Materials for Oxy-Fuel Turbomachine Conditions

Principal Investigators : Gerald H. Meier and Frederick S. Pettit

Graduate Student: Edward J. Magee

SCIES Project : 06-01-SR 124
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Rondle Harp, Program Manager, DOE/NETL
Richard Wenglarz, Manager of Research, SCIES

Project Awarded (07/01/2007, 36 months duration)

$441,882 Total Contract Value ($338,640 DOE)

PROJECTED ADVANCED TURBINE OPERATING PARAMETERS [1]

	Syngas Turbine 2010	Hydrogen Turbine 2015-2020	Oxy-Fuel Turbine 2010	Oxy-Fuel Turbine 2015-2020
Combustor Exhaust Temp, °F (°C)	~+2700 (~+1480)	~+2700 (~+1480)		
Turbine Inlet Temp, °F (°C)	~2500 (~1370)	~2600 (~1425)	~1150 (~620)	~1400 (~760) (HP) ~3200 (~1760) (IP)
Turbine Exhaust Temp, °F (°C)	~1100 (~595)	~1100 (~595)		
Turbine Inlet Pressure, psig	~265	~300	~450	~1500 (HP) ~625 (IP)
Combustor Exhaust Composition, %	CO_2 (9.27) H_2O (8.5) N_2 (72.8) Ar (0.8) O_2 (8.6)	CO_2 (1.4) H_2O (17.3) N_2 (72.2) Ar (0.9) O_2 (8.2)	**H_2O (82)** **CO_2 (17)** O_2 (0.1) N_2 (1.1) Ar (1)	**H_2O (75-90)** **CO_2 (25-10)** O_2, N_2, Ar (1.7)
Deposit on Hardware Resulting from Contaminants	CaO, $CaSO_4$, SiO_2, Al_2O_3	**?**	**?**	**?**

[1] Adapted from M. A. Alvin, et al., Materials and Component Development for Advanced Turbine Systems; Merit Review Paper — May 4, 2007

Gas Turbine Need

- Much of the previous materials development for power generating gas turbines has been performed with natural gas as the fuel of choice and air as the oxidant.

- The use of coal-based oxy-fuel systems will result in combustion gases which are hotter and contain high levels of H_2O and CO_2.

- There is a need to determine the effects of relevant gases on the high temperature degradation of gas turbine alloys and coatings.

- There also is a need to determine the effects of deposit-induced degradation of the alloys and coatings in these atmospheres.

