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Oxidation in Environments with Elevated CO_2 Levels

Gordon R. Holcomb

Materials Research Engineer

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Outline

- **Background**
  - DOE Goals
- **Projects Relating to Oxidation in Environments with Elevated CO_2 Levels**
  - Materials Performance in Oxyfuel Combustion Environments
    - IAES projects at the University of Pittsburgh
  - Materials Performance in Oxyfuel Turbine Environments
    - Zero Emissions Coal Syngas Oxygen Turbo Machinery, Siemens
- **Results**
- **Summary**

DOE/NETL CCS Program Goals

By 2020, have available for commercial deployment, technologies and best practices for achieving:

- 90% CO_2 capture
- 99%+ storage permanence

Pre-combustion Capture (IGCC)

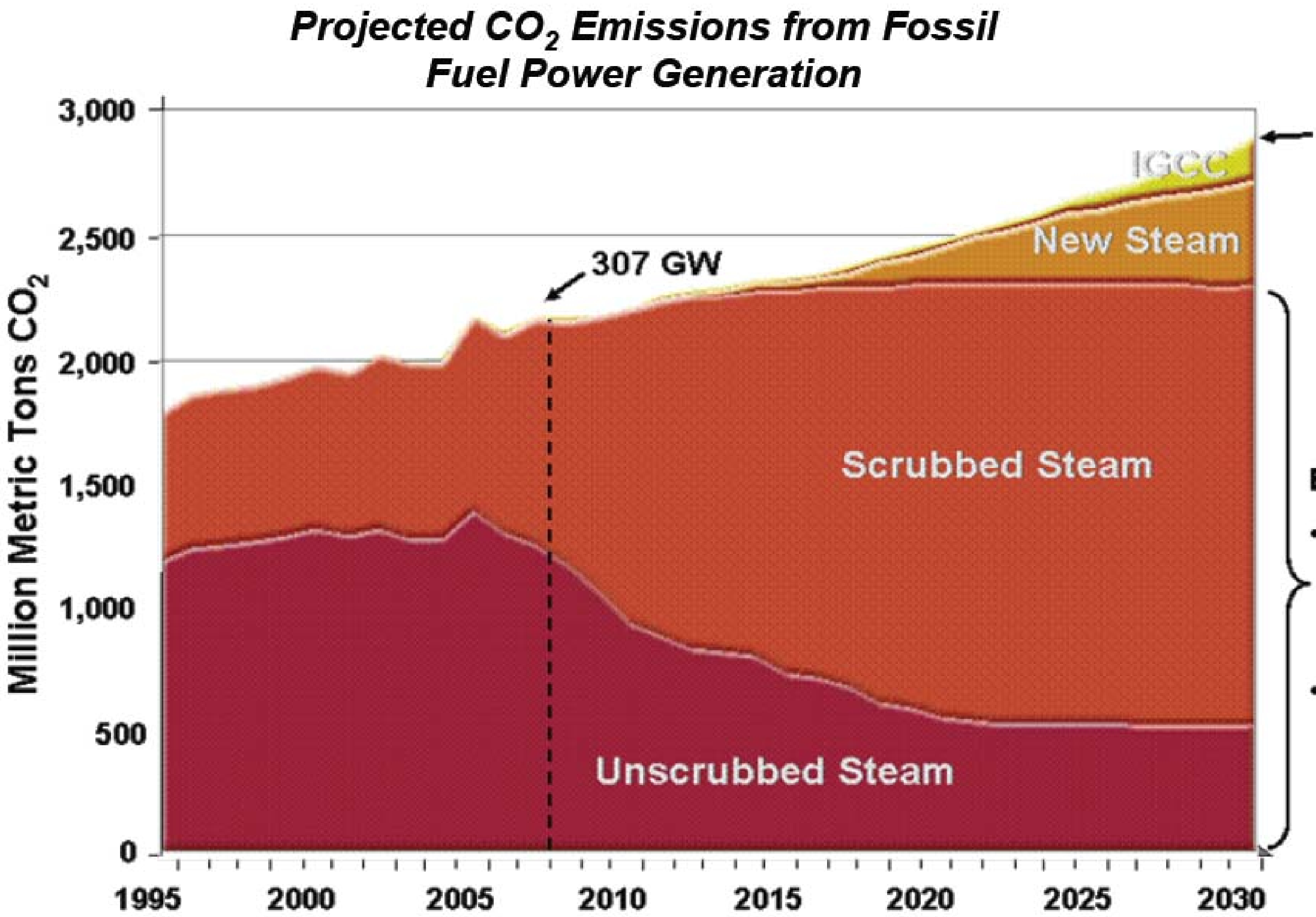
- < 10% increase in cost of electricity (COE)*

Post- and Oxy-combustion Capture

- < 35% increase in COE*

Includes 50 mile pipeline transport and saline formation storage, 100 years of monitoring

U.S. CO_2 Emissions and Existing Coal Plants



Existing units:

- 91.9% of cumulative coal-fired CO_2 2007 – 2030
- 79.4% of 2030 coal-fired CO_2

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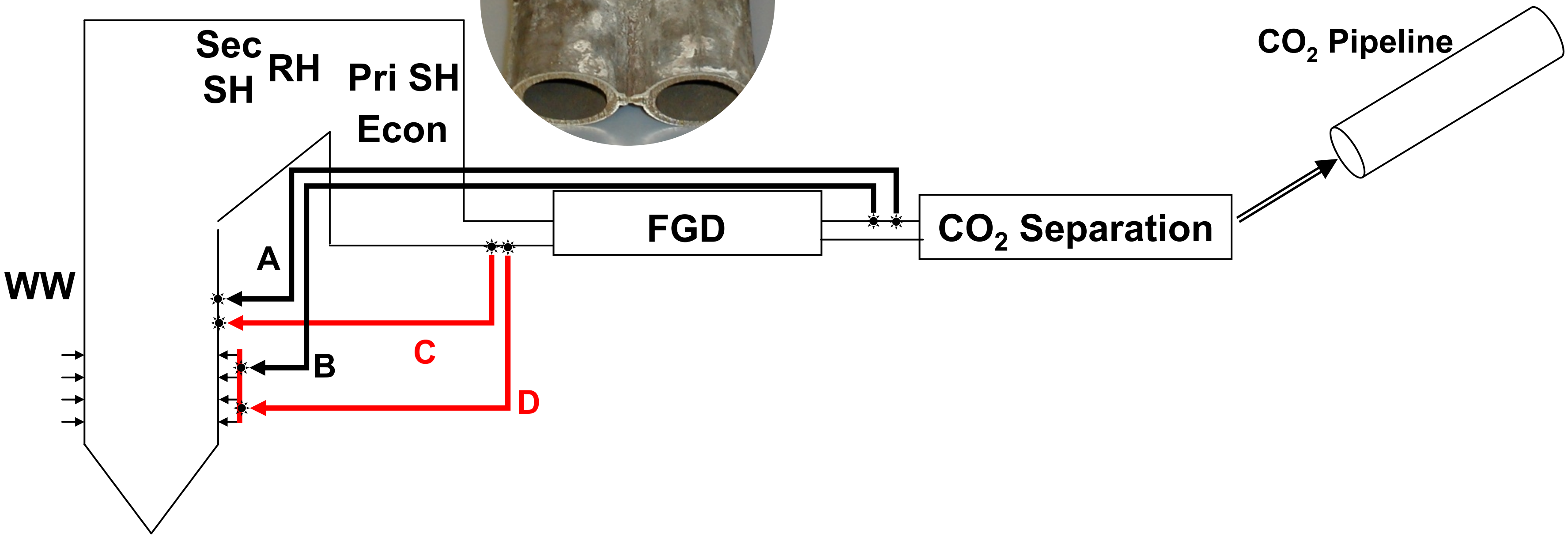
EIA Annual Energy Outlook 2008 Revised Early Release, March 2008

Refit Options and ORD Materials Research

Materials Performance in Oxyfuel Combustion Environments
Fireside Corrosion



A Cold Recirculation with Cleanup and Reheat

B Cold Recirculation with Cleanup, Reheat and Coal Motivation

C Hot Recirculation

D Hot Recirculation with Coal Motivation

Increasing Efficiency
Increasing Corrosion Risk
Increasing Heat Changes

Materials Performance in Oxyfuel Combustion Environments
Fireside Corrosion

- **Goal: determine the effect of Oxyfuel environments on materials of construction for waterwalls and superheaters.**
  - Established Power Plants –will conversion to oxyfuel environments require new equipment with new materials?
  - New Power Plants –what are the best materials for equipment?
- **Oxyfuel combustion can change the boiler environment**
  - Gas composition
    - Can have elevated SO_2/SO_3 (depending on design)
    - Elevated H_2O & CO_2
  - Ash composition

Fireside Corrosion—Initial Experiments
Alloy Composition and Max Use Temperatures

