Metallic Materials Development for SOFC Application

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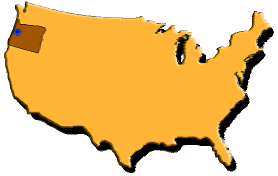
SECA-CTP Program Review
May 11-13, 2004, Boston, MA.

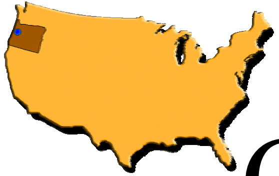
Outline

- Nickel-Base Alloys with Low Coefficient of Thermal Expansion (CTE)
- Corrosion Research Related to SOFC
  - ➢Multiple specimen corrosion testing in dual atmospheres environments
  - ➢Dual environment corrosion mechanisms
  - ➢Chromium vaporization
- Balance of Plant Issues and Interactions with Vertical Teams



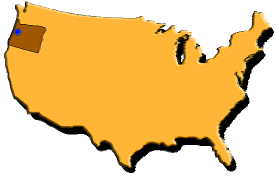
Research Opportunities

- Reactive Element Additions to Ferritic Steels
  - ➢Low solubility additions: Ce, La, Y
  - ➢Higher solubility additons: Ti, Zr,etc
- Nickel-Base Alloys with Low CTE
- Balance of Plant Materials Issues

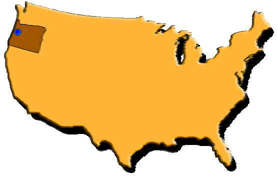


Composition of Ferritic Steels with SOFC Applications

Alloy	**Fe**	**Cr**	**Mn**	**Si**	**Ti**	**Al**	**La+Ce**
AL453	Bal	22.0	0.3	0.3	0.02	0.6	0.1
Crofer 22APU	Bal	22.0	0.5	--	0.08	--	0.06 La
ZMG232	Bal	22.0	minor: Mn, Ni, Zr, La; residual: Al, Si				

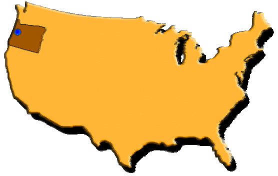


Nickel Base Alloys with Low CTE



Alloy Design Concepts

- **Oxidation Resistance and Low CTE**
- *Oxidation Resistance:* Chromia former
  - **Cr-Mn** Spinel is conductive and minimizes Chrome evaporation
- *Lower CTE*: Additions to Ni
  - **Cr**, Fe, Co, Ta, Nb: raise CTE
  - **Mo, W**, Ti, Al: lower CTE
- ***CTE vs. Oxidation Resistance: a balancing act***
  - Cr for oxidation vs. Mo and W for low CTE



Alloy Design Concepts

- Formulation for CTE

$$\mathbf{CTE} = 13.8732 + 7.2764\text{x}10^{-2}[\mathbf{Cr}] - 7.9632\text{x}10^{-2}\,[\mathbf{W}]$$

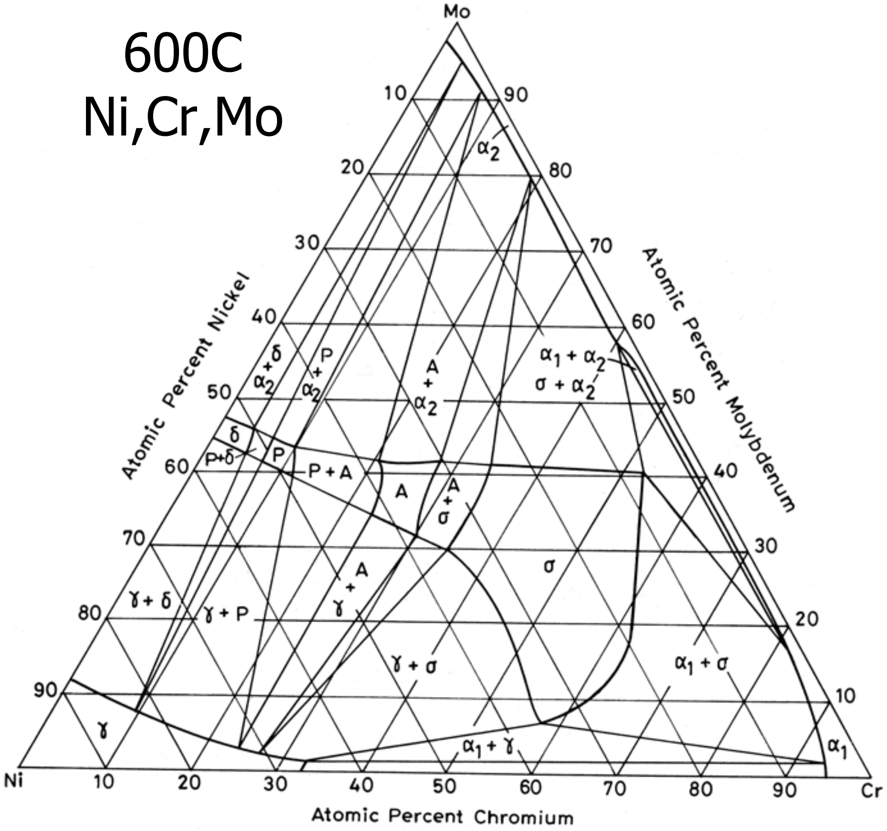
$$- 8.2385\text{x}10^{-2}[\mathbf{Mo}] - 1.835\text{x}10^{-2}[\mathbf{Al}]$$

$$- 1.63381\text{x}10^{-1}\,[\mathbf{Ti}]$$

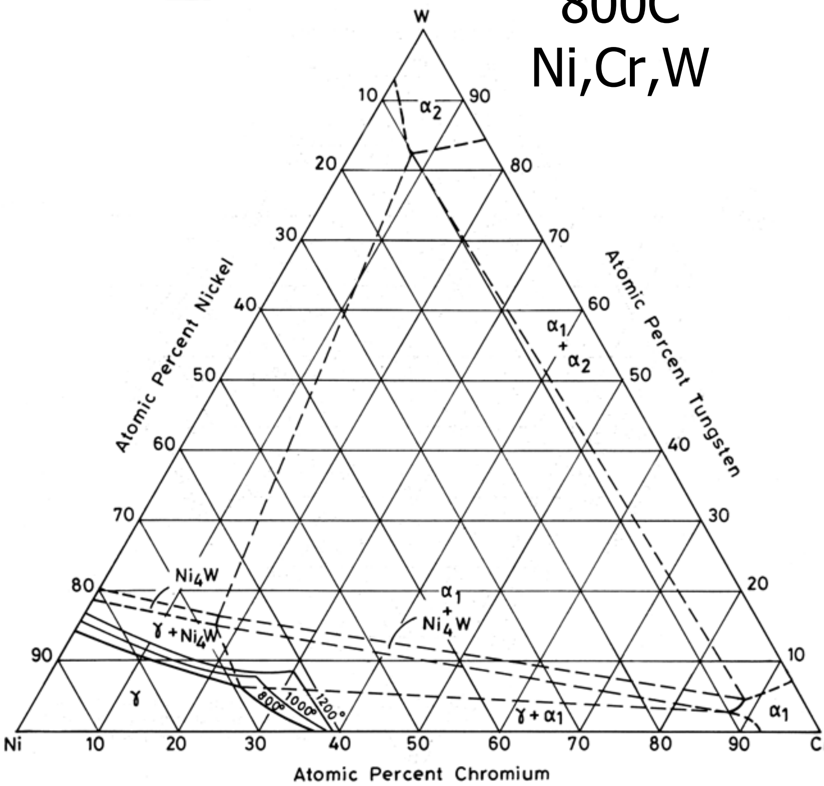
R. Yamamoto et. al., in Materials for Adavanced Power Engineering – 2002, Proc. 7th Leige Conf. Sept 30-Oct 3, 2003, Energy and Technology Vol. 21.

