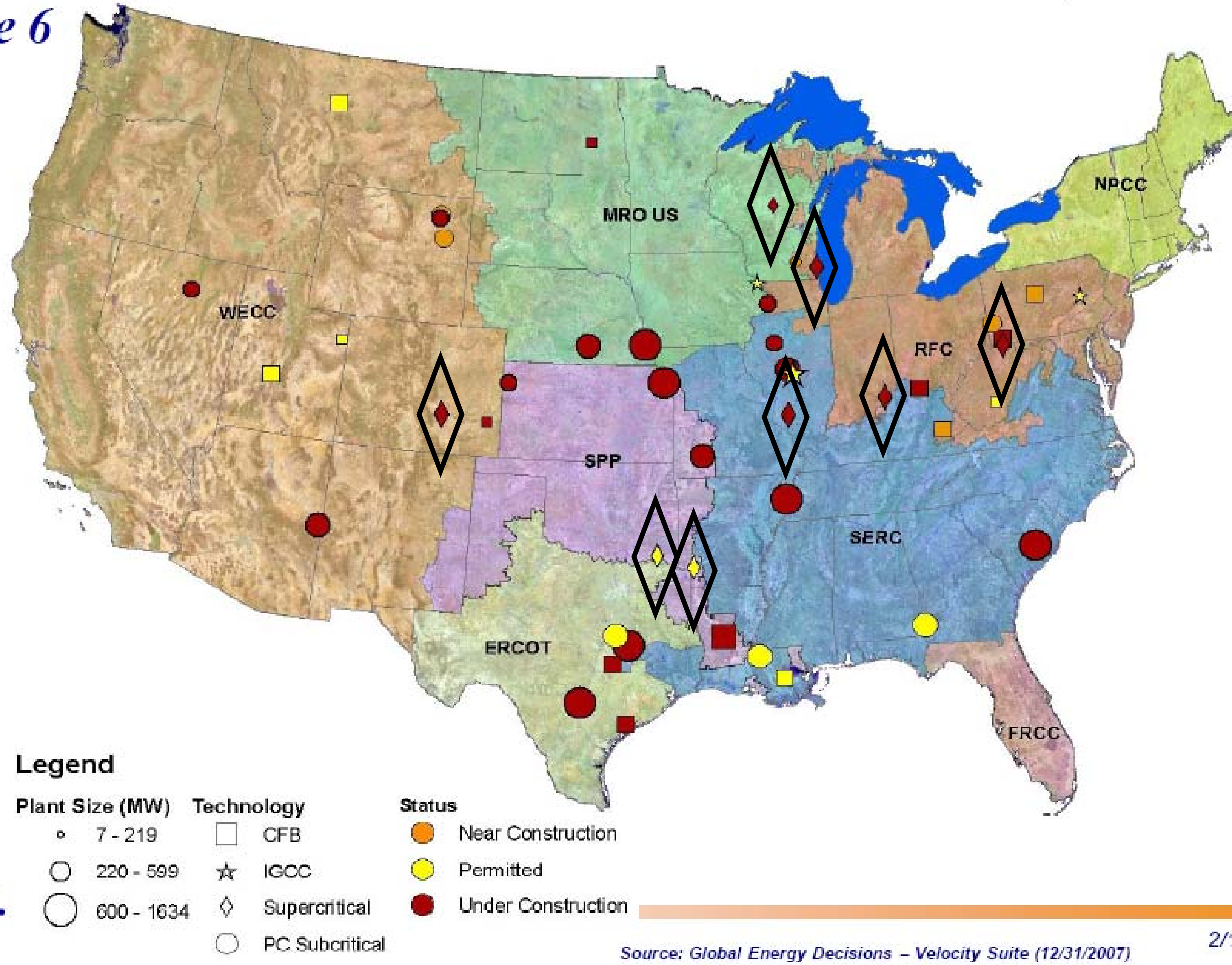


Evaporation at a maximum at 57% H_2O

Summary

- **Nickel-base superalloys for USC applications experience 3 main oxidation behaviors**
  - Scale formation
  - Internal Oxidation
    - Deeper penetration and section loss than scaling
  - Reactive Evaporation
    - Model development—Kinetics, Thermodynamics, Saturation, Alloy Cr Depletion
    - Not important below 650°C
    - Expected to dominate above 700°C
- ***Should evaporation of chromia be a concern in USC boilers and turbines?*** **Yes**