Alloy	Composition, weight %							
	Fe	Cr	Ni	Mo	C	Mn	Other	Max Use T, °C
T22	95.8	2.07	0.19	0.91	0.102	0.49	-	601
T92	87.3	8.84	0.32	0.32	0.124	0.29	1.83 W	650
347	67.1	17.2	11.2	0.28	0.061	1.35	-	760
617	2.24	21.6	54.6	7.74	0.102	0.036	10.9 Co	760

Note: All alloys except 617 supplied as boiler tubes

Fireside Corrosion—Initial Experiments Gas Mixtures

Environ.	Composition, volume %				
	N_2	O_2	CO_2	SO_2	H_2O
Air	74.1	6	14.6	0.3	5
Oxyfuel	0	2.5	60.1	0.9	32.6

675 °C (1247 °F) Equilibrium

O_2	SO_2	SO_3
5.9	*0.16*	*0.14*
2.4	*0.61*	*0.33*

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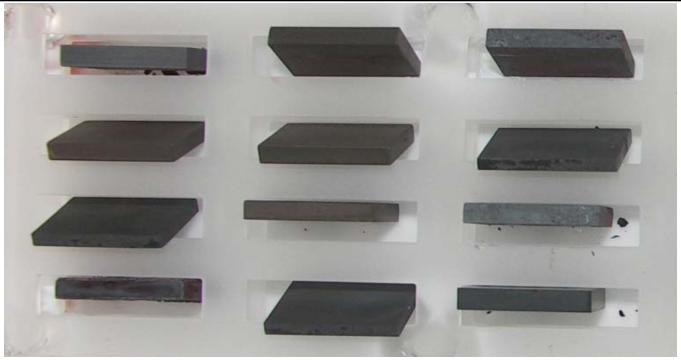
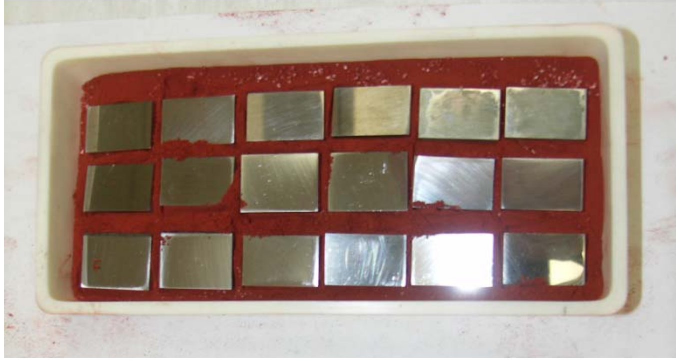
Fireside Corrosion—Initial Experiments

- Temperature = 675 °C (1247 °F), ~ Superheater Fireside
- Gas Linear Velocity = 6 cm/min (not meant to be representative of power plant gas velocities)
- Synthetic ash mixtures:

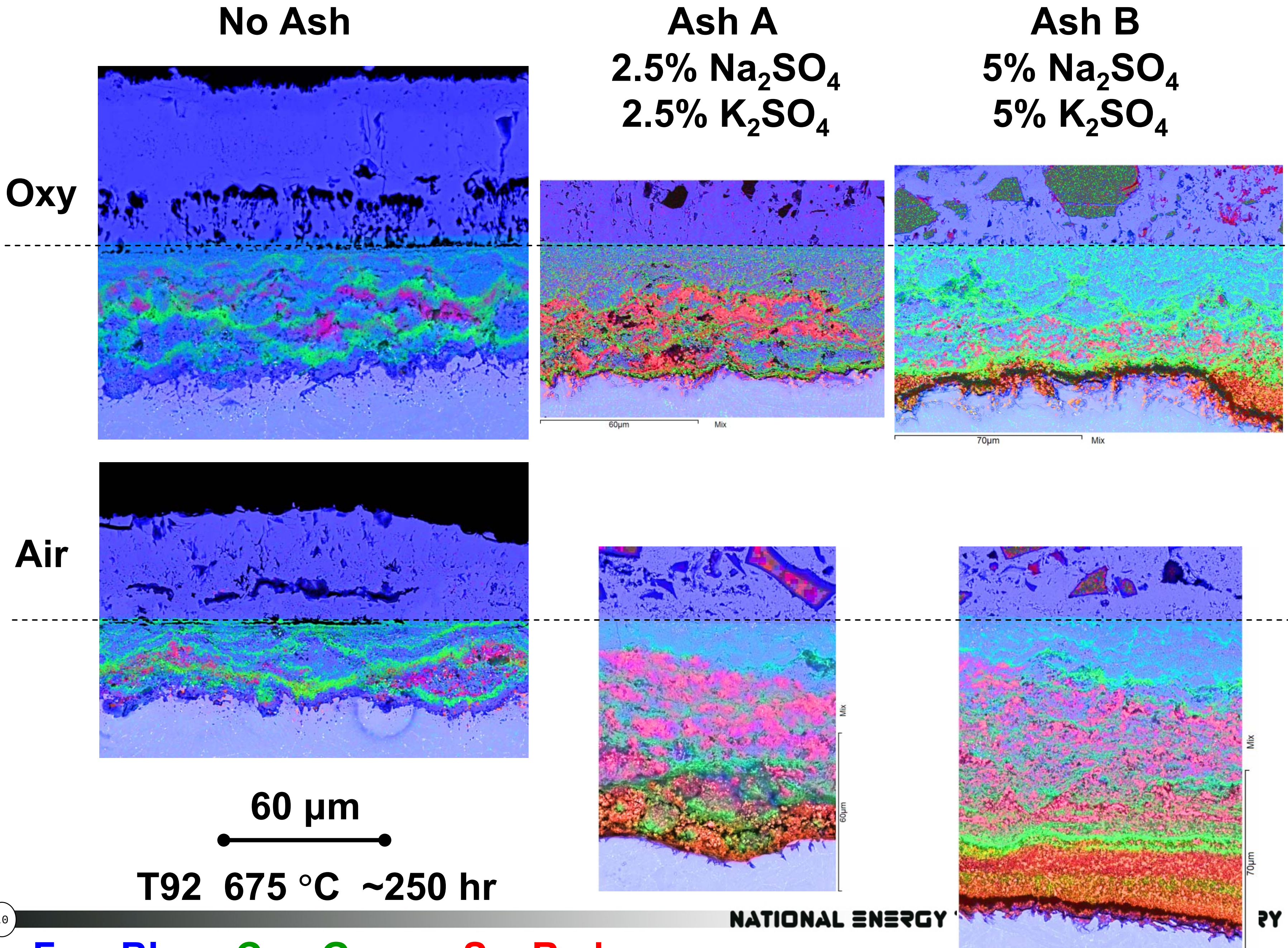
Ash Mixture	Composition, weight %					
	Fe_2O_3	Na_2SO_4	K_2SO_4	Al_2O_3	SiO_2	Calculated Base/Acid
A	31.67	2.5	2.5	31.67	31.67	0.52
B	30	5	5	30	30	0.54