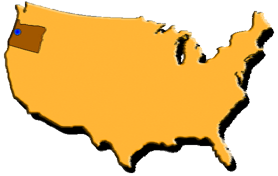
Alloy Design Concepts

600C
Ni,Cr,Mo



800C
Ni,Cr,W

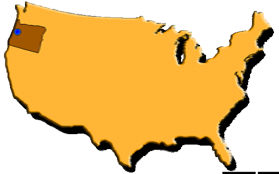




J-Series Ni-Cr-Mo Alloys

Nominal Composition (wt%)

Alloy	Ni	Cr	Mo	Ti	Al	Mn	Y
J1	Bal	12	18	1.1	0.9	0	0
J2	Bal	10	22.5	3	0.1	0.5	0.1
J3	Bal	12.5	22.5	3	0.1	0.5	0.1
J4	Bal	15	22.5	3	0.1	0.5	0.1
J5	Bal	12.5	22.5	1	0.1	0.5	0.1
J6	Bal	12.5	27.7	0	0	0.5	0.1
J7	Bal	22	36.1	0	0	0.5	0.1



JW-Series Ni-Cr-W-Mo Alloys

Nominal Composition (wt%)

Alloy	**Ni**	**Cr**	**W**	**Mo**	**Ti**	**Al**	**Mn**	**Y**
JW5	Bal	12.5	22.5	0	1	0.1	0.5	0
JW8	Bal	15.5	21	10	0	0	0.5	0
JW9	Bal	14	17	10	1.1	0.9	0.5	0

Melt Practice

5000g VIM ingot

500g VIM/VAR ingot

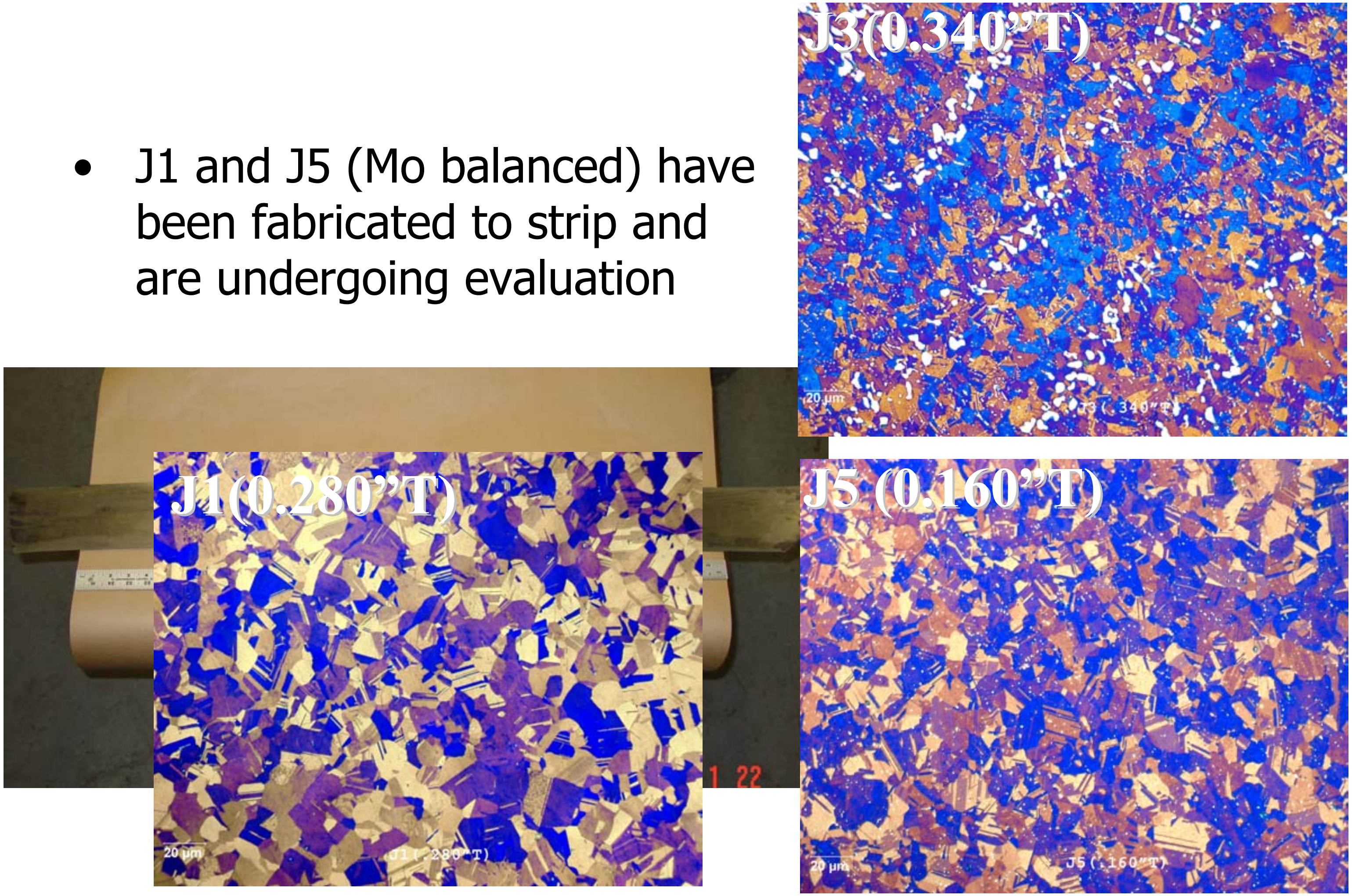
Hot Working

Forging

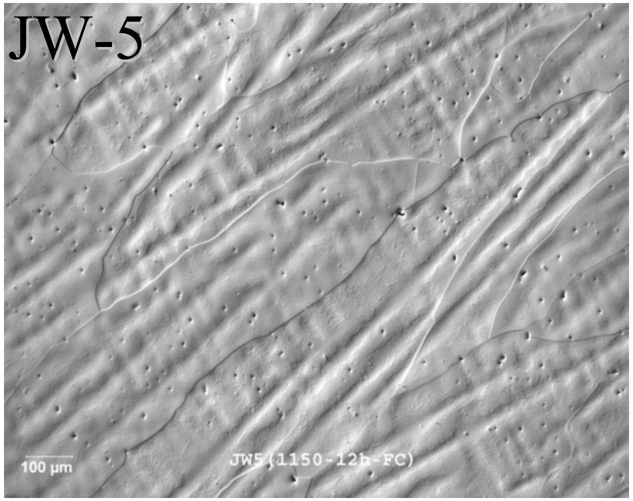
Hot Rolling

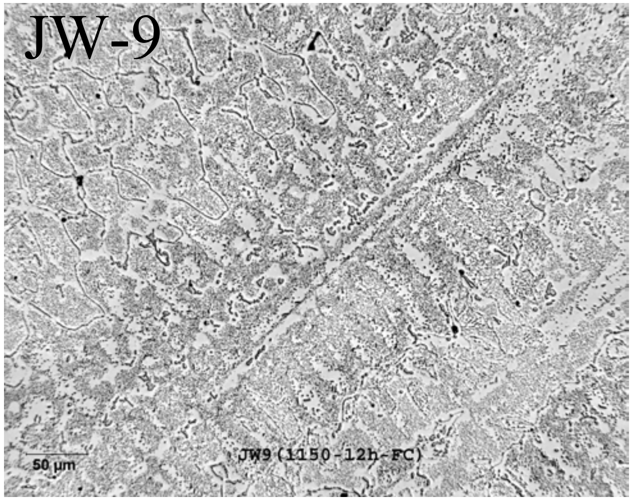
Strip Fabrication

- J1 and J5 (Mo balanced) have been fabricated to strip and are undergoing evaluation



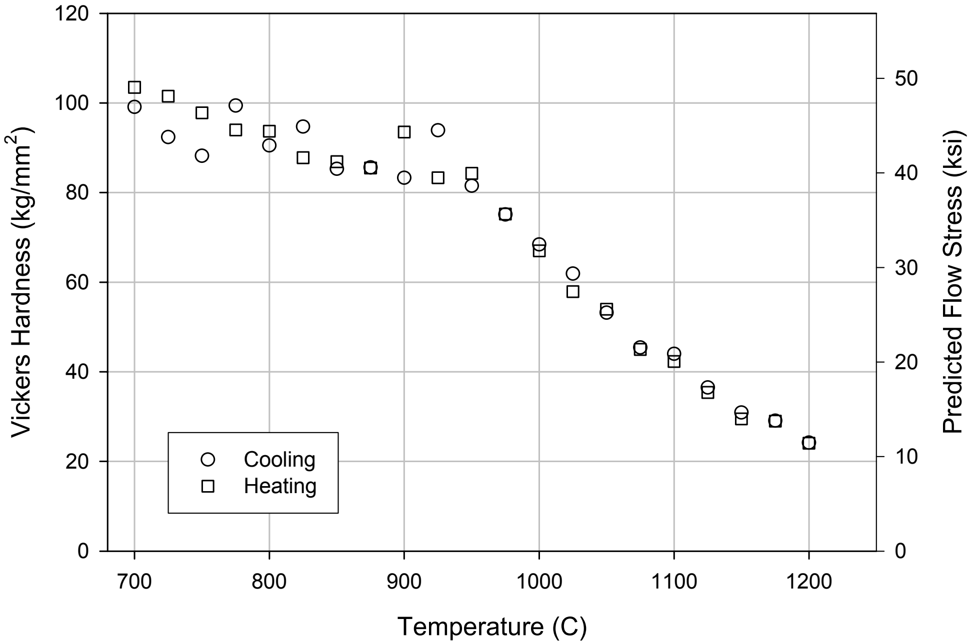
Strip Fabrication





- No JW alloys (W balanced) have been successfully rolled, although several are undergoing evaluation