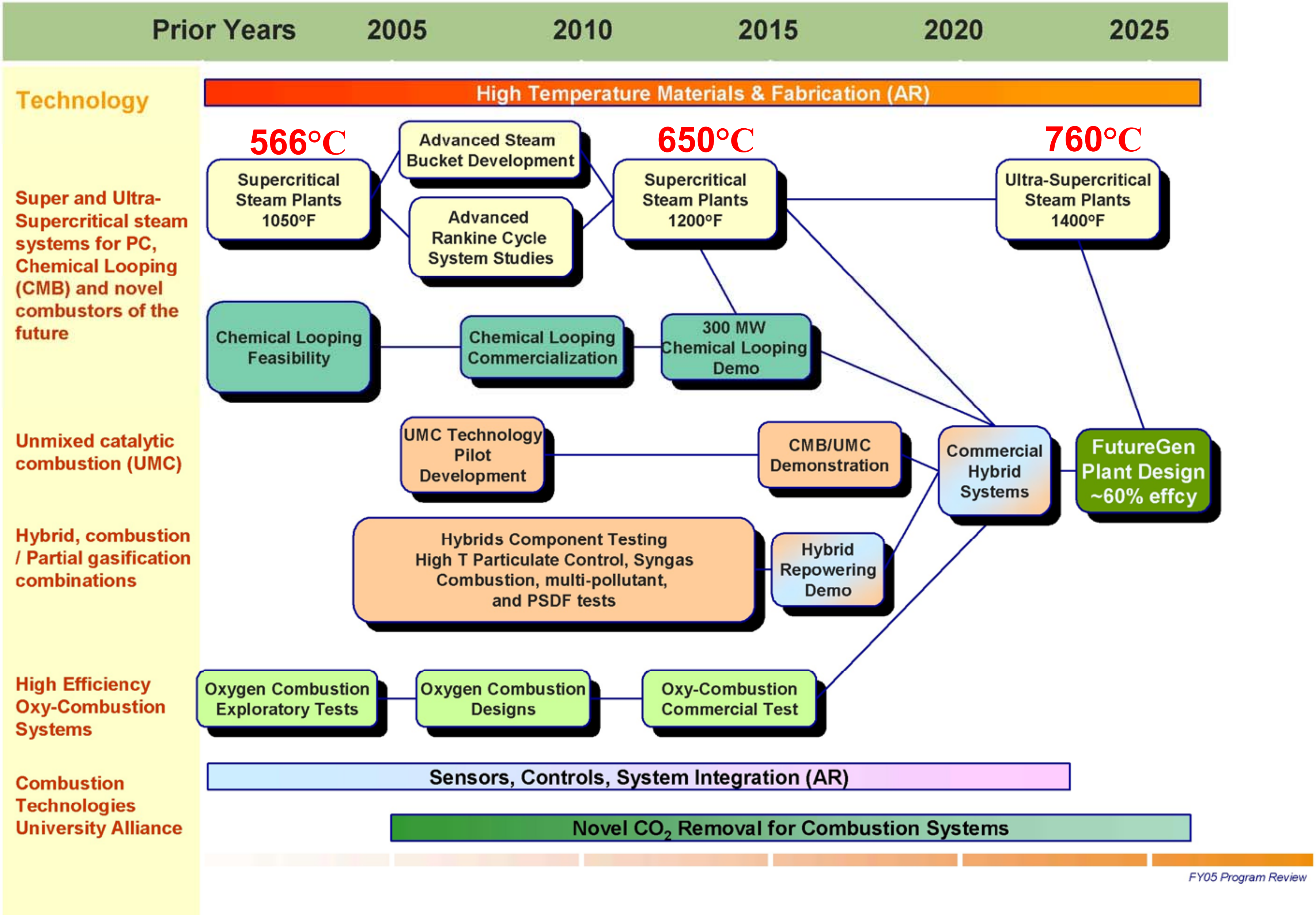
Geographical Map by NERC Regions: Coal-Fired Plants
(Permitted, Near Construction, and Under Construction)
Figure 6



Source: Global Energy Decisions – Velocity Suite (12/31/2007)