No Ash

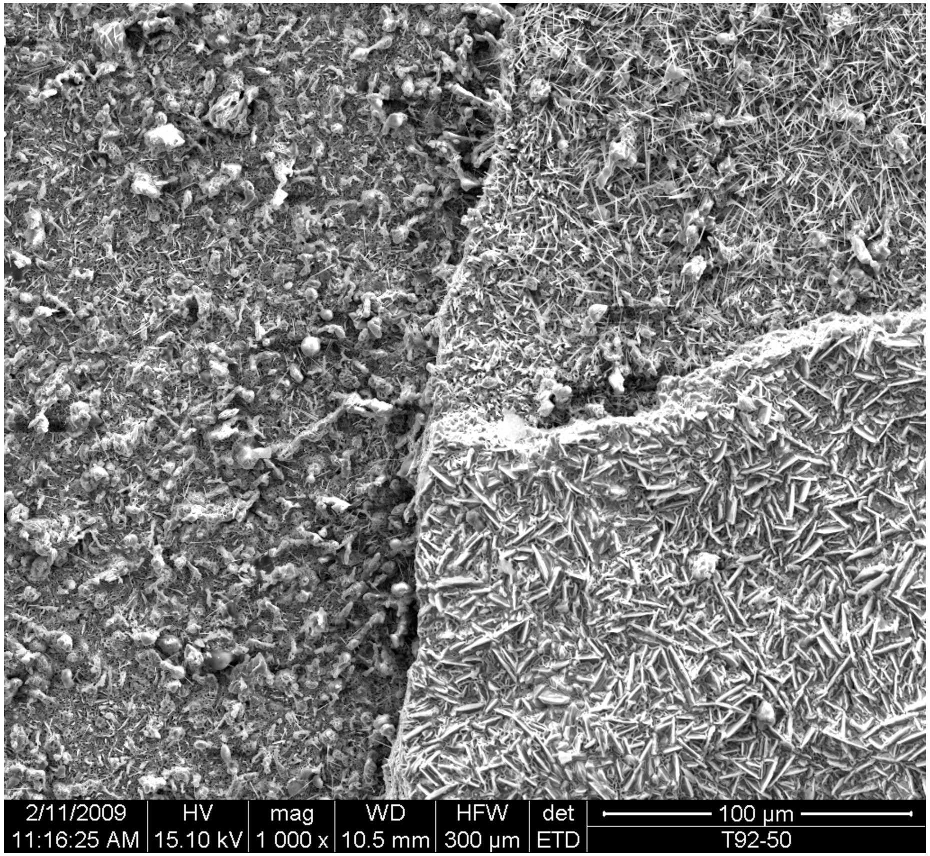


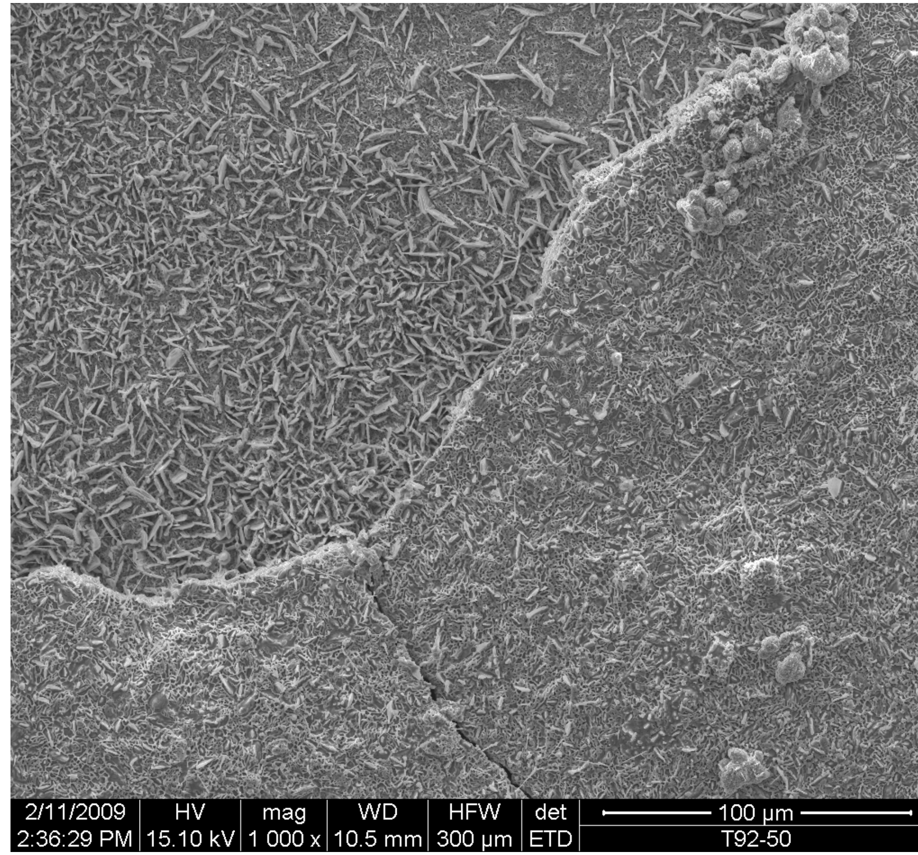


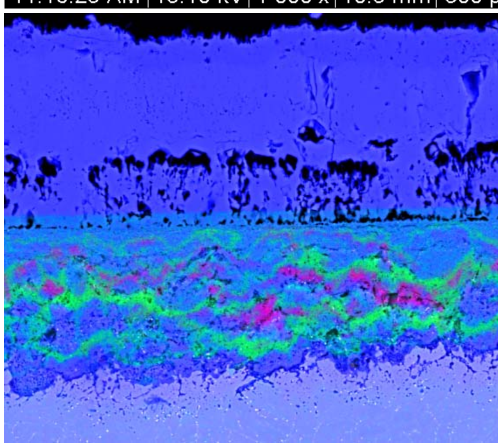
With Ash



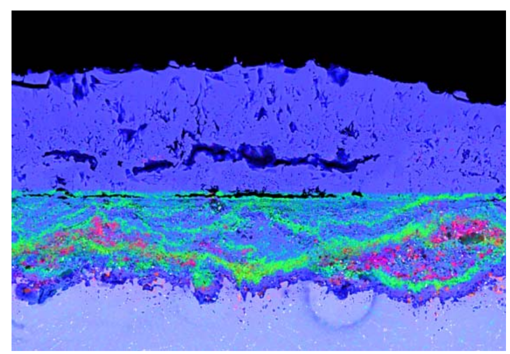
Fe = Blue Cr = Green S = Red







T92
No Ash
Oxy-fired
675 °C
260 hr



T92
No Ash
Air-fired
675 °C
260 hr

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60 µm

Fe = Blue Cr = Green S = Red

Basicity: Salt-Oxide-Metal vs Gas Phase

Basic dissolution: $2NiO + Na_2O + \frac{1}{2}O_2(g) = 2NaNiO_2$

Acidic dissolution: $NiO + Na_2SO_4 = NiSO_4 + Na_2O$

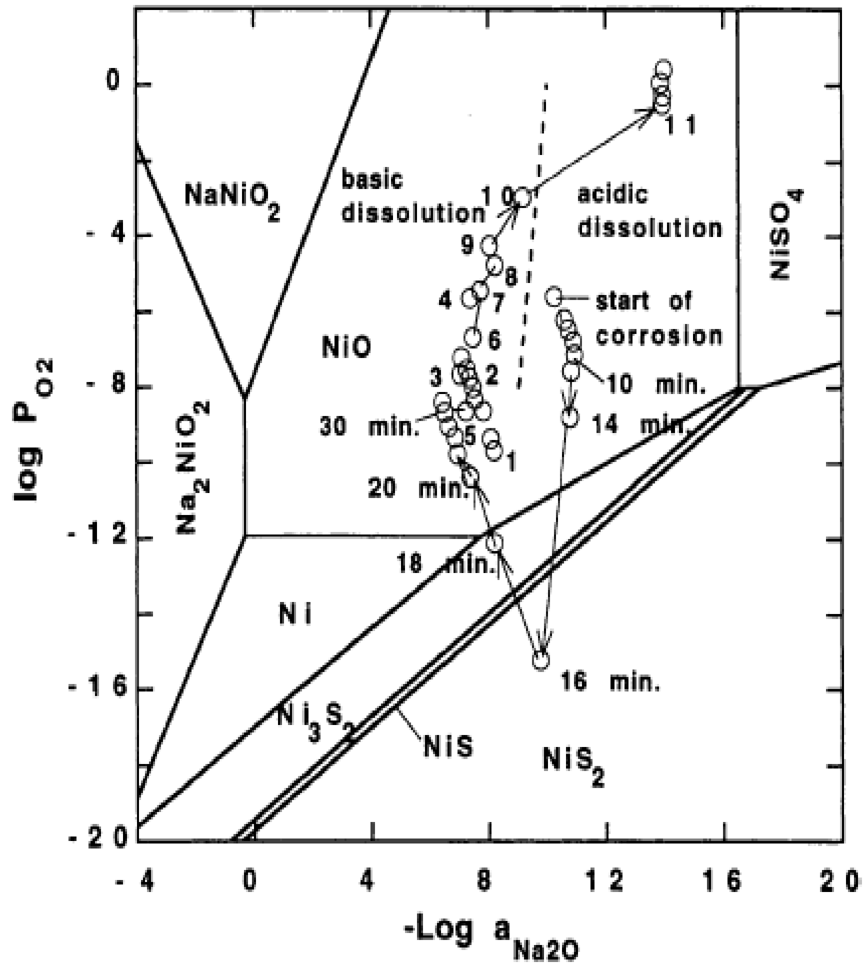
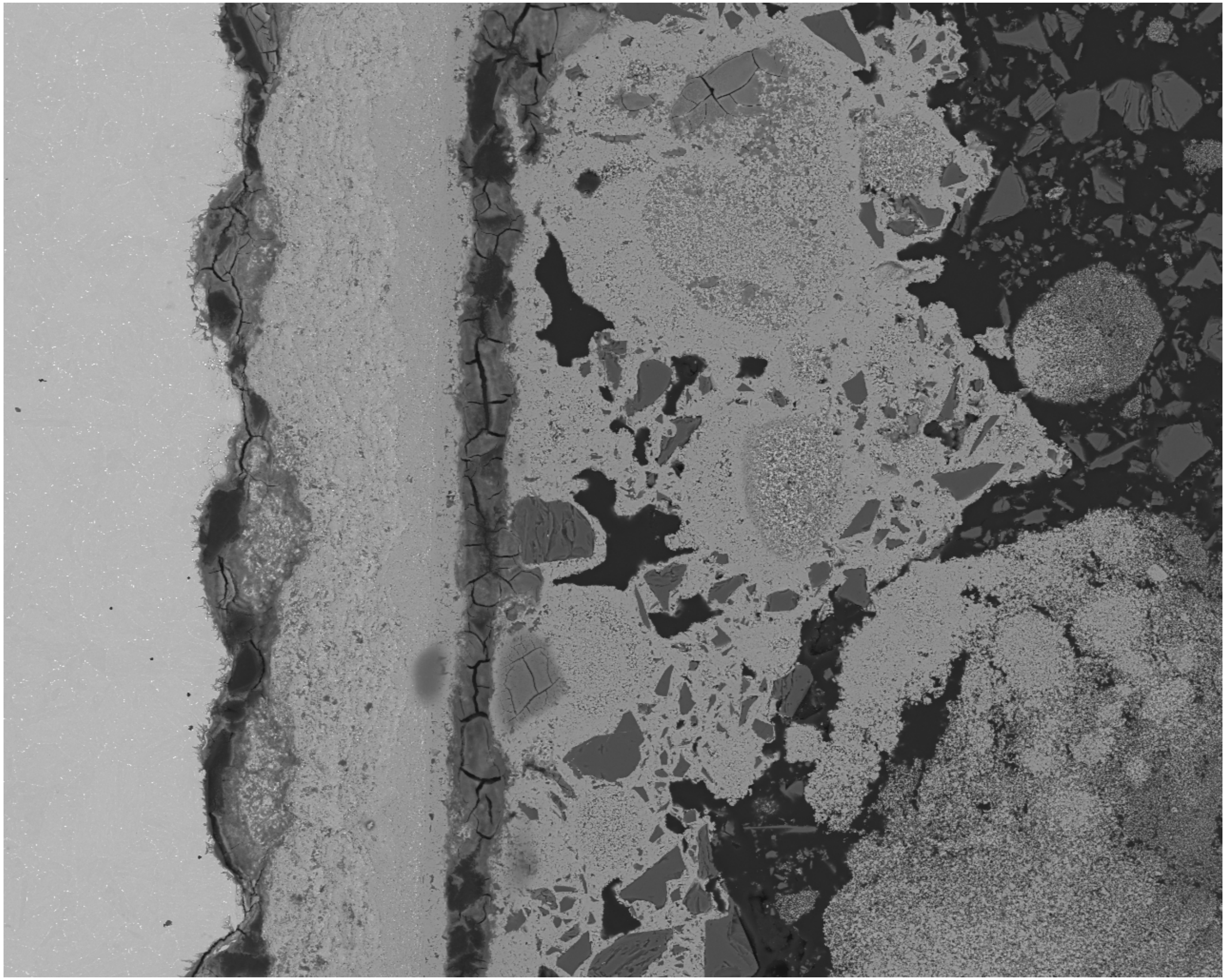