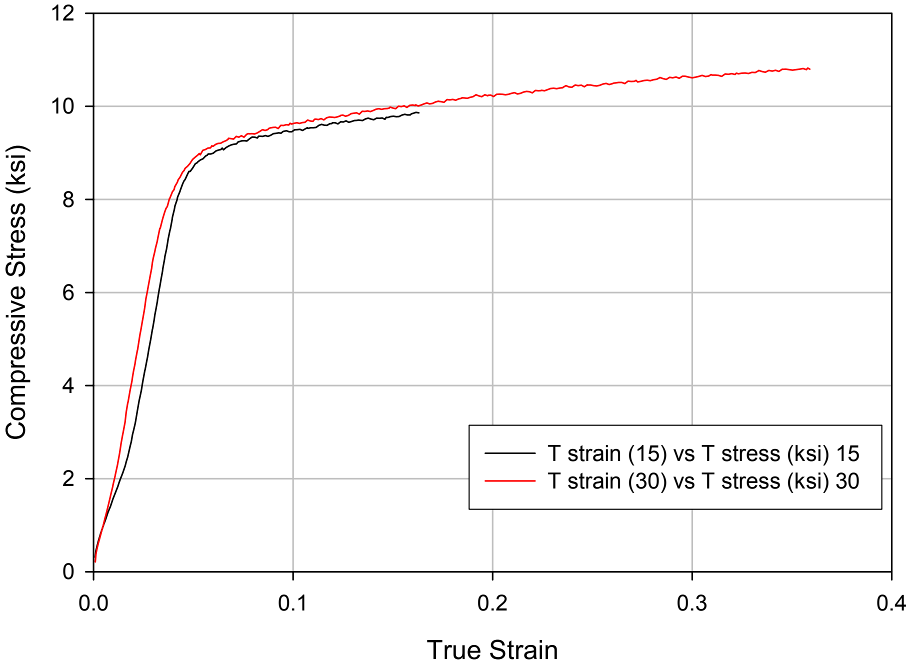
Hot Hardness

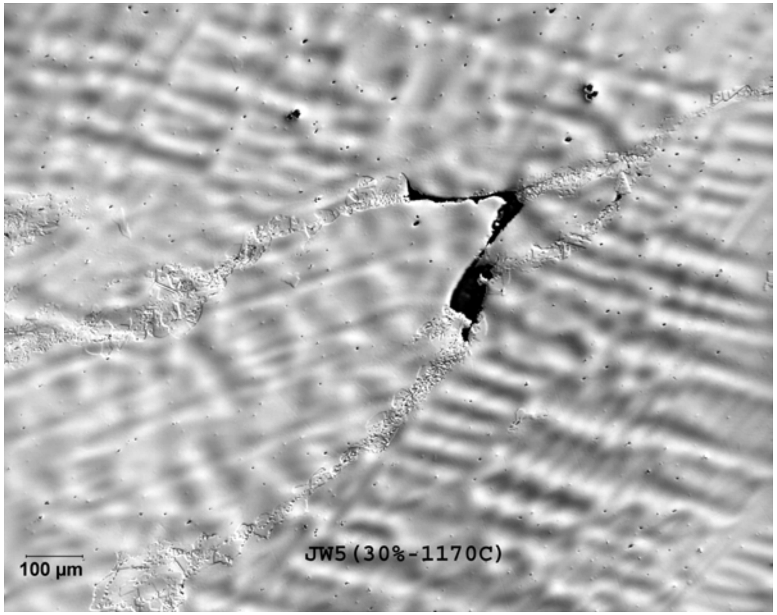


$$\sigma = \frac{H_v}{3} 1.422[ksi]$$

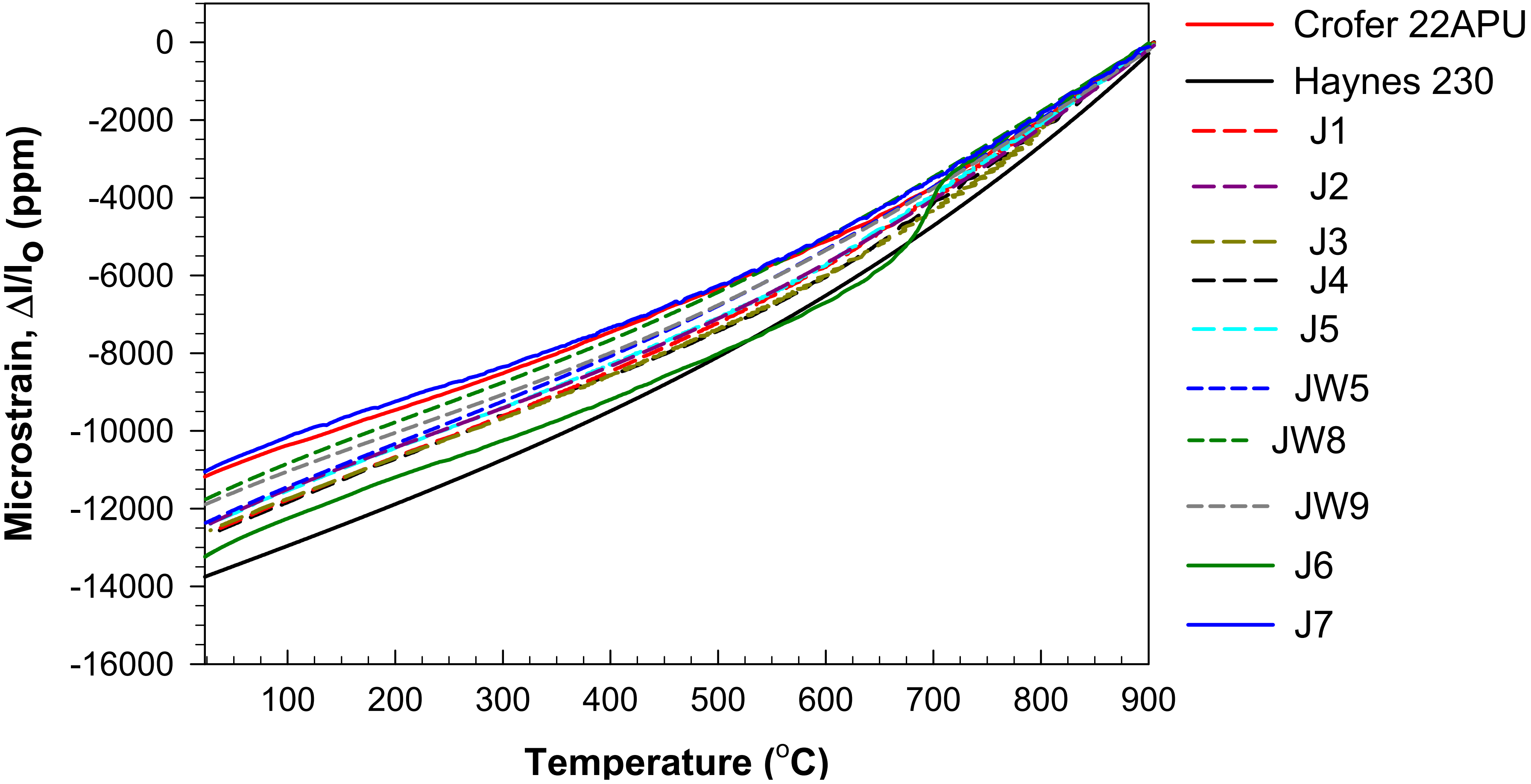
Hot Compression

JW5
1175C





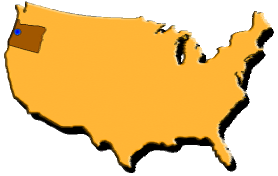
Dilatometry



Dilatometry peformed by Precision Measurements and Instrument Corporation, Corvallis, Or.