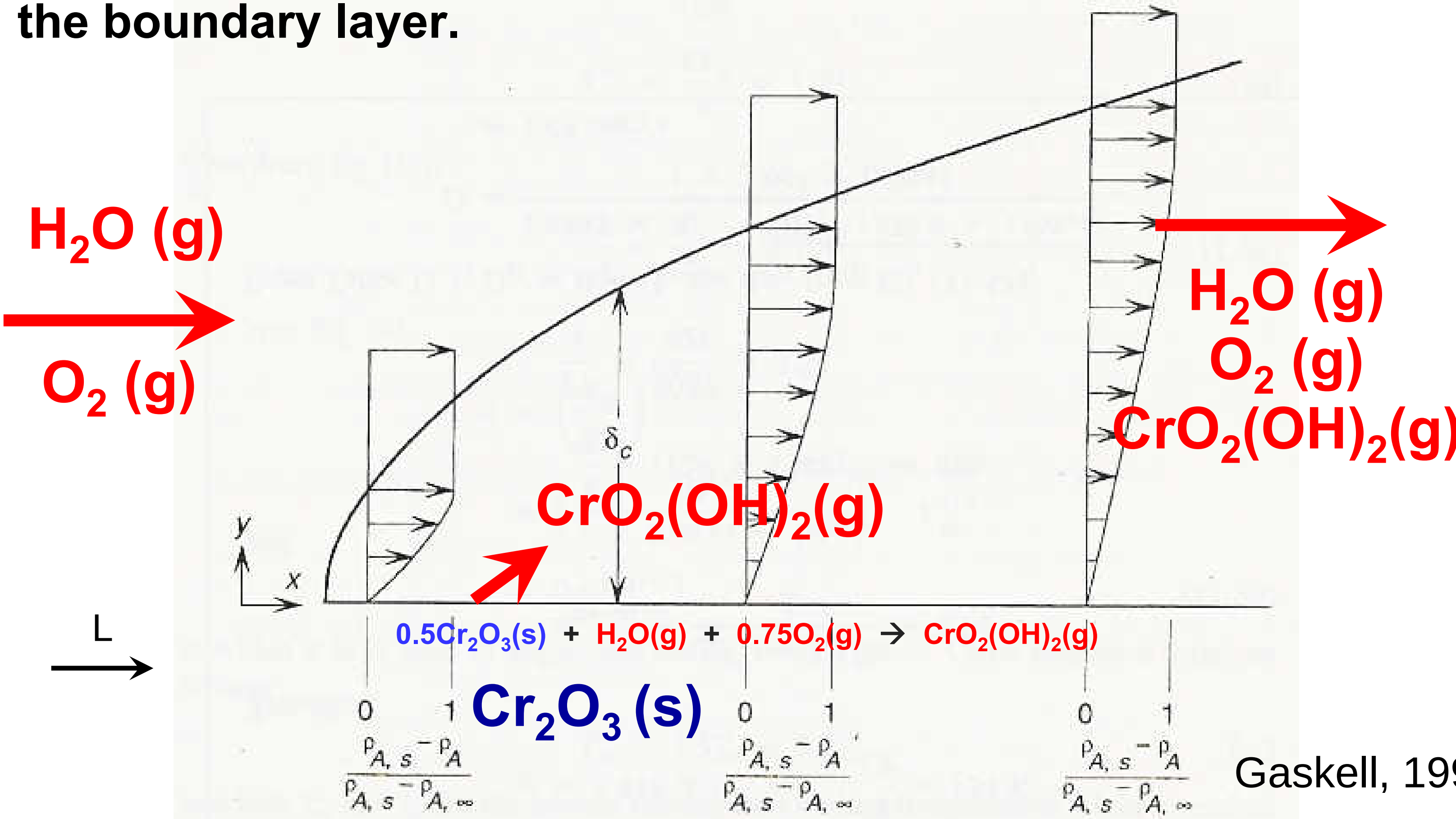
2/18/2008

Combustion Technologies Roadmap



Evaporation Model - Kinetics

- **Controlled by fluid properties and evaporation reaction.**
- **Evaporation is limited by mass transport of the volatile specie in the boundary layer.**



Gaskell, 1993

FIGURE 11.17. Normalized concentration profiles of *A* in the concentration boundary layer on the surface of solid *A* over which fluid *B* is flowing, when *A* is slightly soluble in *B*.