Fig. 4. Trace of basicity and oxygen activity measured on a preoxidized 99% Ni coupon with a Na_2SO_4 film at 1173 K in O_2–0.1% SO_2 gas. The central dashed line in the NiO stable field indicates the minimum in NiO solubility. Numbers in the figure designate the reaction time in hours, except indicated [26].

Rapp, 2002

RATORY

T92 Ash A (2.5% Na_2SO_4 2.5% K_2SO_4) Air-Fired

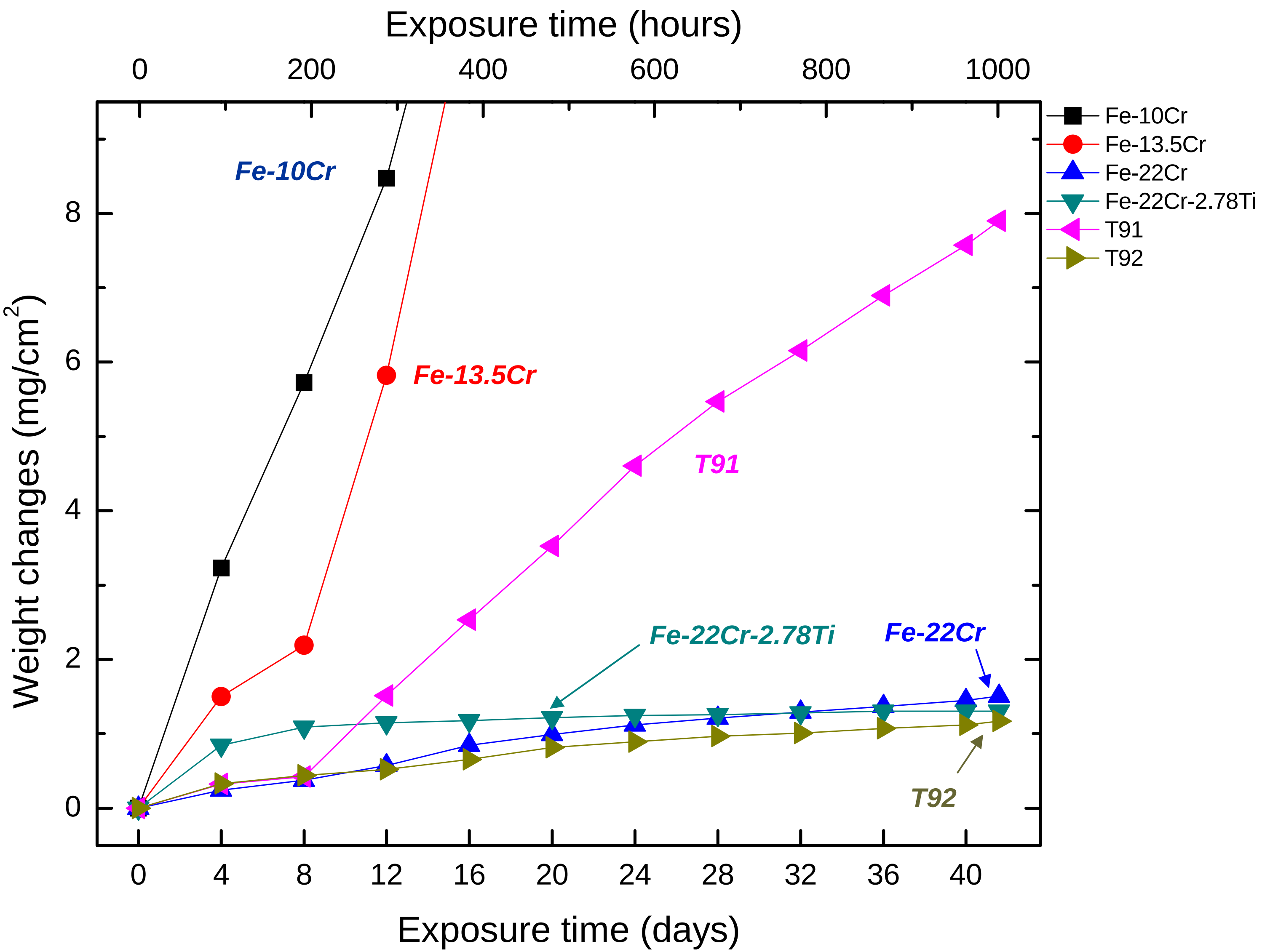


Alloy Scale Ash (high metal content)