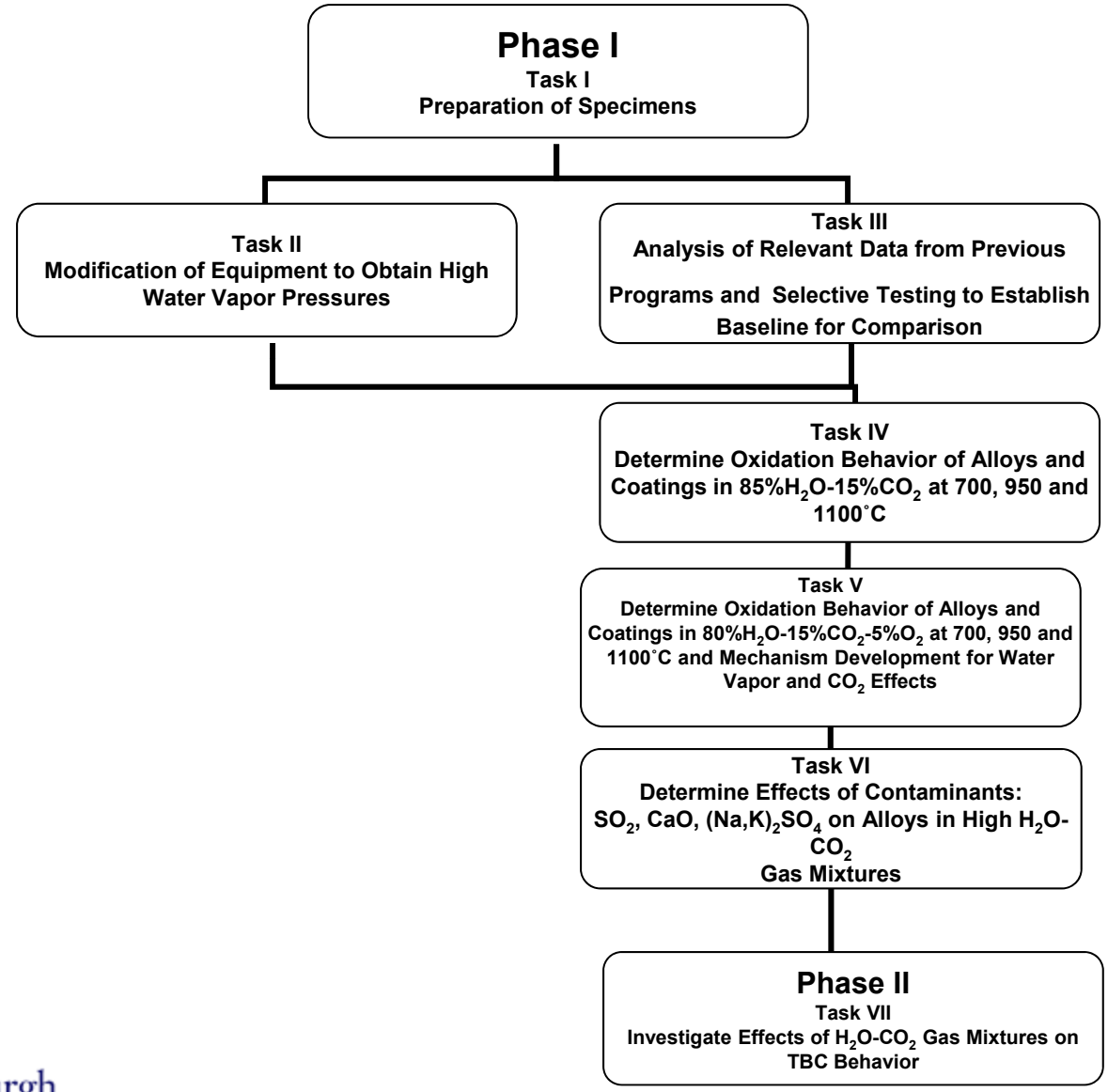
Program Objectives

Evaluate the durability of turbine materials at the temperatures and oxygen pressures typical of those in the high steam and CO_2 levels expected in coal based oxy-fuel systems

Specific Objectives Phase I

1. Evaluating the performance of candidate alloys and coatings in environments starting with 85% steam and 15% CO_2 (by volume) and then for reduced levels of steam to accommodate up to 5% O_2, which may represent excess oxygen needed to assure complete oxy-fuel combustion.
2. Advancing the existing knowledge of how steam (water vapor) affects the selective oxidation of high temperature alloys.
3. Investigate the effects of carbon and hydrogen on the oxidation of alloys exposed to H_2O-CO_2 mixtures.
4. Examine the effects of contaminants such as SO_2 and alkali deposits ($(Na, K)_2 SO_4$, CaO) on the degradation of alloys in H_2O-CO_2 gas mixtures.

Flow Diagram for the Project



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Task 1: Alloy and Coating Compositions

1. Compositions of Alloys (wt%)

Alloy	Ni	Cr	Al	Co	Ta	W	Mo	Ti	B	Hf	Re
IN 738	Bal.	16.0	3.4	8.5	1.7	2.6	7.1	3.4	.001	---	---
René N5	Bal.	7.0	6.2	7.5	6.5	6.0	0.6	1.0	---	0.1	3.0
GTD 111	Bal.	14.0	3.0	9.5	2.8	2.8	1.5	4.9	.01	---	3.0