CTE-J series alloys

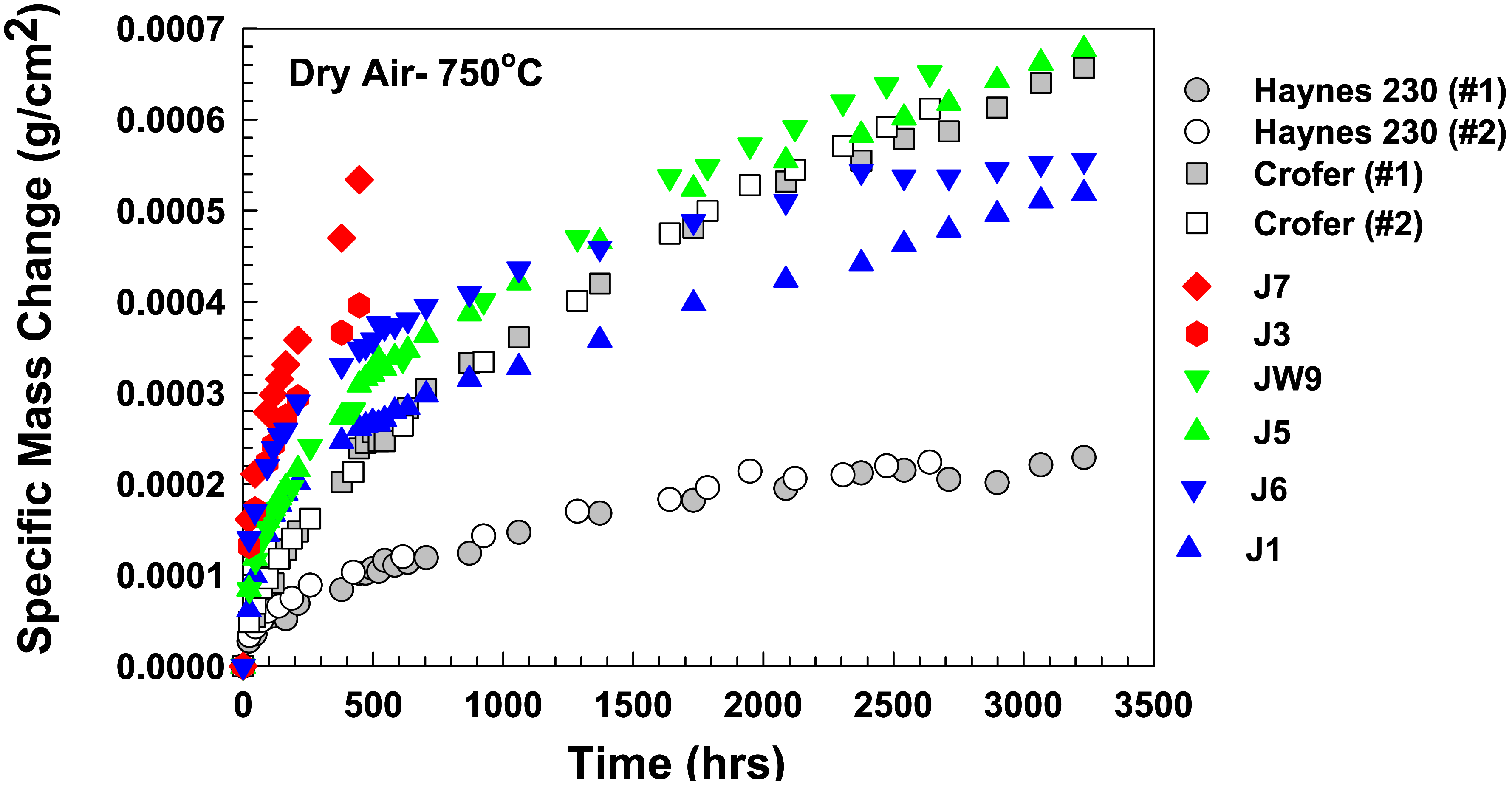
Alloy	**Predicted (23-700^{o}C)**	**Measured (23-700^{o}C)**	**Measured (23-800^{o}C)**	**Measured (23-900^{o}C)**
J1	13.06	12.9	13.6	14.4
J2	12.25	12.5	13.2	14.0
J3	12.44	12.3	13.4	14.3
J4	12.61	12.7	13.6	14.4
J5	12.71	12.6	13.4	14.0
J6	12.50	13.8	14.6	15.7
J7	**12.50**	**11.2**	**11.9**	**12.5**
Crofer	**----**	**11.0**	**11.9**	**12.6**
Haynes 230	**14.2**	**13.3**	**14.3**	**15.4**



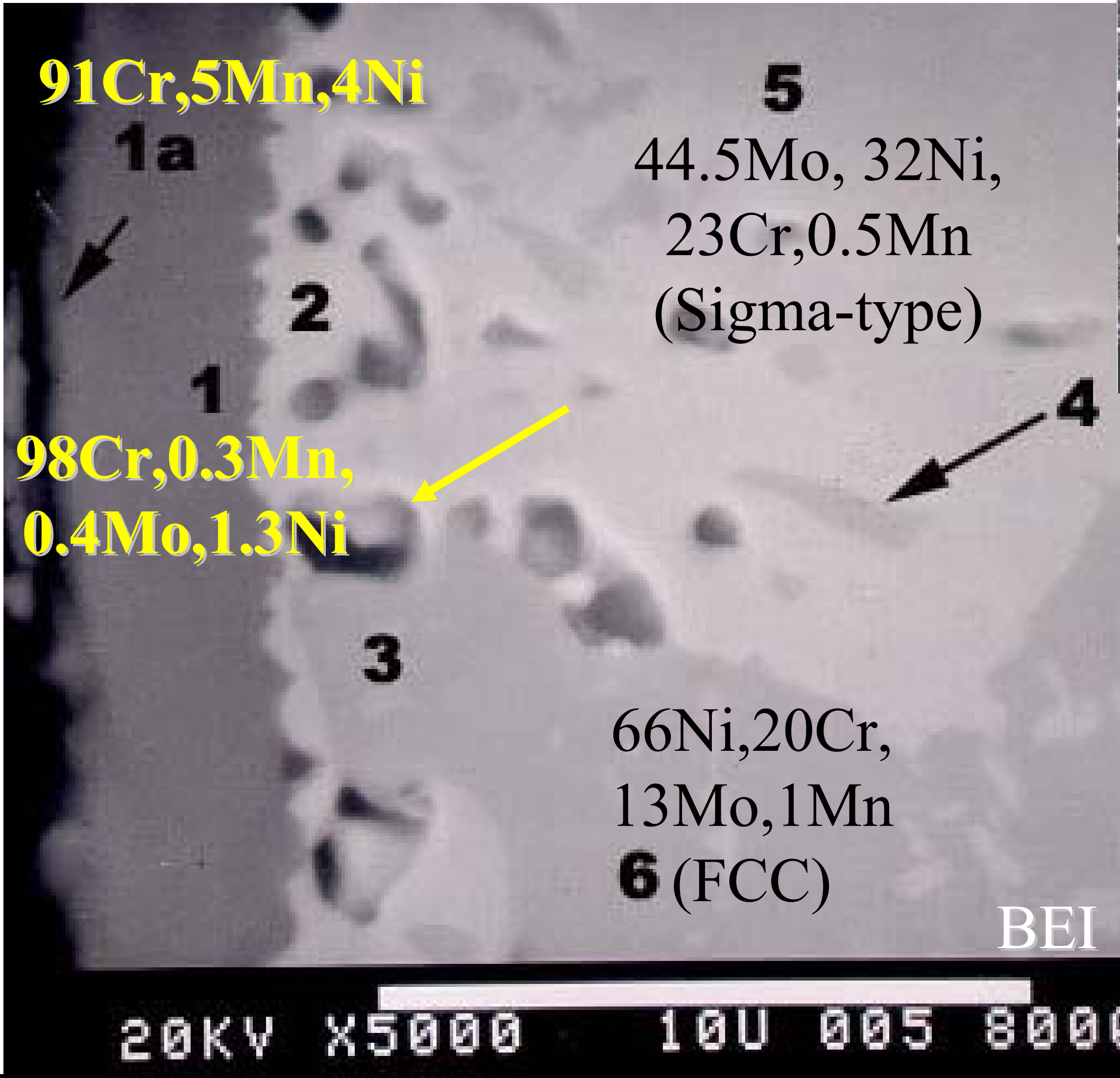
CTE-JW series alloys

Alloy	**Predicted (23-700^{o}C)**	**Measured (23-700^{o}C)**	**Measured (23-800^{o}C)**	**Measured (23-900^{o}C)**
JW5	12.8	12.8	13.4	13.9
JW8	12.5	12.3	12.8	13.4
JW9	**12.5**	**12.0**	**12.7**	**13.3**
Crofer	**----**	**11.0**	**11.9**	**12.6**
J7	**12.5**	**11.2**	**11.9**	**12.5**
Haynes 230	**14.2**	**13.3**	**14.3**	**15.4**