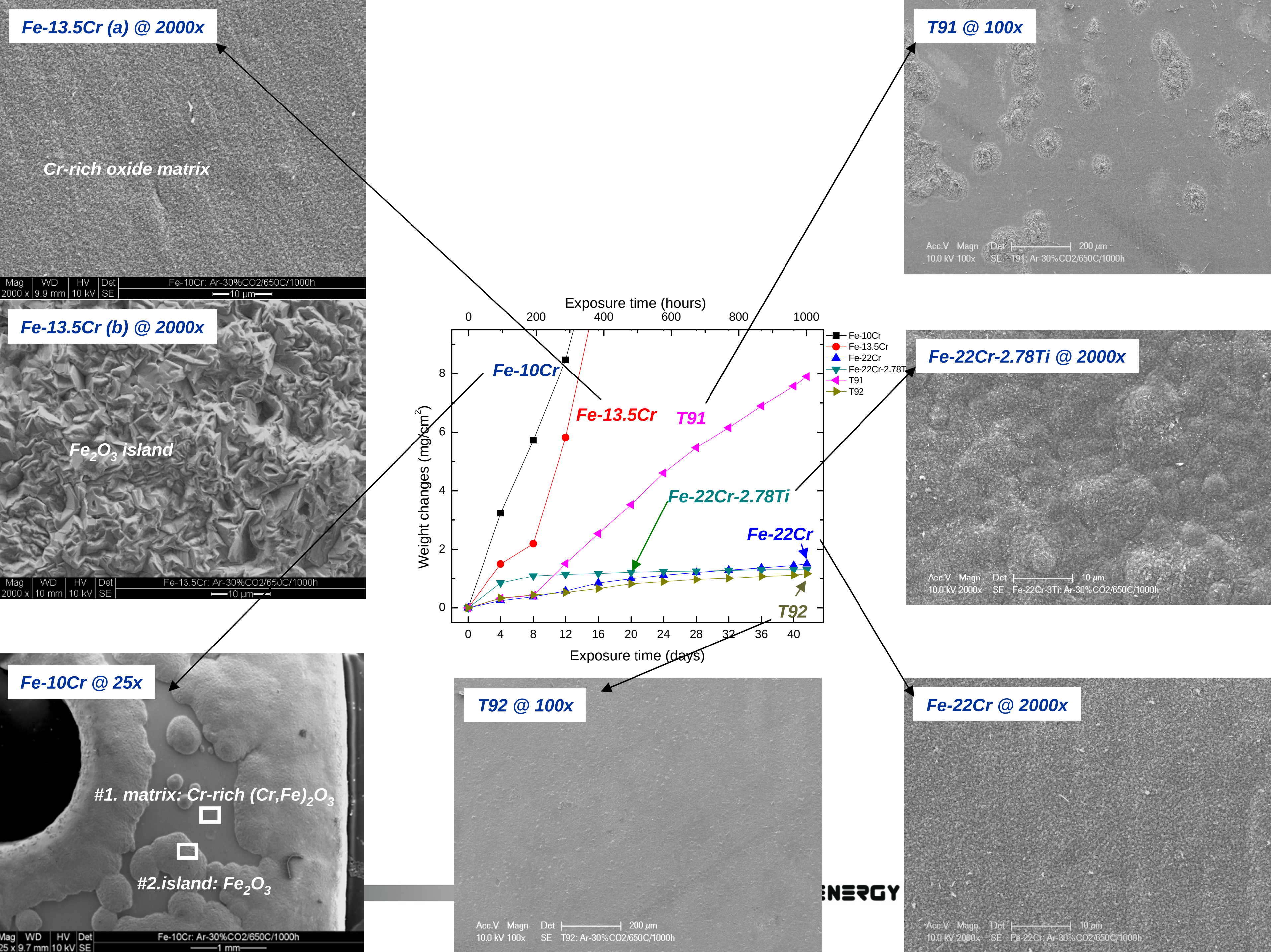
Ar-30% CO_2 Gas Mixtures

- **AIES Project at University of Pittsburgh**
  - Professor Gerald Meier
  - Post Docs Nan Mu and Keeyoung Jung
- **Some results on the effect of CO_2 gas**
- **See their poster in the after lunch poster session for more information**

Isothermal Oxidation at 650 °C in Ar-30%CO_2



Meier, University of Pittsburgh, 2009

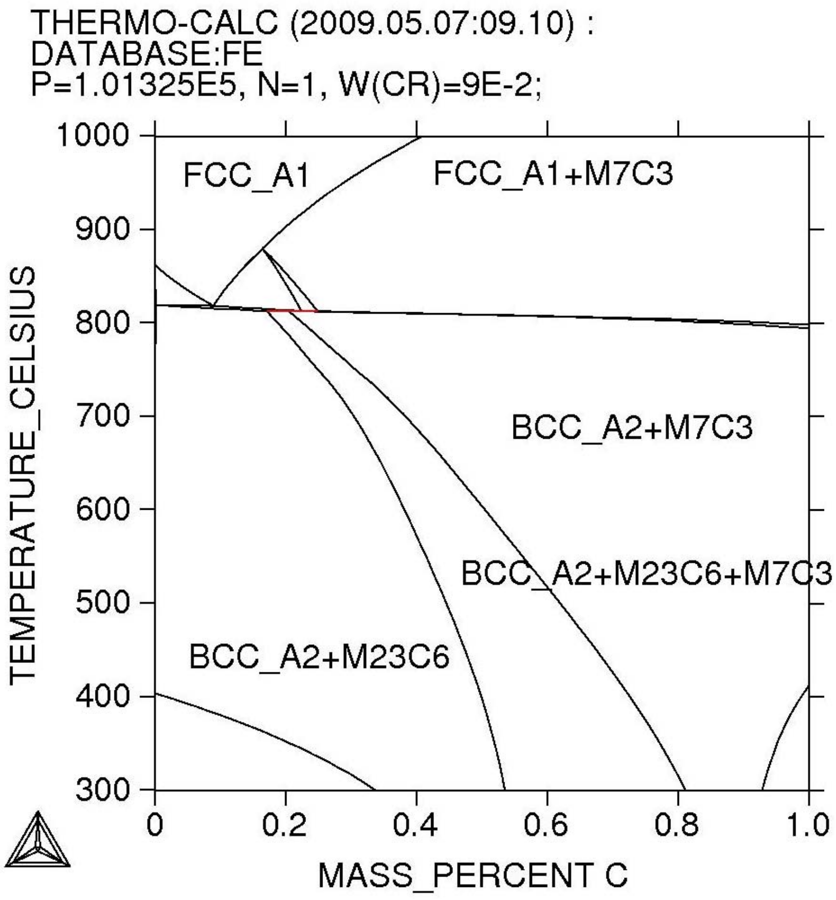


Fe-13.5Cr (a) @ 2000x
Cr-rich oxide matrix
Mag 2000 x | WD 9.9 mm | HV 10 kV | Det SE | Fe-10Cr: Ar-30%CO2/650C/1000h | 10 µm
Fe-13.5Cr (b) @ 2000x
Fe$_2$O$_3$ island
Mag 2000 x | WD 10 mm | HV 10 kV | Det SE | Fe-13.5Cr: Ar-30%CO2/650C/1000h | 10 µm
Fe-10Cr @ 25x
#1. matrix: Cr-rich (Cr,Fe)$_2$O$_3$
#2.island: Fe$_2$O$_3$
Mag 25 x | WD 9.7 mm | HV 10 kV | Det SE | Fe-10Cr: Ar-30%CO2/650C/1000h | 1 mm
T91 @ 100x
Acc.V Magn Det 200 µm
10.0 kV 100x SE T91: Ar-30%CO2/650C/1000h
Fe-22Cr-2.78Ti @ 2000x
Acc.V Magn Det 10 µm
10.0 kV 2000x SE Fe-22Cr-3Ti: Ar-30%CO2/650C/1000h
T92 @ 100x
Acc.V Magn Det 200 µm
10.0 kV 100x SE T92: Ar-30%CO2/650C/1000h
Fe-22Cr @ 2000x
Acc.V Magn Det 10 µm
10.0 kV 2000x SE Fe-22Cr: Ar-30%CO2/650C/1000h
Exposure time (hours)
0 200 400 600 800 1000
Weight changes (mg/cm^2)
0 2 4 6 8
Exposure time (days)
0 4 8 12 16 20 24 28 32 36 40
Fe-10Cr
Fe-13.5Cr
Fe-22Cr
Fe-22Cr-2.78Ti
T91
T92

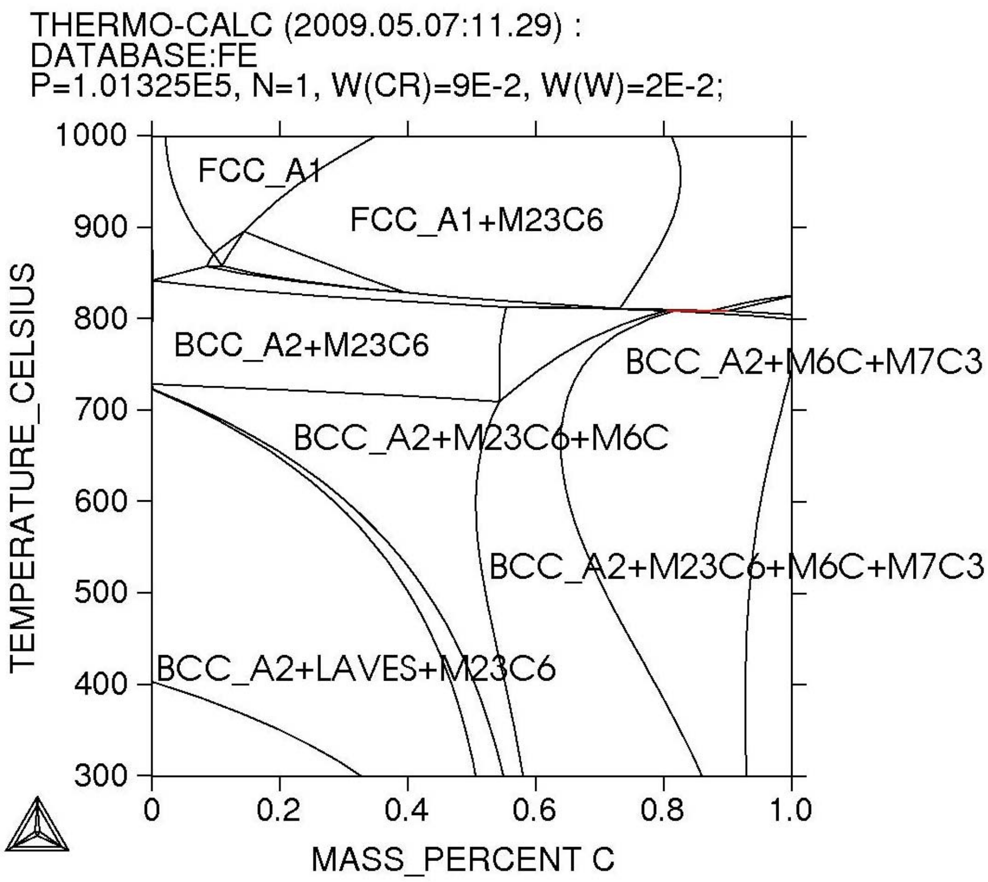
Speculation on Elevated CO_2

- For Fe-Cr alloys
- $4M + 3CO_2 = 2M_2O_3 + 3\underline{C}$
- Dissolved C forms internal carbides (primarily Cr-C)
- Metal matrix is reduced in Cr
- Oxidation behavior more like a lower Cr alloy
- Additions such as W and Ti, that form very stable carbides, might act as a sink for C and maintain a higher Cr level in the metal matrix