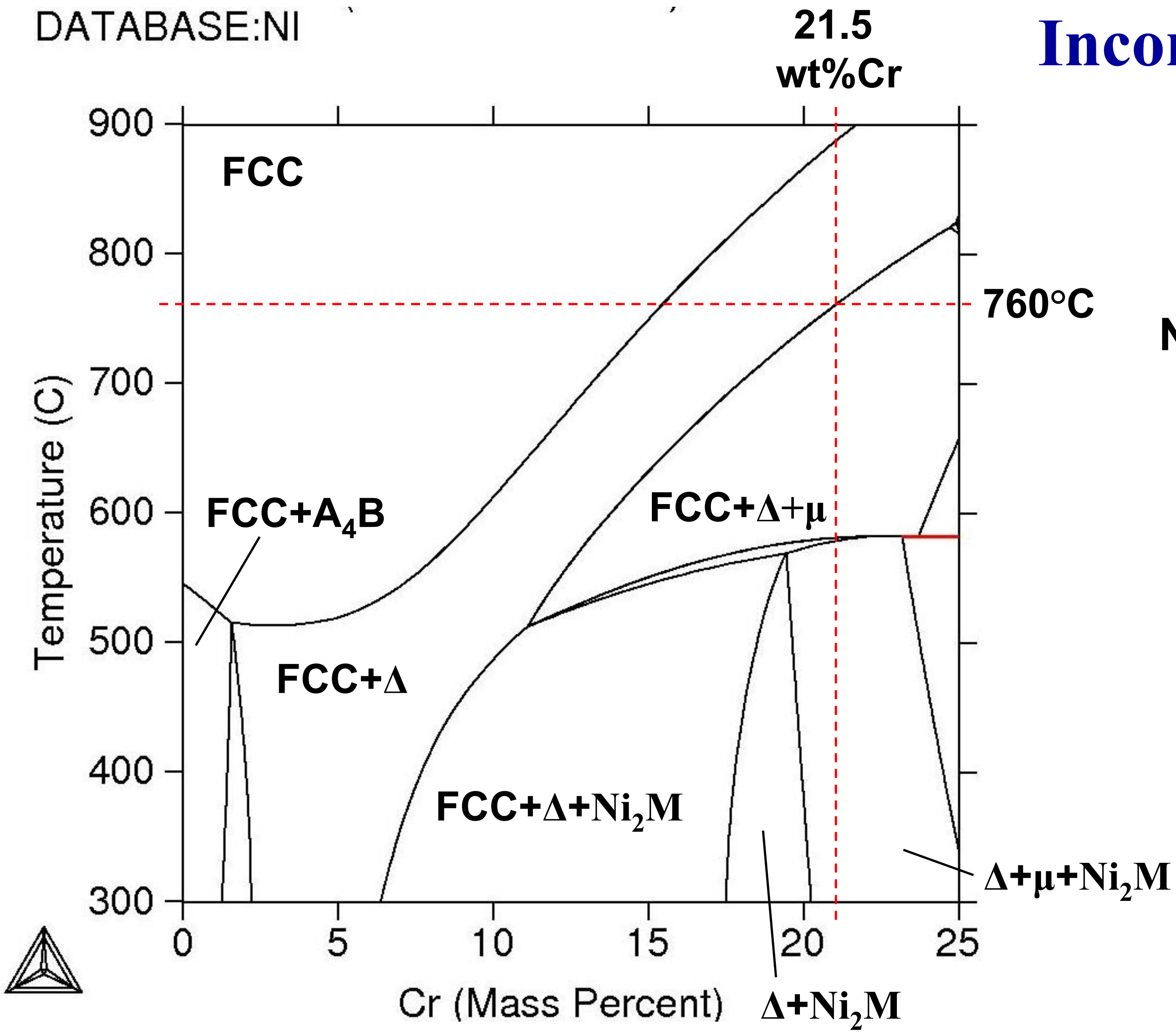
Nickel-base Superalloy Compositions

Alloy	Fe	Cr	Ni	Co	Mo	C	Si	Ti	Al	B ppm	Mn	Other
Haynes 230	1.5	22	Bal	2.5	2	0.1	0.4		0.3	75	0.5	0.02 La 14 W
Haynes 282	0.75	19.5	Bal	10	8.5	0.06	0.075	2.1	1.5	50		0.15 Cu
Inconel 617	1.5	22	Bal	12.5	9	0.1	0.5	0.3	1.15	30	0.5	0.25 Cu
Inconel 625	2.5	21.5	Bal	0.5	9	0.05	0.25	0.2	0.2		0.25	3.65 Nb
Inconel 718	Bal	19	52	0.5	3.05	0.04	0.175	0.9	0.5	30	0.175	5.125 Nb 0.15 Cu
Inconel 740	0.7	25	Bal	20	0.5	0.03	0.5	1.8	0.9		0.3	2 Nb
Nimonic 105	0.5	14.85	Bal	20	5	0.085	0.5	1.2	4.7	65	0.5	0.075 Zr 0.1 Cu
Udimet 720Li		16	Bal	14.75	3	0.015		5	2.5	150		1.25 W 0.0375 Zr

Other Alloy Compositions

Alloy	Analysis	Fe	Cr	Ni	Co	Mo	Nb	Mn	Si	Ti	Al	Other
SAVE12-9.5Cr	XRF	83.0	9.5	0.4	2.6	0.04	0.05	0.5	0.4	0.02		2.9 W 0.3 V
SAVE12-10.5Cr	XRF	82.9	10.3	0.2	3.0		0.06	0.5	0.8	0.01		2.9 W 0.3 V
HR6W	XRF	24.2	23.6	43.4	0.4	0.2	0.2	1.0	0.3	0.2	0.04	6.1 W 0.1 Cu
T92	Nom		9	<0.4		0.5		0.5	<0.5		<0.04	1.75 W 0.2 V 0.07 Cb
TP347HFG	Nom	Bal	18	11			*	2.0	1.0			Nb+Ta≥10xC