2. Compositions of Coating Materials (wt%)

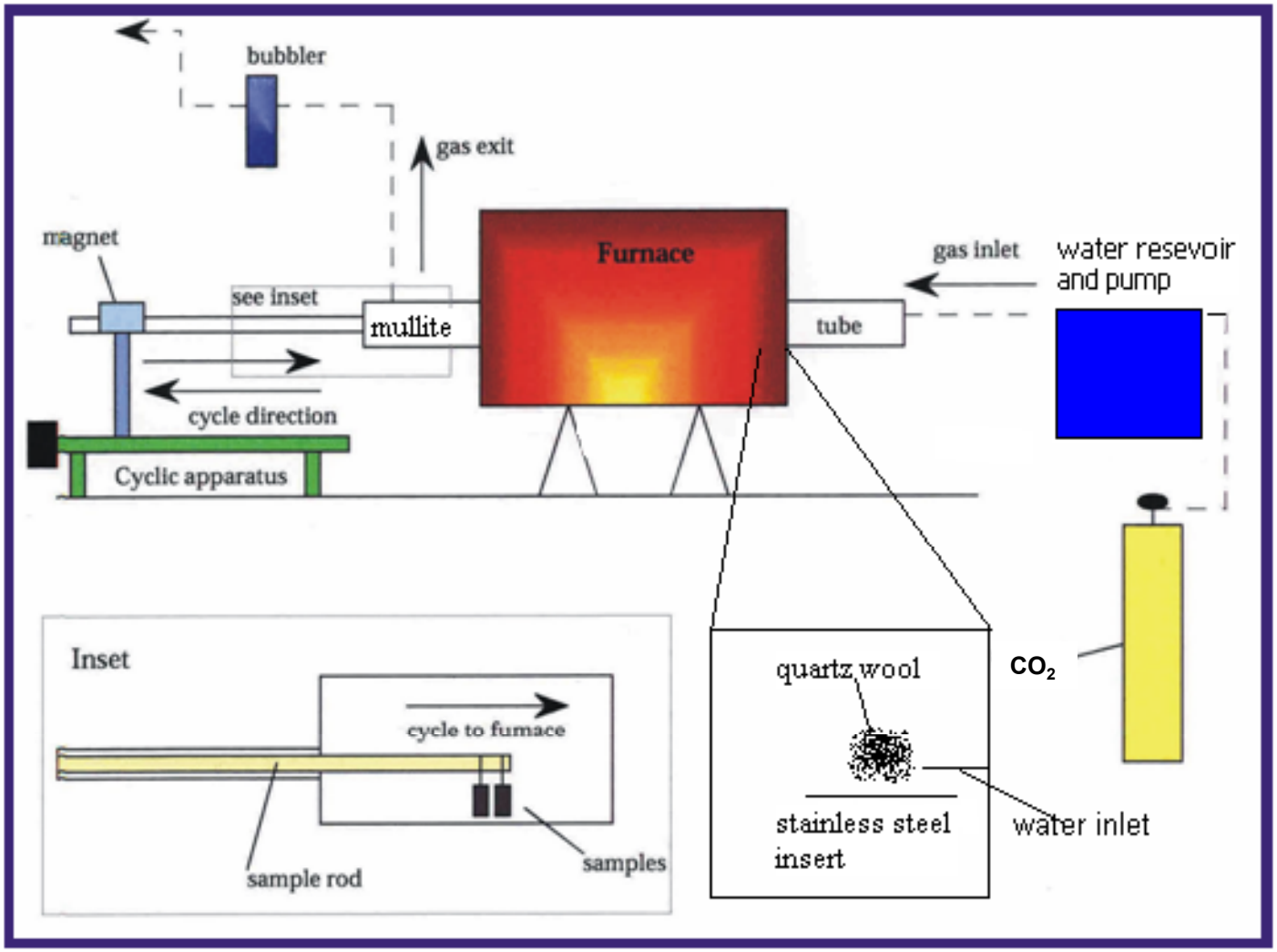
coating	Ni	Co	Cr	Al	Y	Pt
NiCoCrAlY	Bal.	22.5	16.5	13.5	0.5	-
Pt-modified Aluminide †	42	-	-	23	-	35

† At the surface of coating

3. Simple Model Alloys

Ni-Cr-Al, Fe-Cr (single phase)