Fe-9Cr and Fe-9Cr-2W Comparison

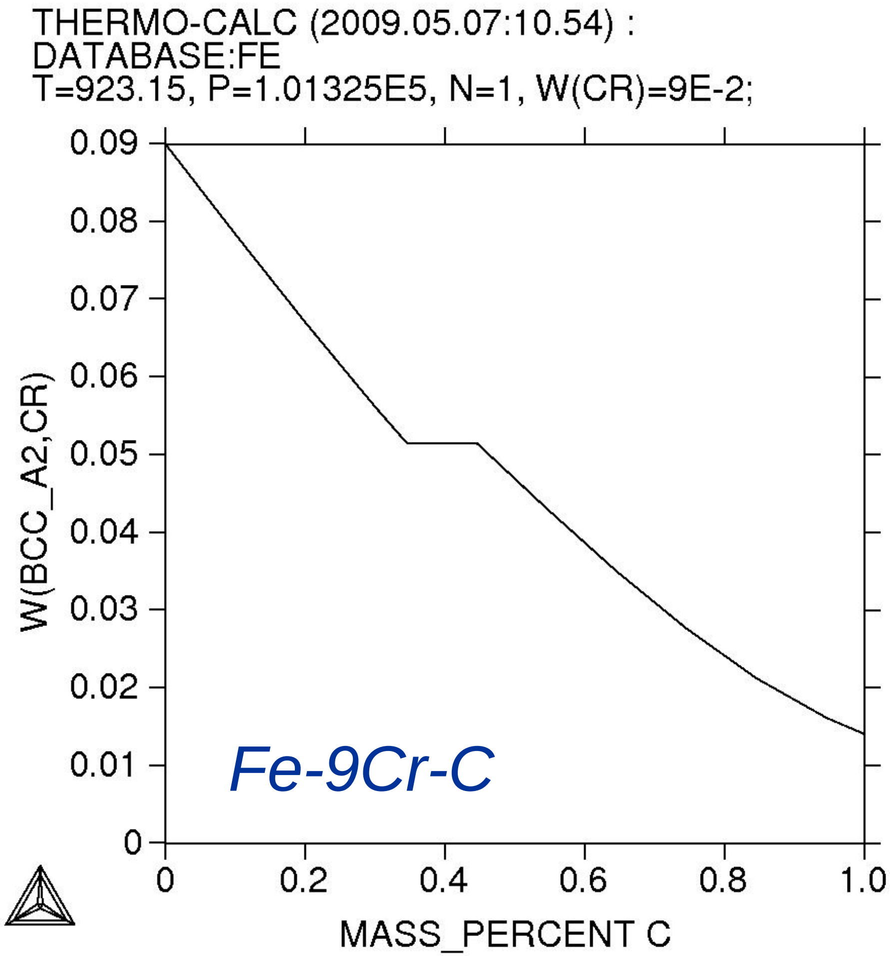


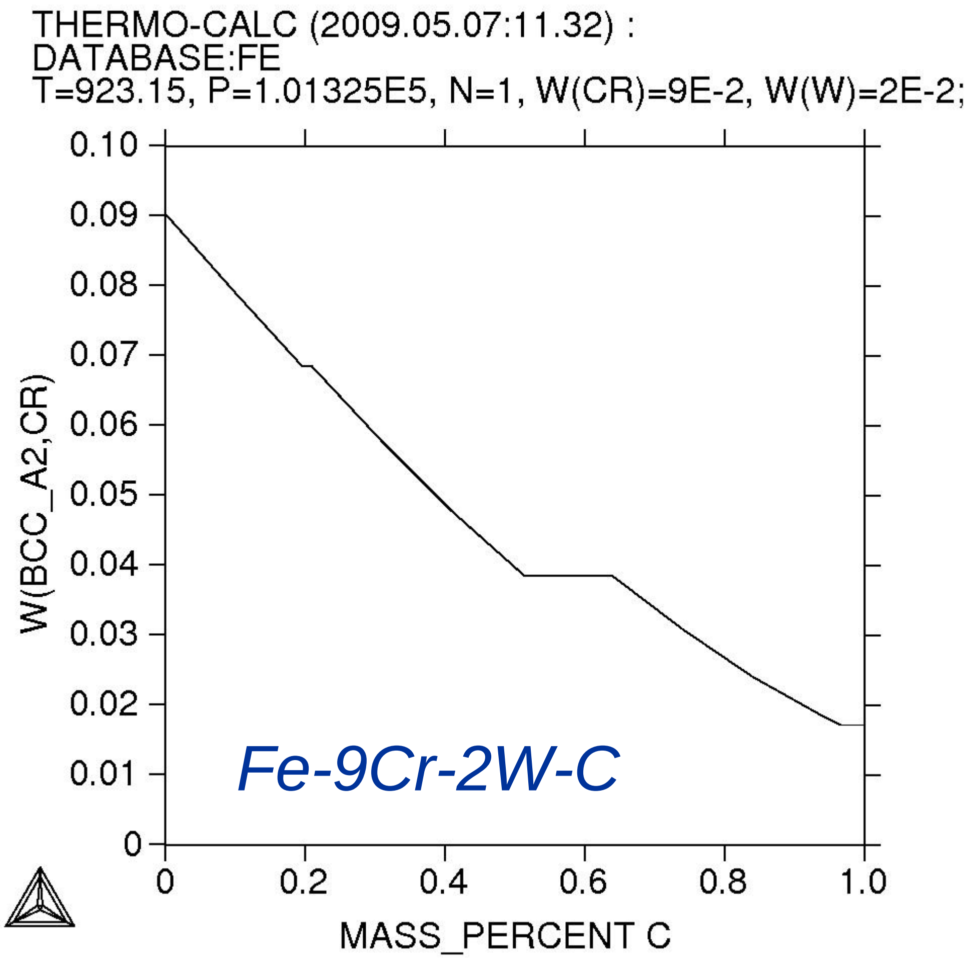
Fe-9Cr-C



Fe-9Cr-2W-C

Fe-9Cr and Fe-9Cr-2W Comparison

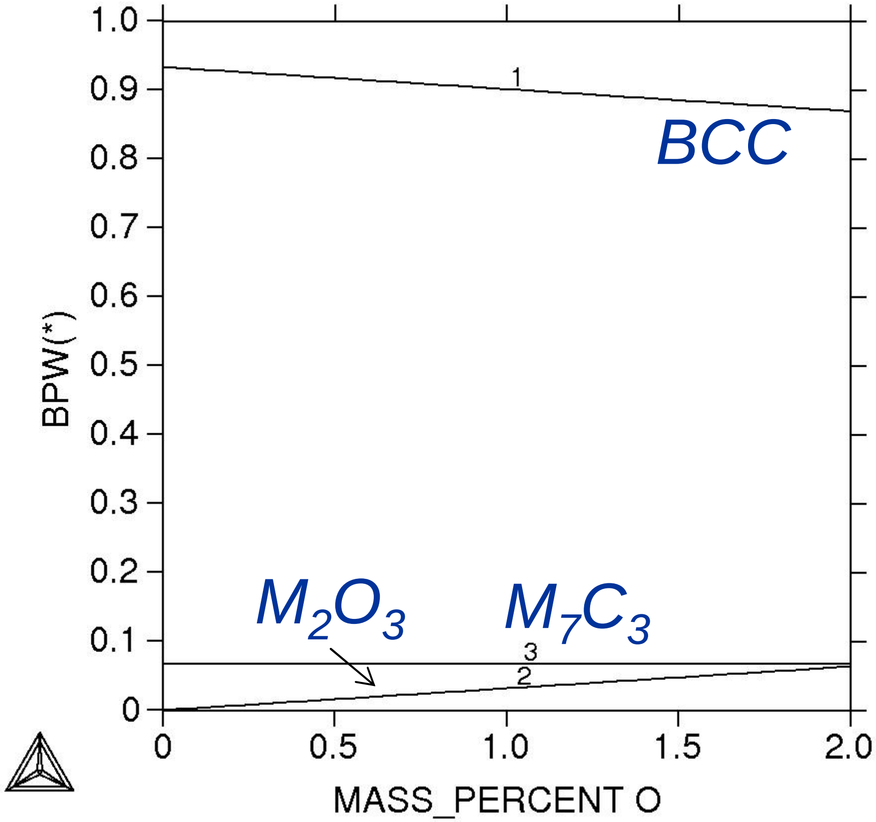




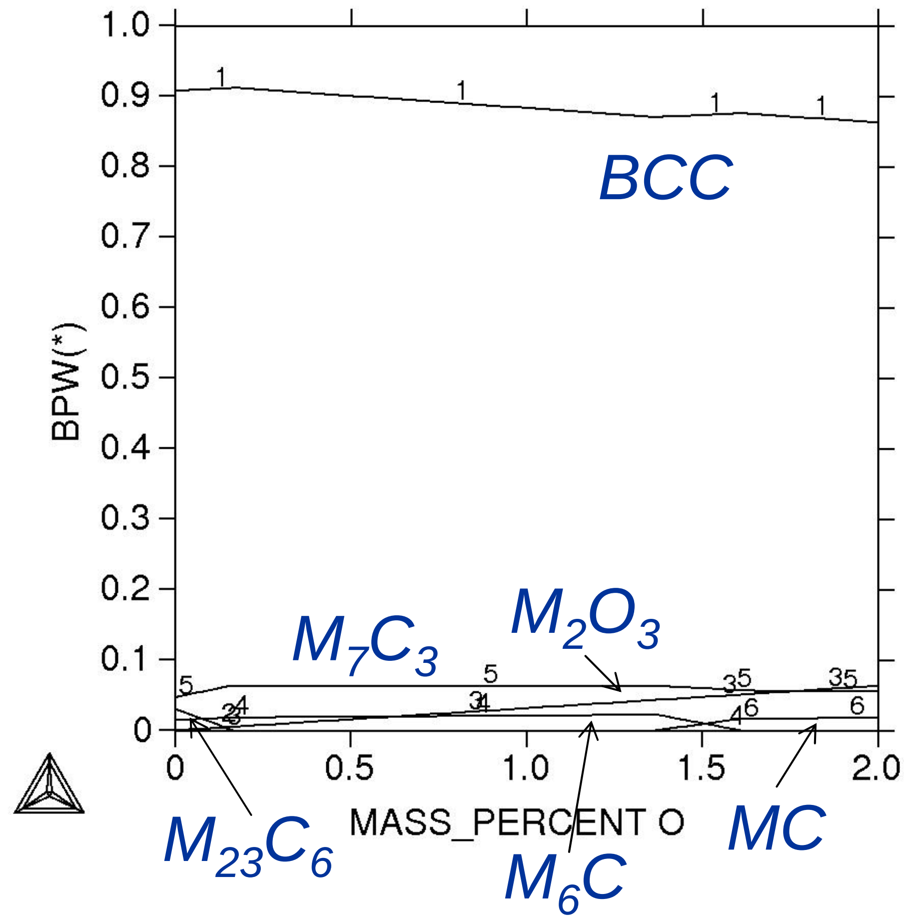
Amount of Cr in the BCC phase (metal matrix)

Fe-9Cr and Fe-9Cr-2W Comparison

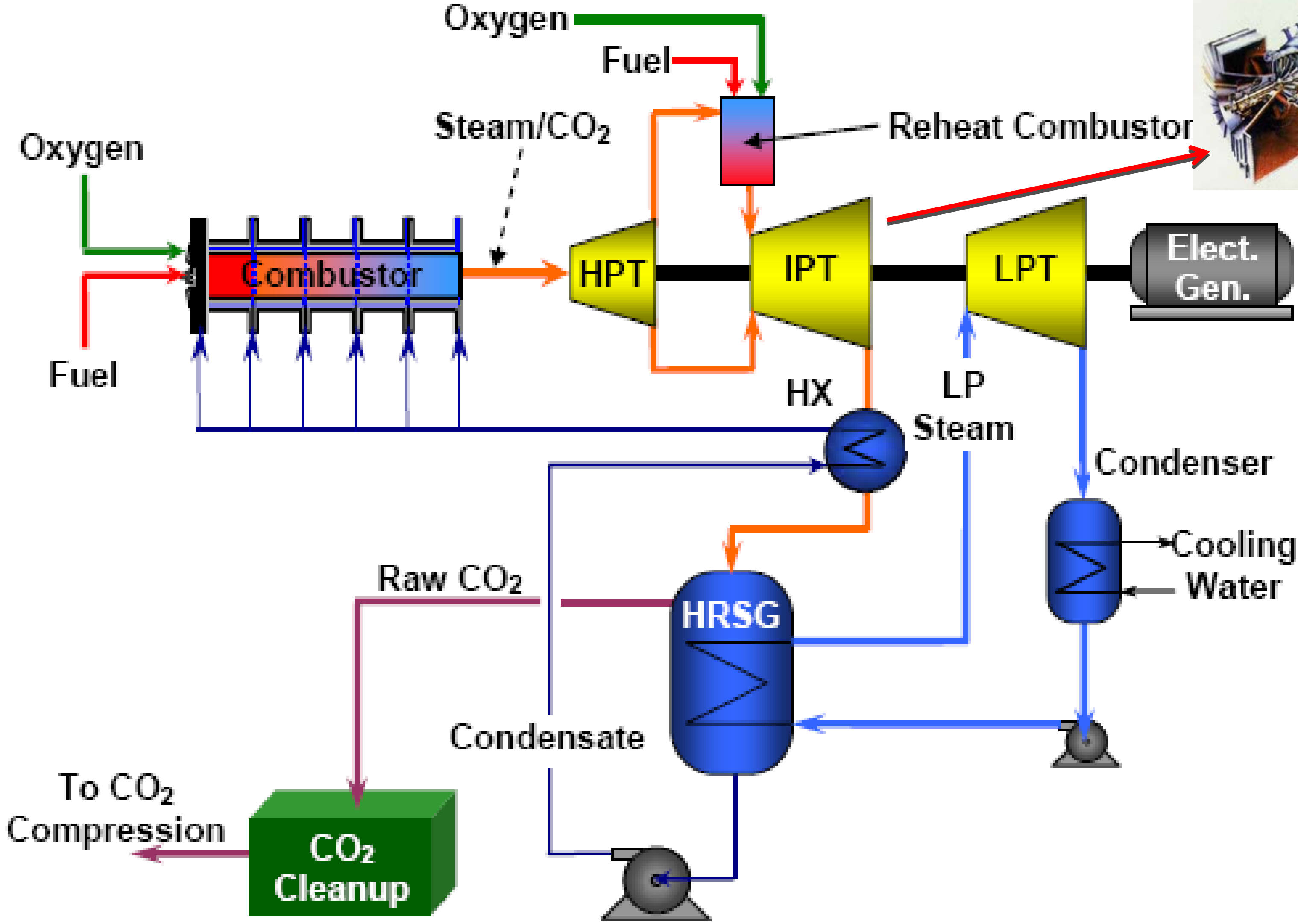
Fe-9Cr-0.6C-O



Fe-9Cr-2W-0.6C-O



Materials Performance in Oxyfuel Turbine Environments



Anderson et al., 2008