Inconel 625



$A_4B \approx Ni_4Mo$

$\Delta \approx Ni_3(Nb\text{-}Mo)$

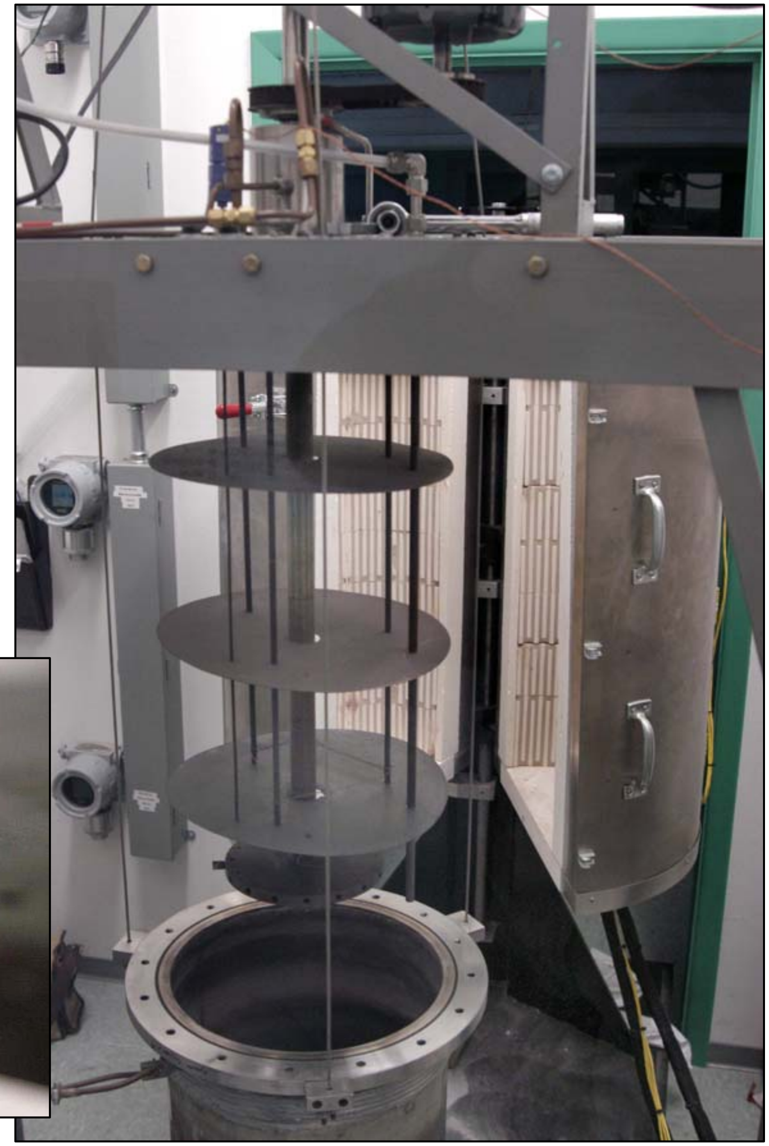
$Ni_2M \approx Ni_2(Cr\text{-}Mo)$

$\mu \approx NiMoCr$

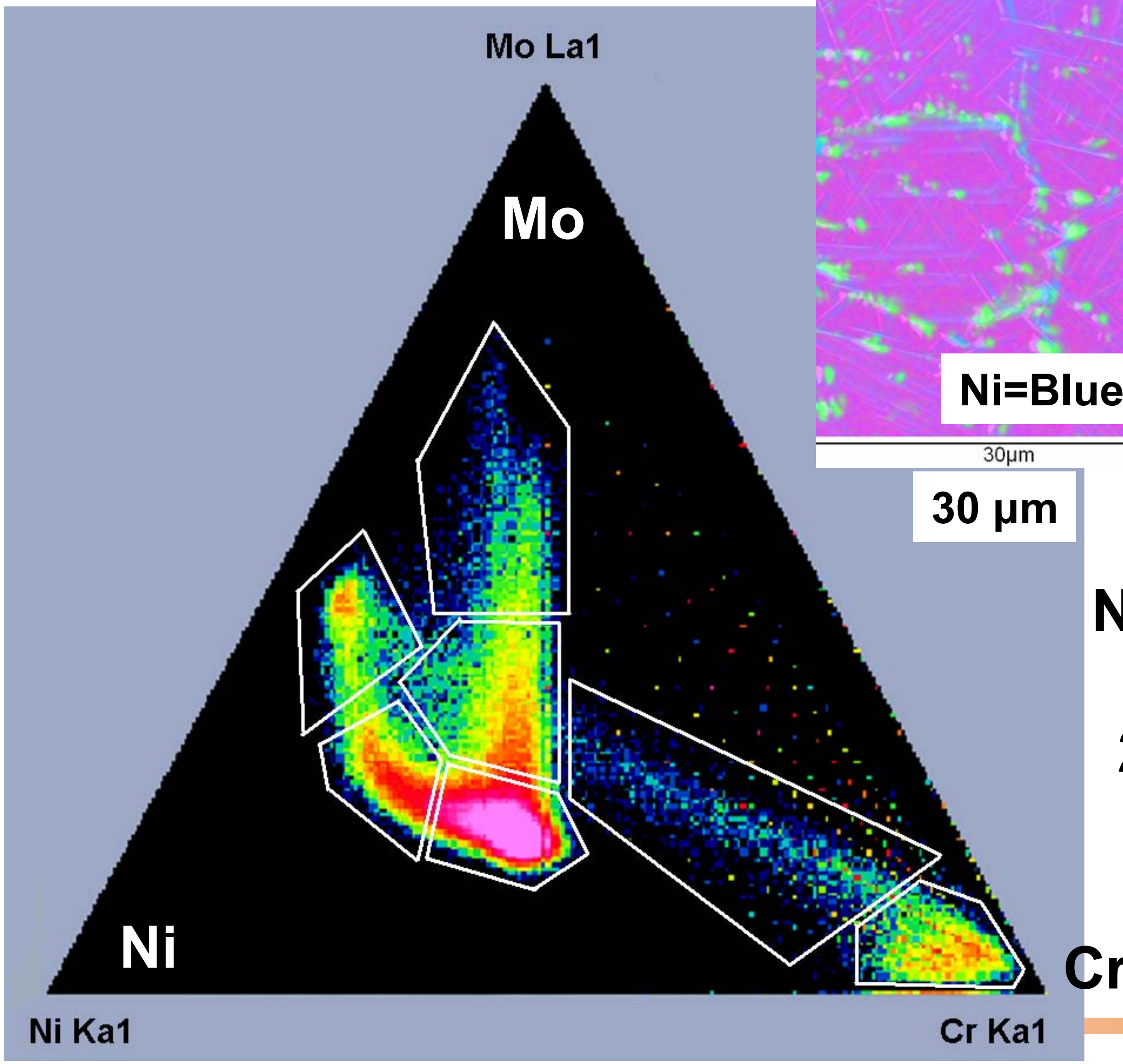