Oxidation behavior – 750°C



J7:800°C-300h

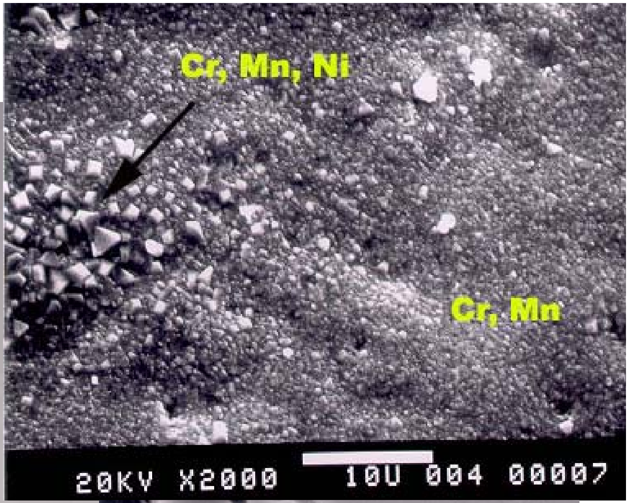


91Cr,5Mn,4Ni

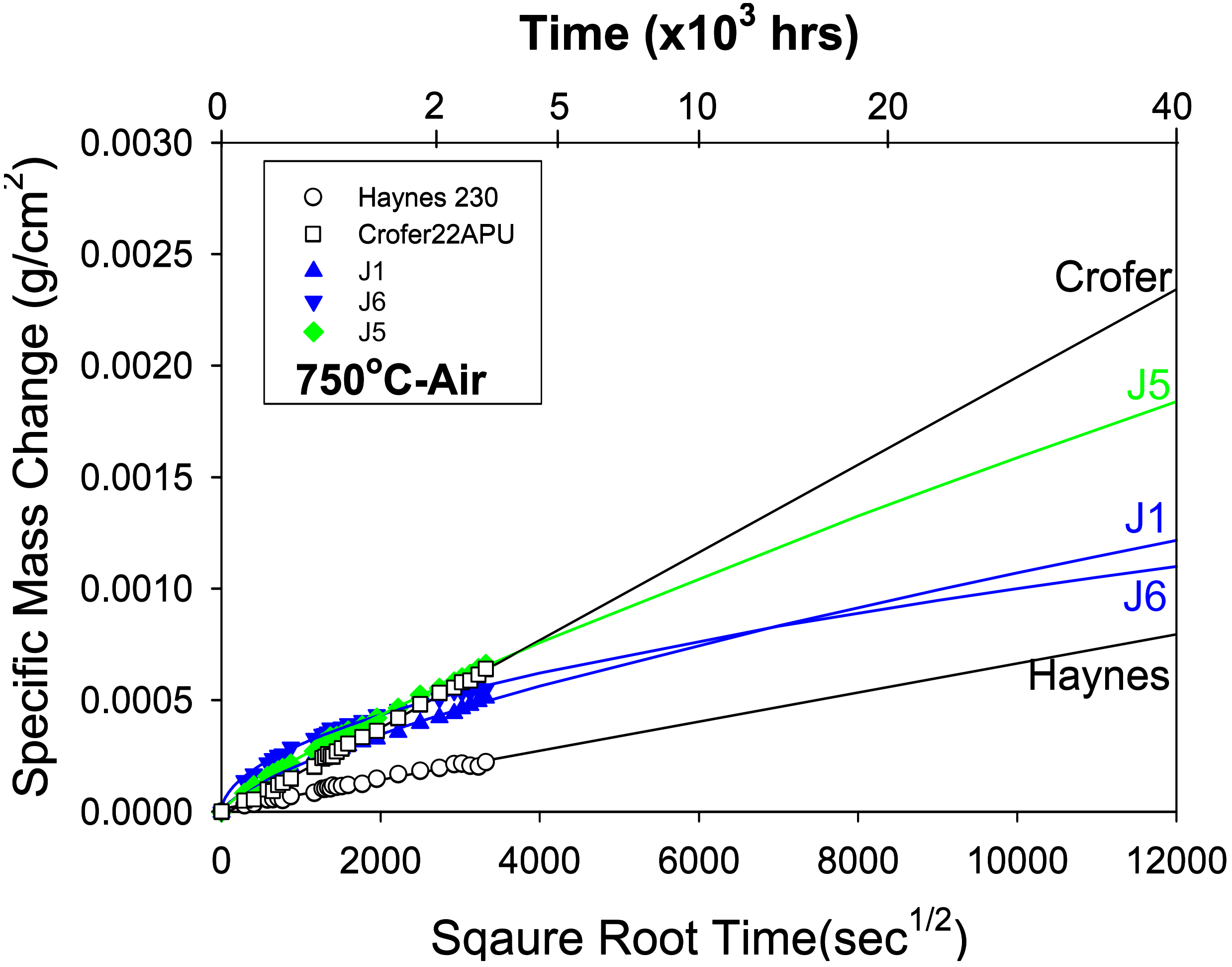
98Cr,0.3Mn, 0.4Mo,1.3Ni

44.5Mo, 32Ni, 23Cr,0.5Mn (Sigma-type)

66Ni,20Cr, 13Mo,1Mn (FCC)



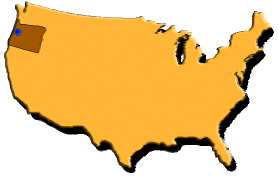
40,000h Extrapolated Behavior



Low CTE Nickel-Alloy Development

Summary and Research in Progress

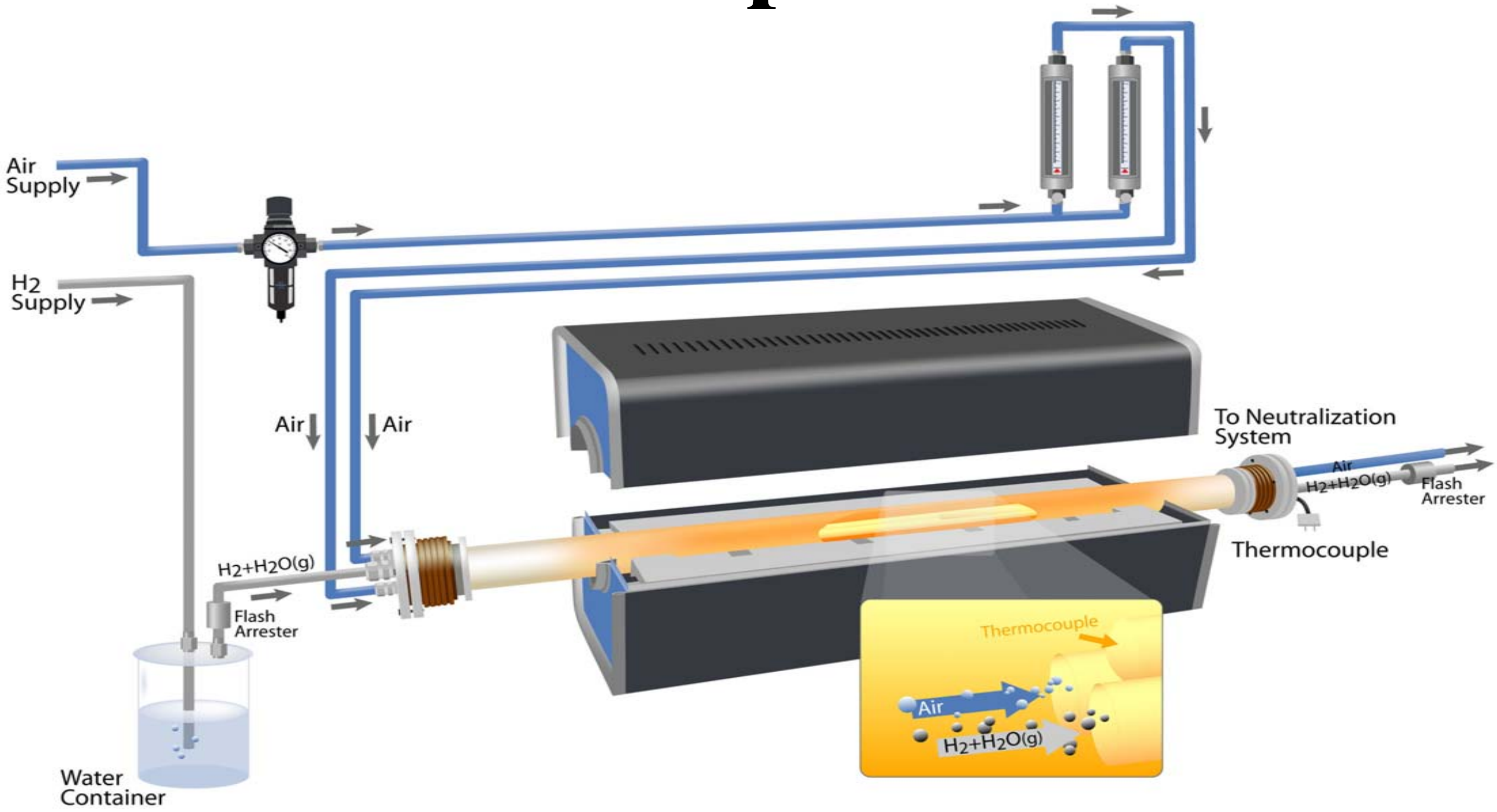
- Ni-alloys with CTE between Haynes 230 and Crofer formulated and produced
- 750^{o}C dry air exposure – on going (currently 3000+hrs)
  - ➢ ASR
- Mechanism studies initiated
  - ➢ Alloy modification and microstructural control for low CTE and oxidation resistance (significantly improve oxidation resistance of low CTE alloys).
- Evaluation in moist environment
- Evaluation in dual environment