Test Matrix

Test matrix for 1000 hour exposures in H_2O-10% CO_2-0.2% O_2

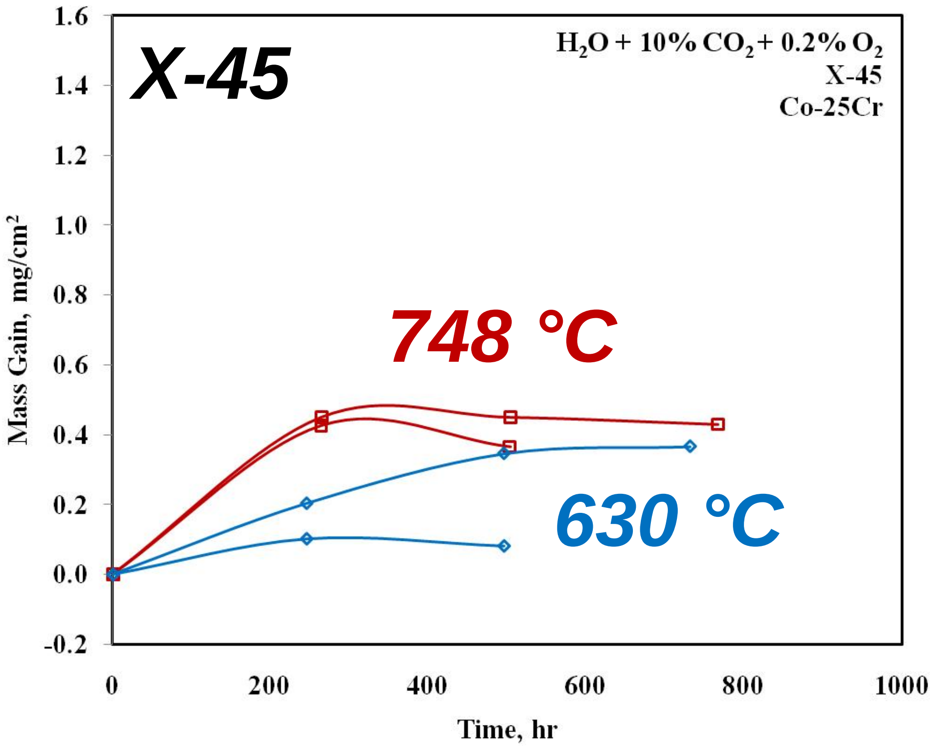
T °C	Type	ECY-768		X-45		IN-738			IN-939		U-520		Total
		Un	TB	Un	BC	Un	BC	TB	Un	TB	Un	BC	
630	LCF										8		8
	Ox	2		2		2			2	1	2	1	12
693	LCF									8			8
	Ox	2	1	2	1	2	1	1	2	1	2	1	16
748	LCF		8		8		7						23
	Ox	2	1	2	1	2	1	1	2	1	2	1	16
821	LCF							8					8
	Ox	2	1	2	1	2	1	1	2		2		14
Spare	Ox	2	1	2	1	2	1	1	2	1	2	1	16
Total	LCF		8		8		7	8		8	8		47
	Ox	10	4	10	4	10	4	4	10	4	10	4	74