Isopleth with Mo = 9 wt% and Nb = 3.65 wt%

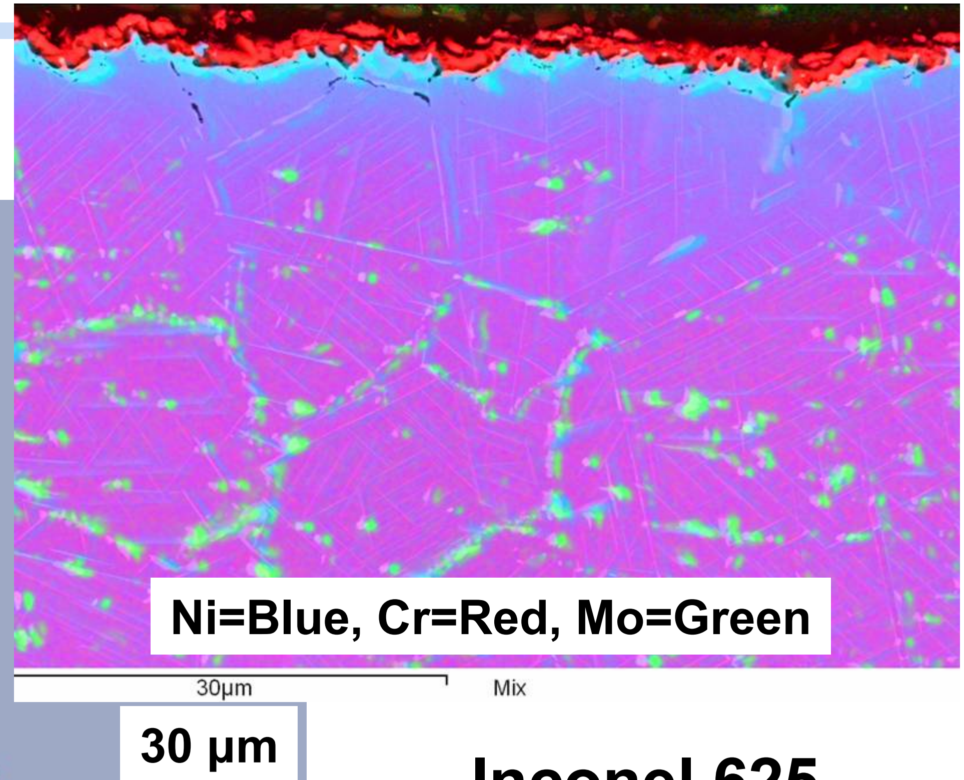
High Velocity Exposures in Moist Air

- Rotating disk up to 40 m/s
- Moist environments
- Cr evaporation model
  - Turbulent: $v^{0.8}$
  - Laminar: $v^{0.5}$