CORROSION RESEARCH RELATED TO SOFC

- Multiple Specimen Corrosion Testing in Dual Atmospheres

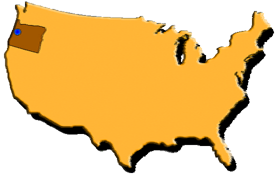
Experimental Setup for Tubular Specimens



List of Publications on Tube Tests

“Understanding the Corrosion Behavior of Chromia-forming 316L Stainless Steel in a Dual Oxidizing-reducing Environment Representative of SOFC Interconnect ,” M. Ziomek-Moroz, S.D. Cramer, G.R. Holcomb, B. S. Covino, Jr., S.A. Matthes, S.J. Bullard, J.S. Dunning, D.E. Alman, P. Singh, 2003 Fuel Cell Seminar, p. 522

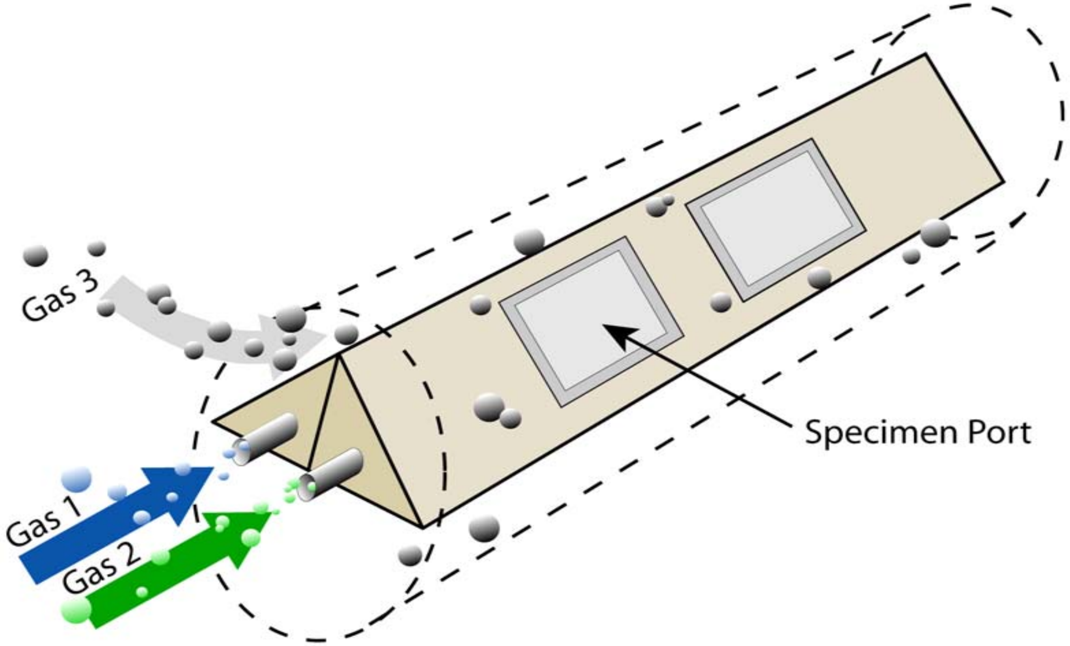
“Corrosion of Stainless Steel in Simulated Solid Oxide Fuel Cell Interconnect Environments,” M. Ziomek-Moroz, S.D. Cramer, G.R. Holcomb, B. S. Covino, Jr., S.J. Bullard, P. Singh, CORROSION 2004, Paper 04534



List of Publications on Tube Tests, cont’d

“ Study of Scale Formation on AISI 316L in Simulated Solid Oxide Fuel Cell Bi-polar Environments,” M. Ziomek-Moroz, B. S. Covino, Jr., S.D. Cramer, G.R. Holcomb, S.J. Bullard, P. Singh, C.F. Windisch, Jr., Proceedings of the 29th International Technical Conference on Coal Utilization & Fuel Systems, in press

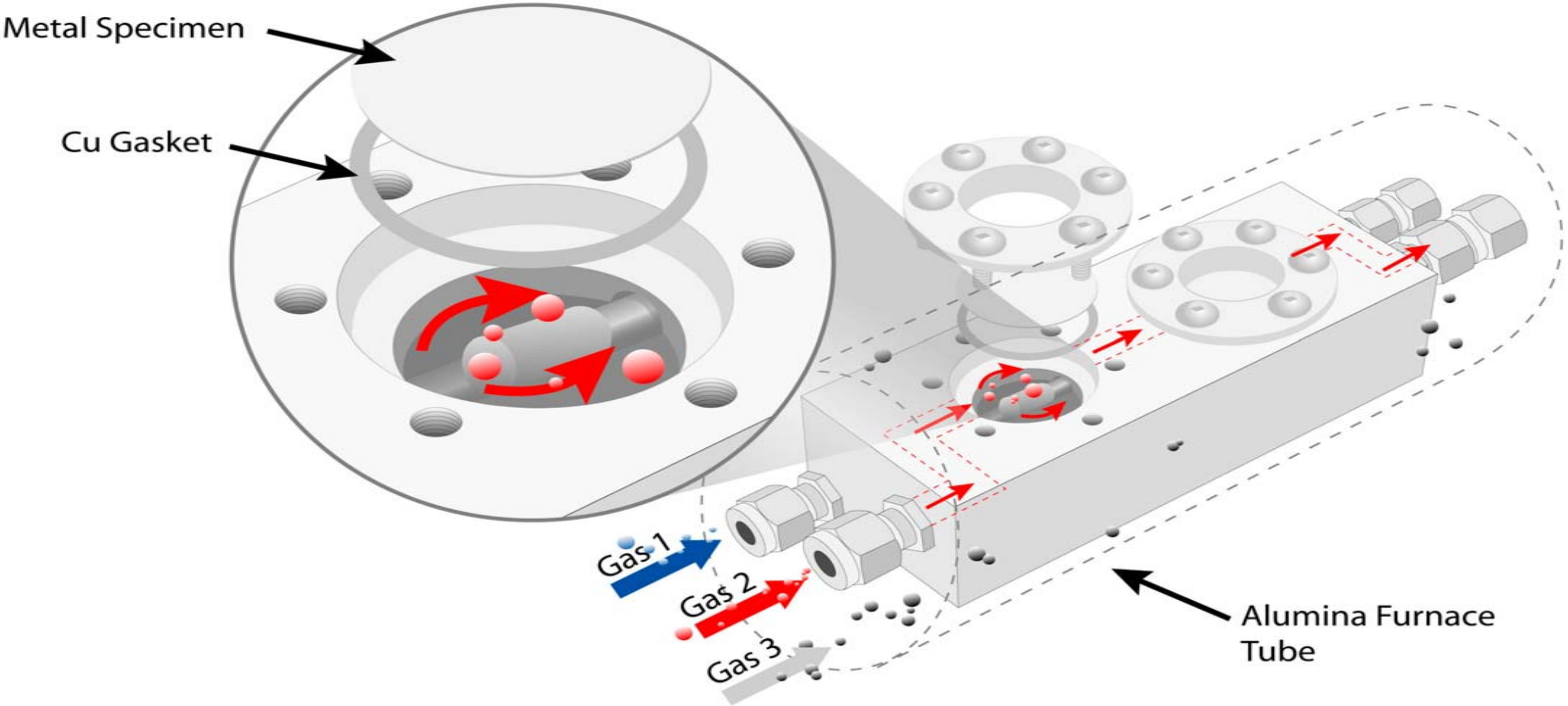
Dual Atmosphere Test – Apparatus with Cements as Seal Materials

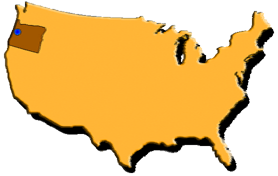


Non-proprietary major constituents present in seal materials

Ceramabond 552	***Ceramabond 569***	Pyro-putty 600	***Ceramabond 685N***	Ceramabond 571P
Aluminum oxide	***Aluminum oxide***	Aluminum oxide	***Zirconia***	Magnesium oxide

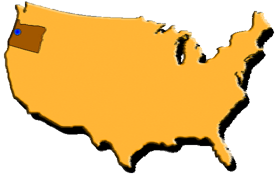
Latest Dual Atmosphere Test Apparatus





Cr Vaporization Related To SOFC

- Goal: Quantify effect of Manganese additions on reducing Chromium evaporation
- Thermodynamic analysis
- Experiment
  - ➢Nickel-Chromium alloys