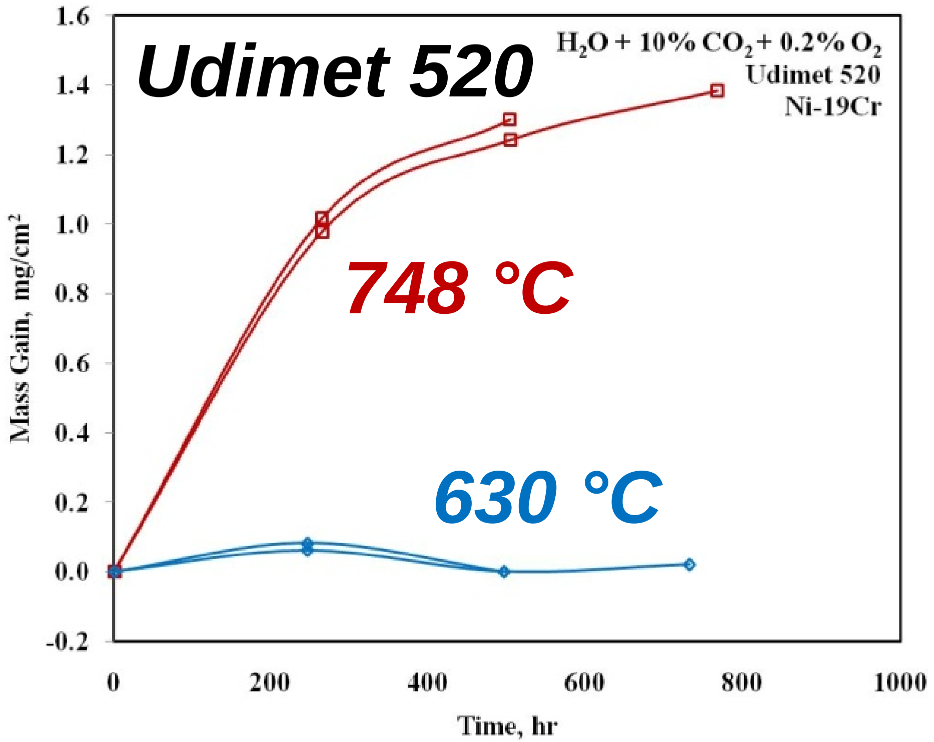
Alloys

Nominal Composition

Alloy	Ni	Co	Cr	Al	Ti	Mn	Ta+Nb	W	Fe	Mo	C
X-45	10.1	Bal	24.8			0.6		7.8	1.0		0.25
ECY-768	9.7	Bal	23.8	0.1	0.2		3.5	7.0	0.2		0.59
Inconel 738	Bal	8.5	15.8	3.5	3.3		1.7	2.5		1.7	0.12
Inconel 939	Bal	18.9	22.5	1.9	3.8		2.4	2.0			0.14
Udimet 520	Bal	12.5	19.0	2.0	3.0			1.2		6.3	0.06

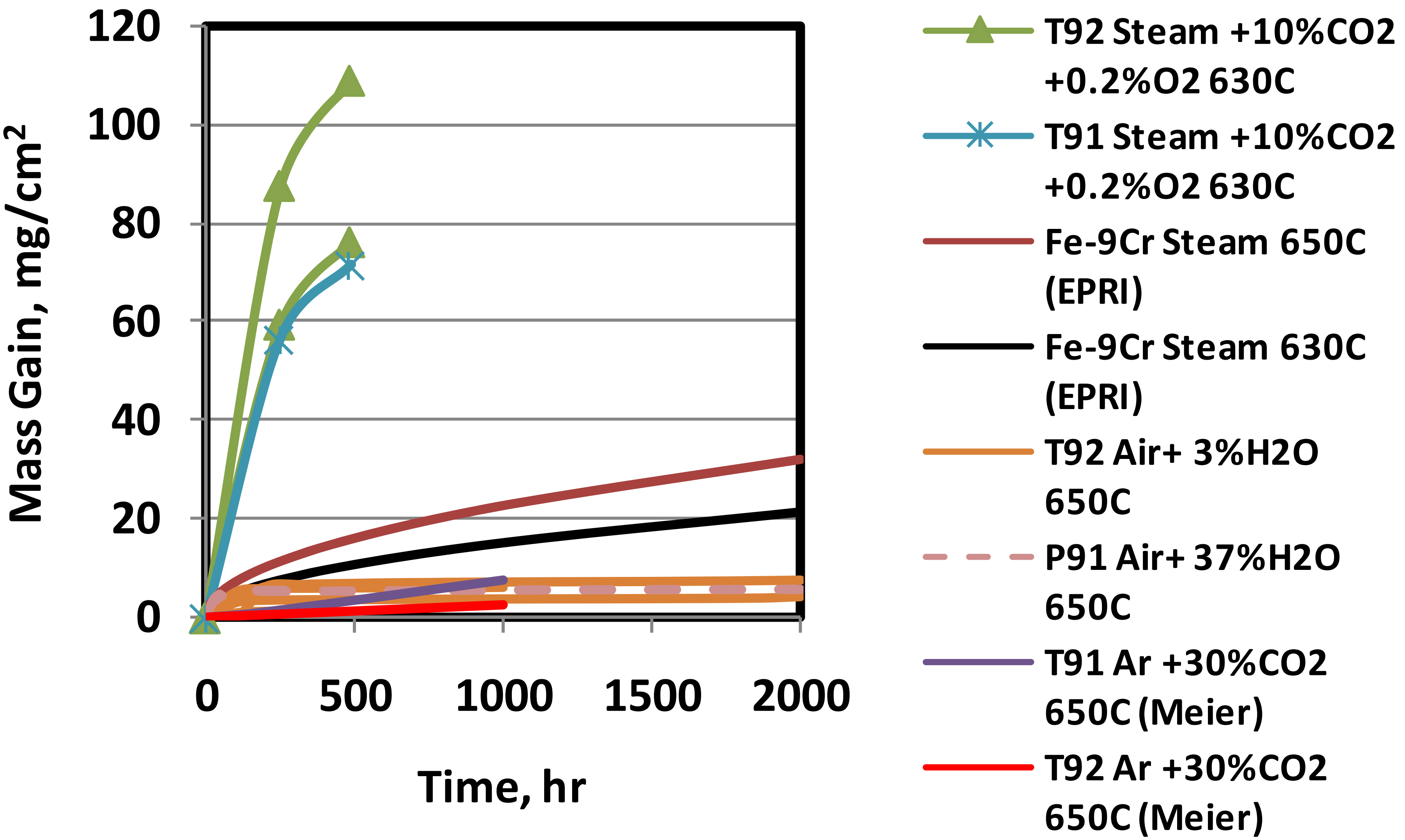
Oxidation Coupons





Alloy	Ni	Co	Cr	Al	Ti	Mn	Ta+Nb	W	Fe	Mo	C
X-45	10.1	Bal	24.8			0.6		7.8	1.0		0.25
ECY-768	9.7	Bal	23.8	0.1	0.2		3.5	7.0	0.2		0.59
Inconel 738	Bal	8.5	15.8	3.5	3.3		1.7	2.5		1.7	0.12
Inconel 939	Bal	18.9	22.5	1.9	3.8		2.4	2.0			0.14
Udimet 520	Bal	12.5	19.0	2.0	3.0			1.2		6.3	0.06

T91/T92 Environment Comparison



EPRI Data from Dooley (Report #1013666, 2007)

Summary

- **Three Environments with Elevated CO_2**
- **Oxyfuel Combustion (air- vs oxy-fired atmospheres)**
  - Stratified Scales wrt Cr, Fe, and S
  - Speculated on cycles of acid and basic fluxing
- **Fundamental Studies at Univ of Pittsburgh (Ar-CO_2)**
  - Wide variation in oxidation wrt Cr content and model vs commercial alloys
  - Speculated on the role of W and other carbide formers
- **Oxyfuel Turbines (Steam + 10% CO_2 + 0.2% O_2)**
  - Exposure tests underway
  - Cobalt-base alloys showing less mass gain at 748 °C than nickel-base alloys