Inconel 625



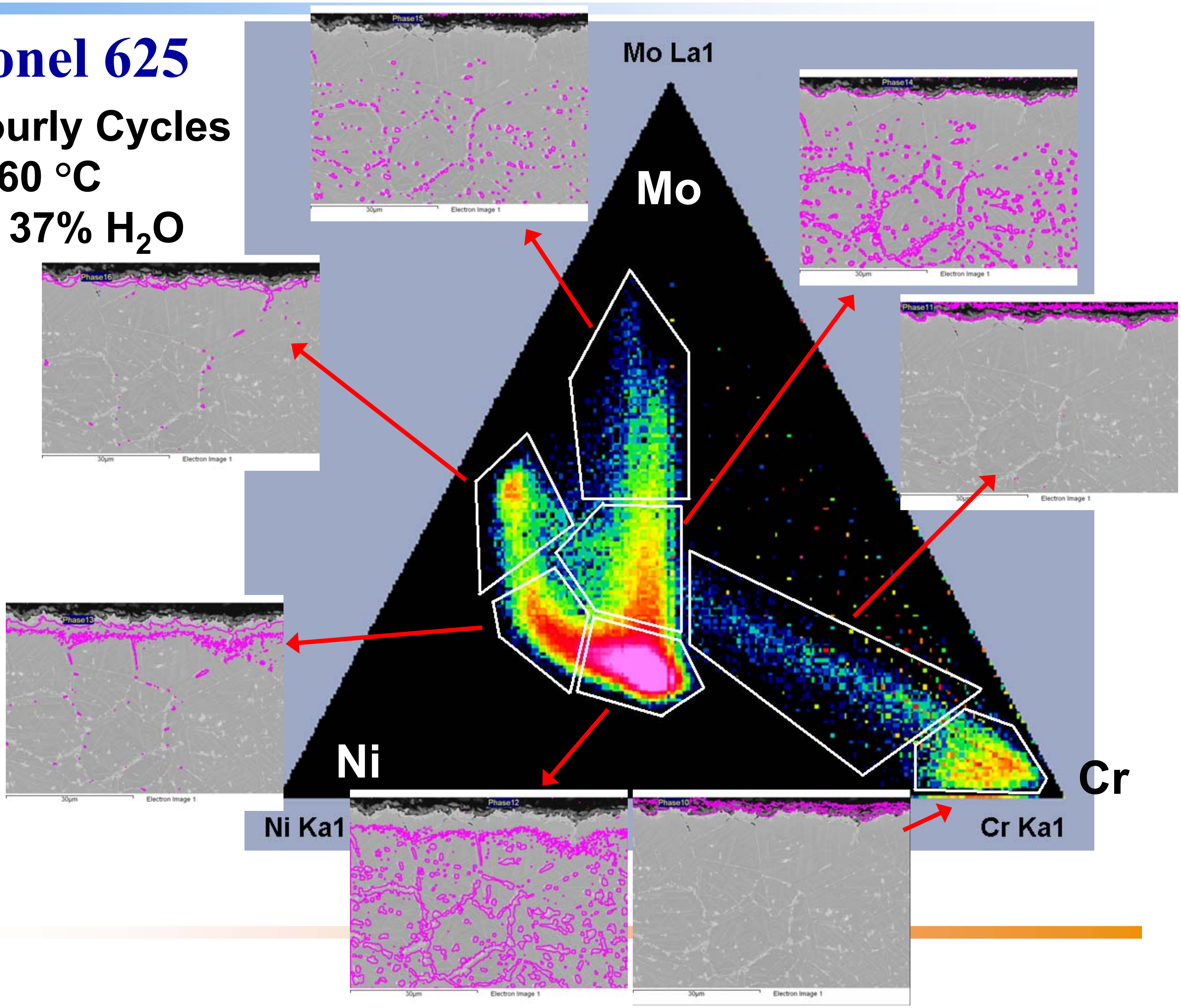


Inconel 625
Ni-21.5Cr-9Mo-3.65Nb

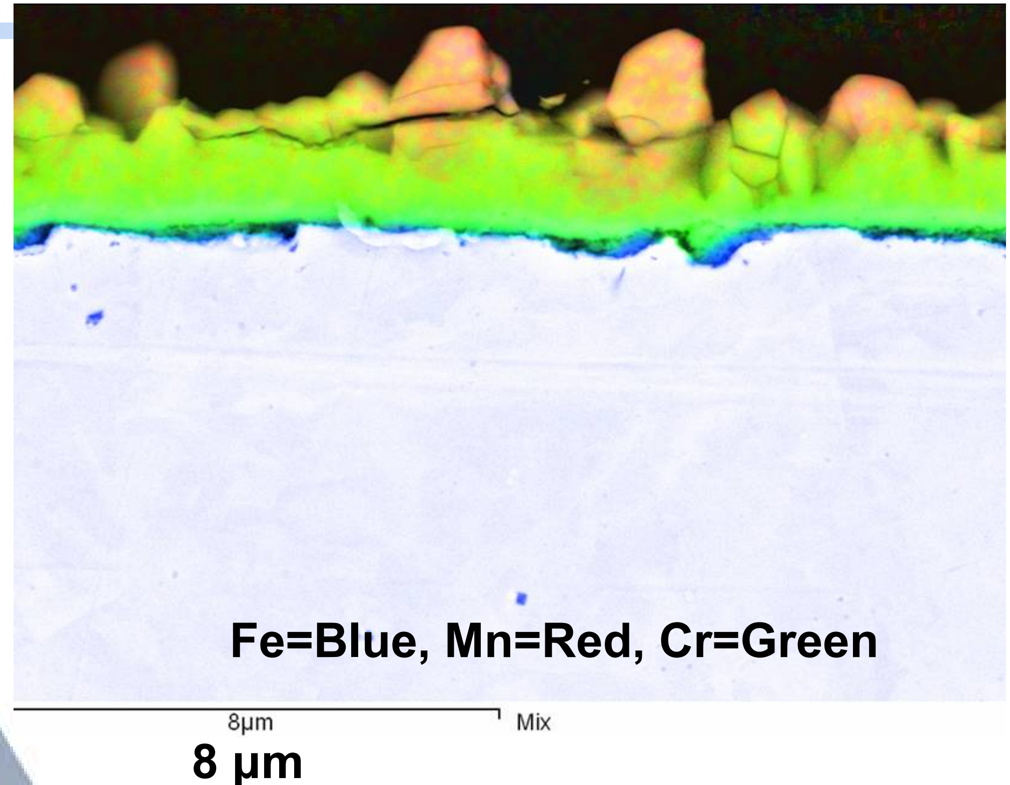
2000 Hourly Cycles
760 °C
Air + 37% H_2O