Knudsen Effusion (Maximum Evaporation)

$$Evaporation\left(\frac{g}{cm^2\,\sec}\right)=\frac{m}{tA}=p\sqrt{\frac{M}{2\pi RT}}=44.33\boxed{p}\sqrt{\frac{M}{T}}$$

m = mass of vapor (g)

t = time (sec)

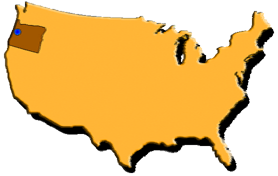
A = area (cm^2)

p = partial pressure (atm)

M = molecular weight of vapor (g/mol)

T = temperature (K)

R = Gas Constant



Real Evaporation Rates

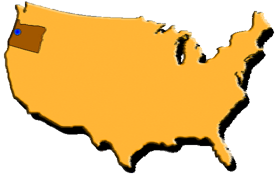
- Langmuir Effusion:

$$Langmuir\ \ Effusion = \alpha\ Knudsion\ \ Effusion$$

✂= vaporization coefficient, ~10^{-3}

- Effective Film Thickness Model:

$$Evaporation = \frac{D\left[p - p_{bulk}\right]}{1.5\ L\ N_{Sc}^{-1/3}\ N_{\mathrm{Re}}^{-1/2}\ R\ T}$$

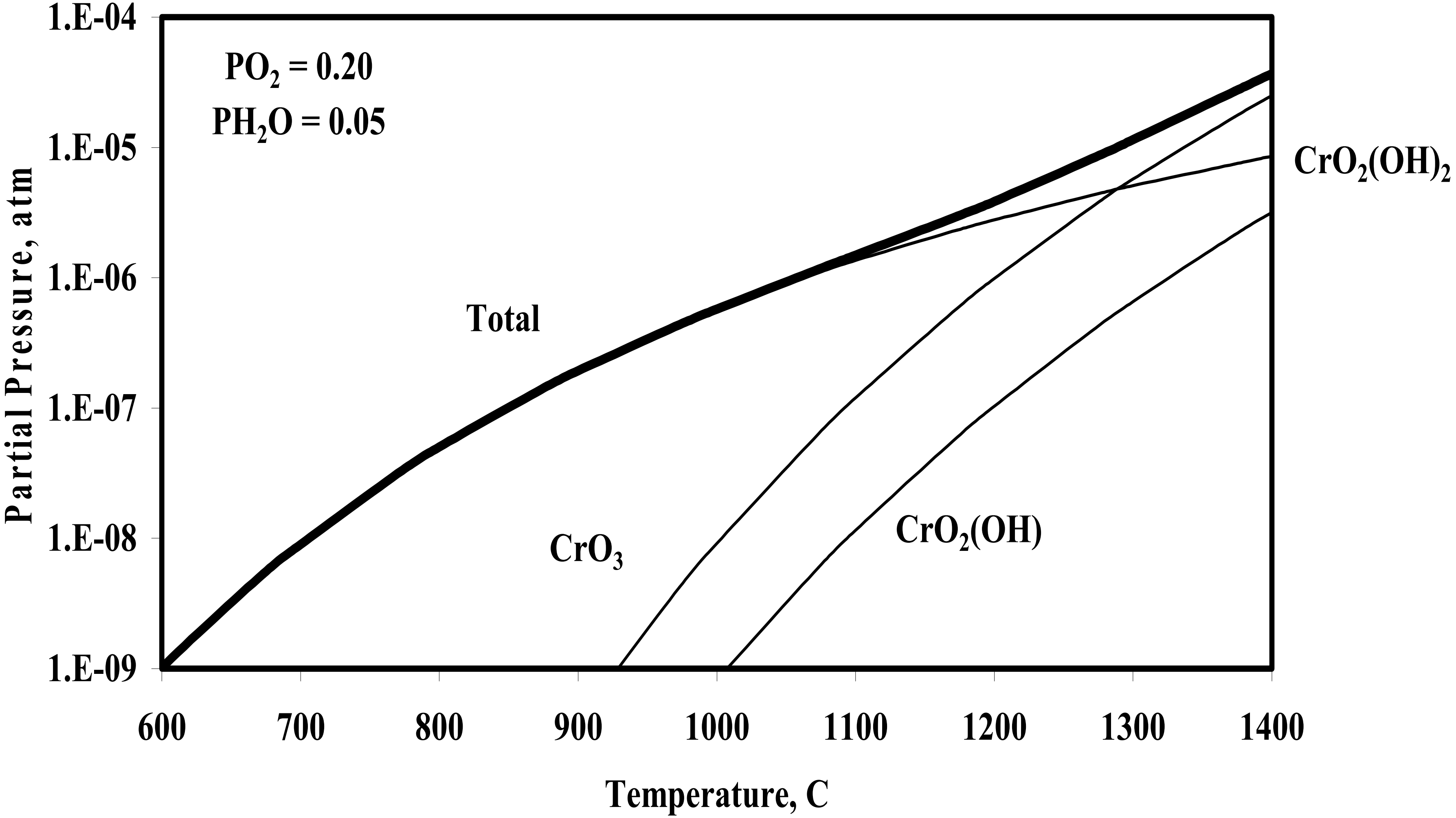


Finding P of Cr species

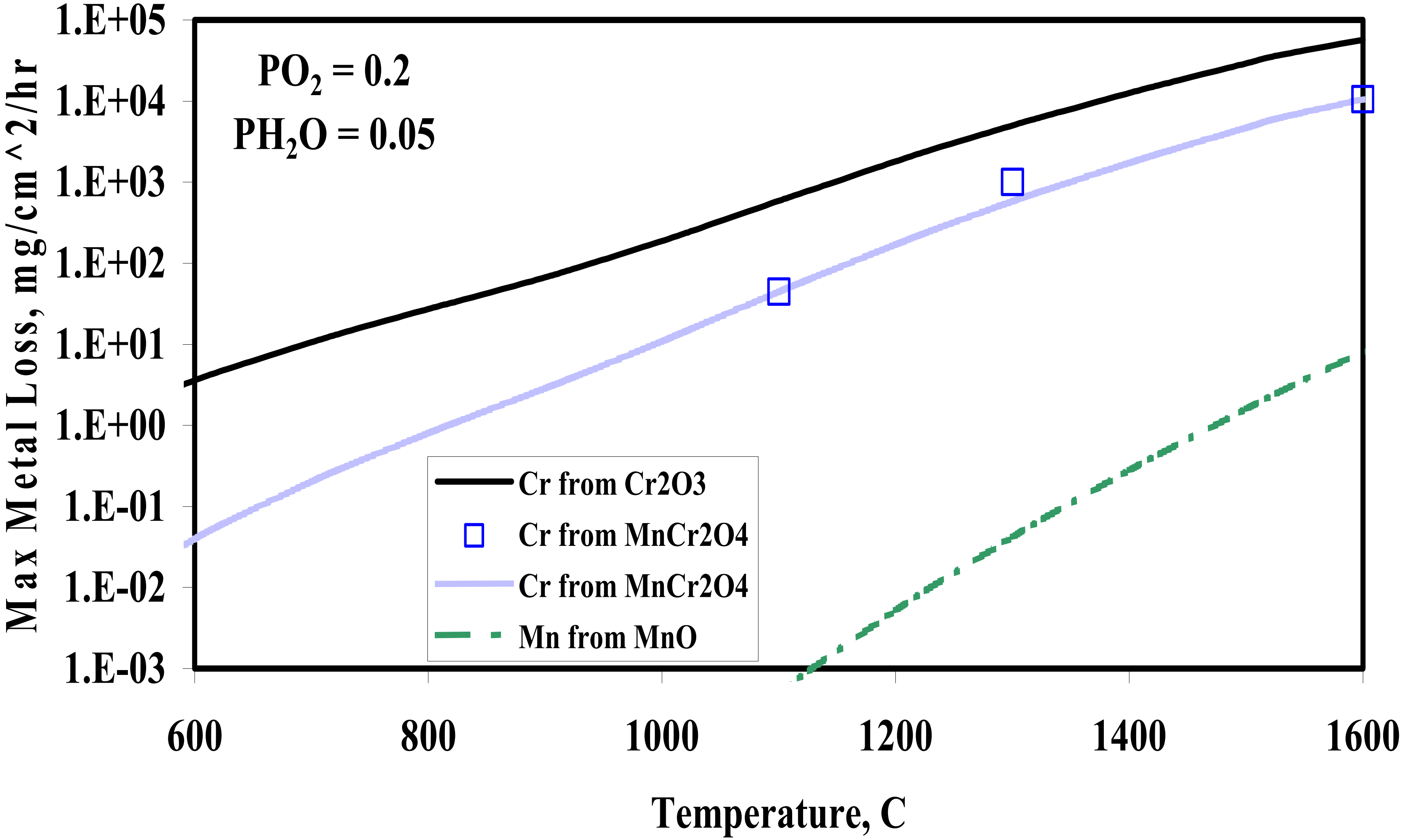
$$Cr_2O_3(s) + 2H_2O(g) + \frac{3}{2}O_2(g) = 2CrO_2(OH)_2(g)$$

$$\sum \Delta G_f^{\circ} = -RT\ln\frac{P^2_{CrO_2(OH)_2}}{P^2_{H_2O}\,P^{3/2}_{O_2}}$$