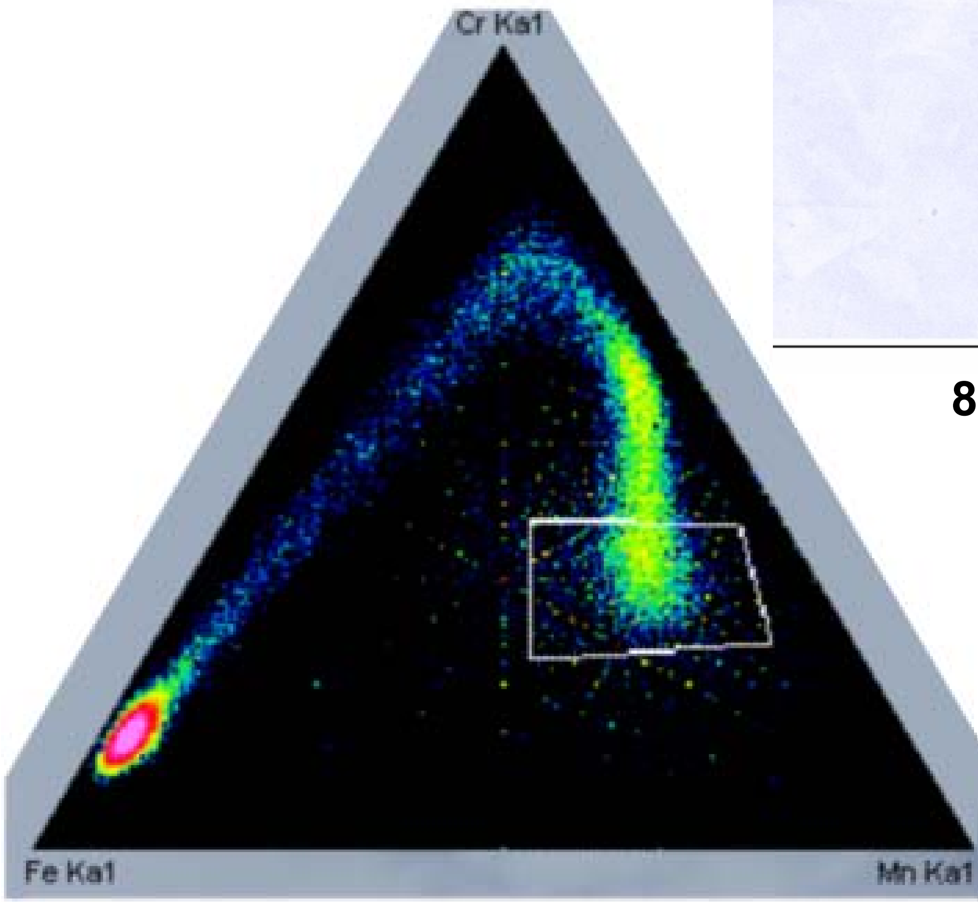
Inconel 625

2000 Hourly Cycles
760 °C
Air + 37% H_2O



T92





2000 Hourly Cycles
760 °C
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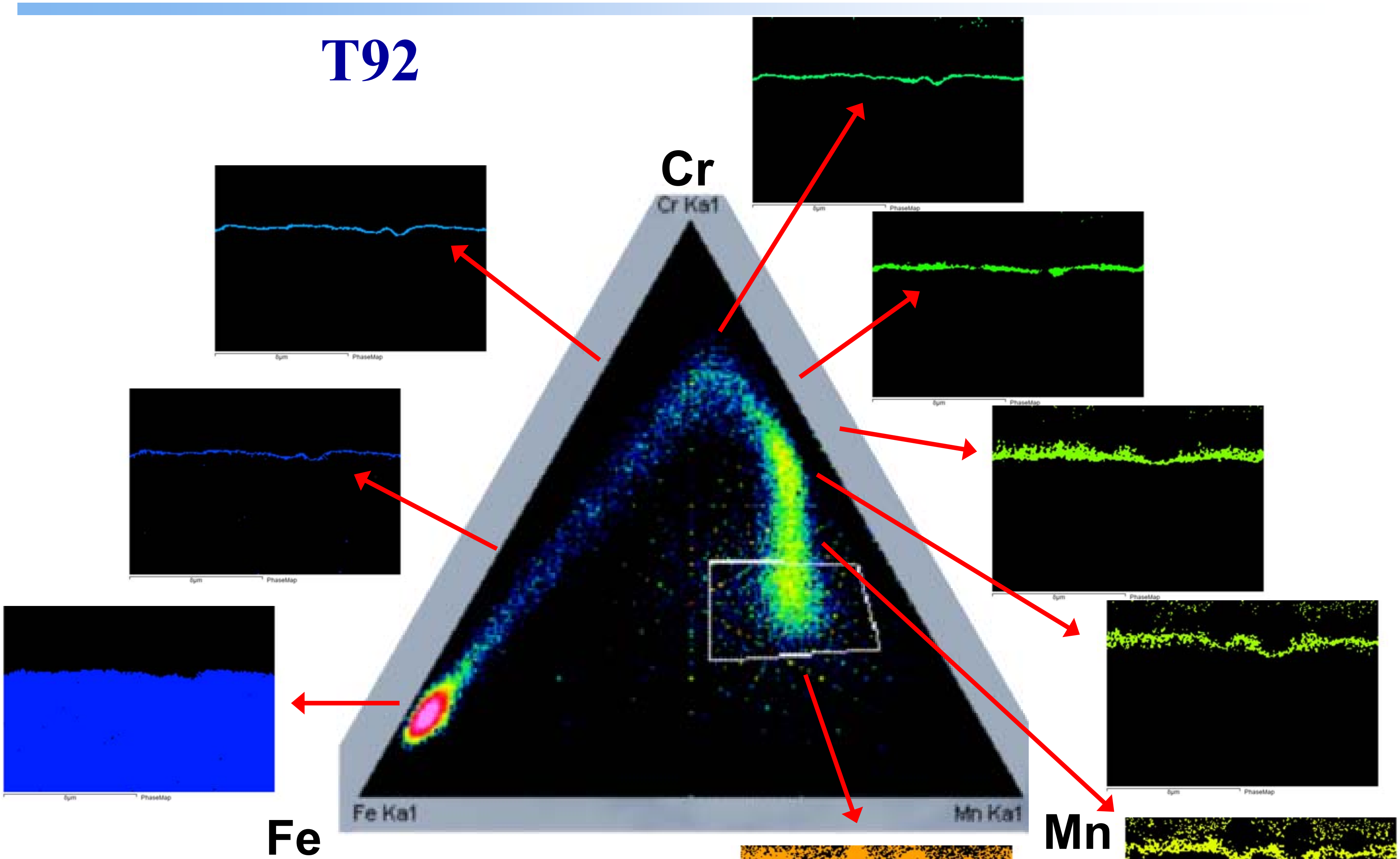
T92



Fe-9Cr-2W-0.5Mo-0.5Mn
2000 Hourly Cycles
760 °C in Air + 37% H_2O

Evaporation Model – Some Verification

Table 5 – Comparison of experimental and predicted evaporation rates (all on a Cr_2O_3 basis).

Alloy and Conditions	Experimental Slope ($kg\ m^{-2}s^{-1}$)	Evaporation based on Glusko[16] $CrO_2(OH)_2(g)$ data ($kg\ m^{-2}s^{-1}$)	Evaporation based on Gindorf [20] $CrO_2(OH)_2(g)$ data ($kg\ m^{-2}s^{-1}$)	Evaporation based on Ebbinghaus[17] $CrO_2(OH)_2(g)$ data ($kg\ m^{-2}s^{-1}$)
Haynes 230 UNS NO6230 760°C 38% H_2O in air 1.9×10^{-3} m/s	-3.46×10^{-10} (21)	-6.50×10^{-11}	-7.00×10^{-10}	-1.38×10^{-08}
Haynes 230 UNS NO6230 760°C 37% H_2O in air 7.6×10^{-3} m/s	-1.11×10^{-9} (21)	-1.27×10^{-10}	-1.37×10^{-9}	-2.69×10^{-08}
304L UNS S30403 600°C 10% H_2O in O_2 2.5×10^{-2} m/s	-5.68×10^{-10} (7)	-3.79×10^{-11}	-5.23×10^{-10}	-1.03×10^{-08}

Asteman et al., 2000

Advanced Steam Turbines – Mitigation Techniques

- **Reduce Cr activity → spinels**
  - Manganese-Chromium Spinel Formation
  - $0.5MnCr_2O_4 + H_2O + 0.75O_2 = CrO_2(OH)_2 + 0.5\ MnO$
  - Lowers Evaporation by a factor of:
    - 55 at 700°C
    - 35 at 800°C

Holcomb & Alman, 2006

- **Reduce Cr activity → coatings**
- **Thermal barrier coatings to reduce metal temperature and give a much thicker diffusion boundary layer**
- **Steam chemistry—Reduce dissolved oxygen (DO)**
  - Limited by water dissociation and other steam cycle corrosion