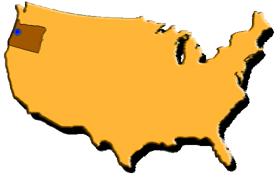
Partial Pressure of Cr Gas Species



Max Metal Loss (Knudsen)



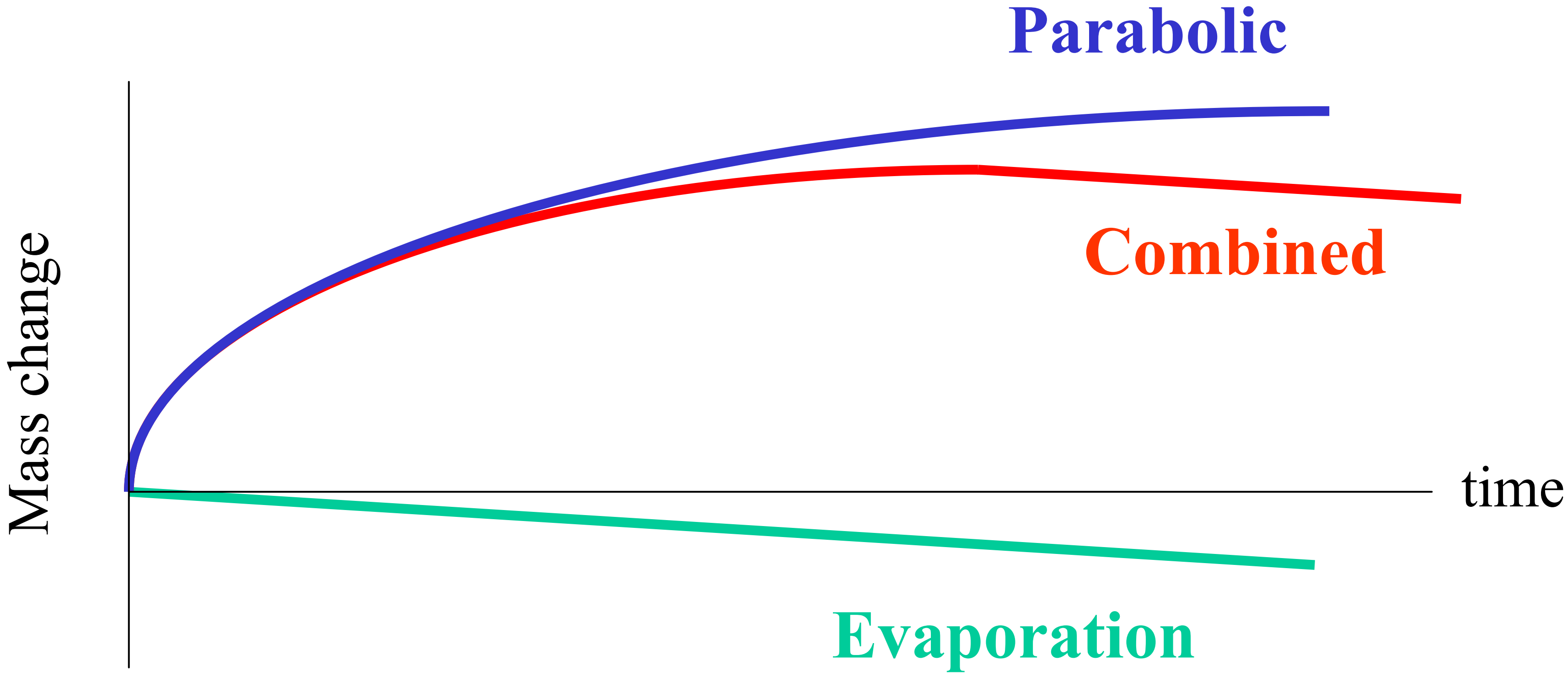
Temperature, °C	Maximum Cr Loss, mg/cm^2/hr, from Cr_2O_3	$NiCr_2O_4$	$MnCr_2O_4$	Reduction Factor from $NiCr_2O_4$	Reduction Factor from $MnCr_2O_4$
$P_{O2} = 0.21$, $P_{H2O} = 0$					
600	0.00428	0.0000913	0.0000472	47	91
700	0.116	0.00240	0.00220	48	53
800	1.66	0.0334	0.0490	50	34
900	14.6	0.289	0.623	51	23
1000	88.8	1.72	5.15	52	17
$P_{O2} = 0.20$, $P_{H2O} = 0.05$					
600	3.58	0.0764	0.0396	47	91
700	10.7	0.221	0.203	48	53
800	27.1	0.547	0.801	50	34
900	67.2	1.33	2.86	51	23
1000	188	3.65	10.9	52	17
$P_{O2} = 0.10$, $P_{H2O} = 0.20$					
600	8.53	0.182	0.0942	47	91
700	25.2	0.522	0.479	48	53
800	61.7	1.24	1.82	50	34
900	134	2.63	5.68	51	23
1000	287	5.55	16.6	52	17
$P_{O2} = 0.001$, $P_{H2O} = 0.344$					
600	0.464	0.00990	0.00512	47	91
700	1.37	0.0284	0.0261	48	53
800	3.35	0.0675	0.0989	50	34
900	7.24	0.143	0.308	51	23
1000	15.5	0.301	0.901	52	17

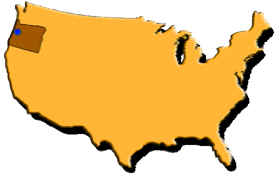


5 Alloys

- Ni-25Cr
  - Base alloy, enough Cr for Cr_2O_3 layer
- Ni-25Cr-0.1Y
  - Y to aid scale adhesion
- Ni-25Cr-0.1Y-0.4Mn
- Ni-25Cr-0.1Y-1Mn
  - Mn above 0.6 gives some $MnCr_2O_4$ in the scale
- Ni-25Cr-0.1Y-3Mn
  - Mn above 3 gives $MnCr_2O_4$ layer

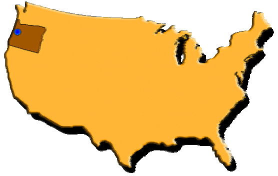
Long Term Wt Change Experiments





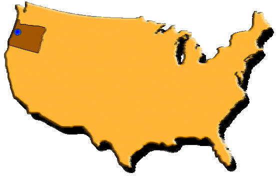
Long Term Exposures

- 950°C
  - Faster kinetics and relative evaporation
- Air plus water
  - 20% O_2 + 5% H_2O
- Up to several thousand hours to obtain linear mass loss (the evaporation rate)



Balance of Plant (BOP) Issues

- Information Gathering
- Low Cost, High Temperature Preheaters & Heat Exchangers
- Cr Evaporation
- Data Base



Information Gathering

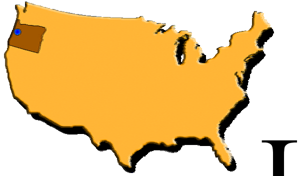
Contacts with SOFC industry

Vertical Teams

- SOFCo (Greg Rush, Steve Kung)
- Cummings Power Generation (Charles Vesely)
- Delphi Automotive Systems (Diane England)
- Fuel Cell Energy (Pinakin Patel)
- GE Power Systems (Nguyen Minh)

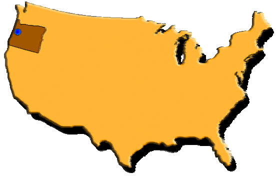
Others

- Nanodynamics, Inc (micro-FC: David Bothell)
- Fucello, Inc (1-4 kW SOFC: Don Pohanska)
- Porvair (heat exchangers: Charles Frame)
- Exothermics (heat exchangers)
- Edison Welding Institute(joining technologies)



Low Cost, High Temperature Heat Exchangers (HX)

- Pre-heat fuel and air to operating temperatures (650^{o}C-900^{o}C)
- HX for aerospace applications can cost $100,000 per unit. SECA goal of fuel cell cost of $400/kW need HX cost of $200 per unit for a 10kW System



Generic BOP Issues

- Cr Evaporation identified as BOP issue
  - Poison from down stream components
  - Low cost corrective measures needed
- Develop data base of materials that can help meet cost goals of $200 per unit for a 10 kW system.