Task 2: Exposure Apparatus



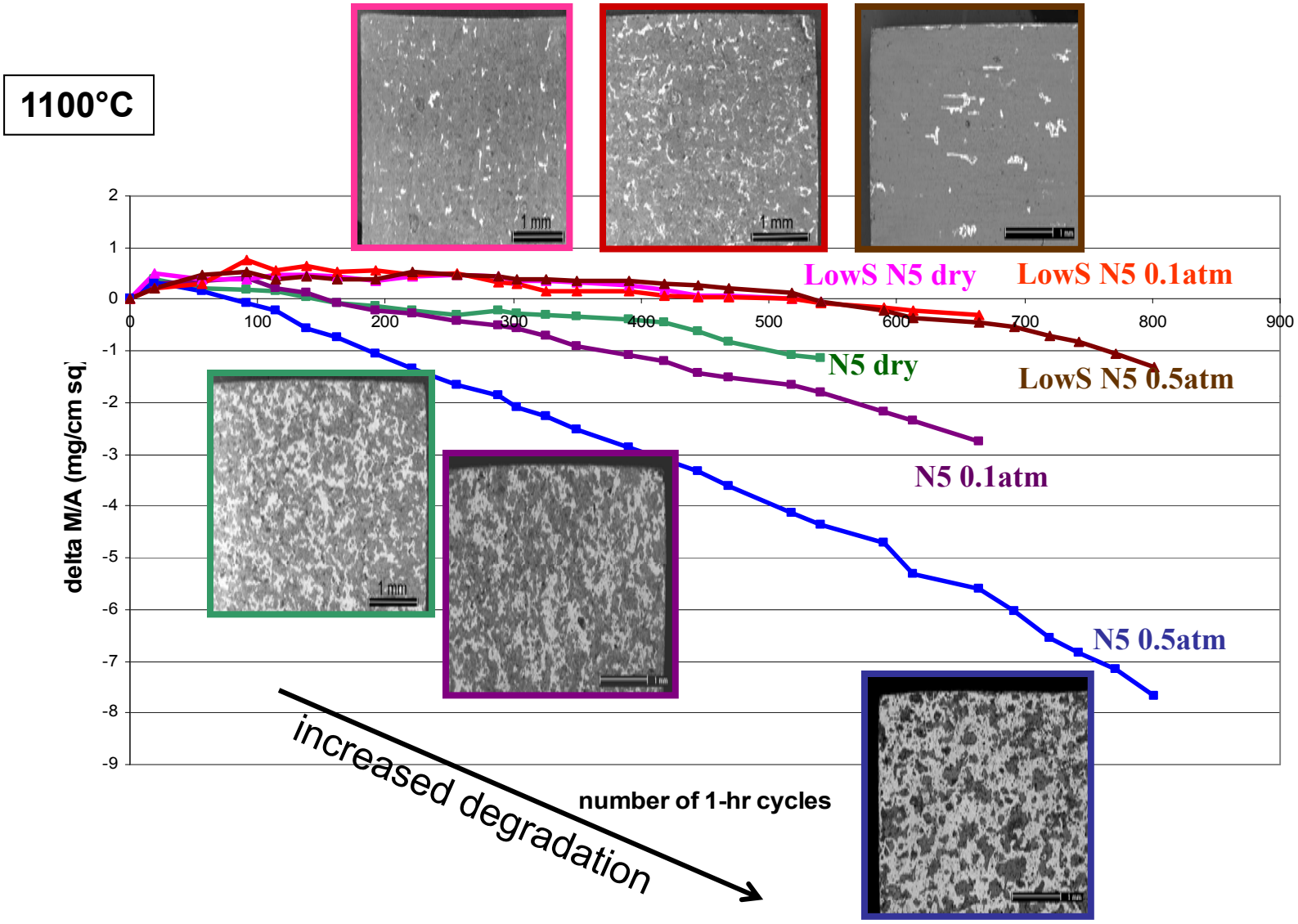
Task 3: Analysis of Relevant Data

The results of previous and ongoing projects have been analyzed with respect to the effects H_2O and CO_2 high-temperature alloy oxidation.

Water Vapor Effects on High Temperature Oxidation

- **The effects depend on the alloy system.**
- **In the case of Al_2O_3- and Cr_2O_3-formers, water vapor affects the oxidation resistance adversely.**
  - Adherence of alumina is degraded (Chromia adherence is often improved)
  - Selective oxidation is often disrupted.
  - Transient oxidation is often accelerated
  - Evaporation of oxide films is accelerated (chromia, silica)
  - Dual atmosphere effects observed in fuel cells and boiler tubes

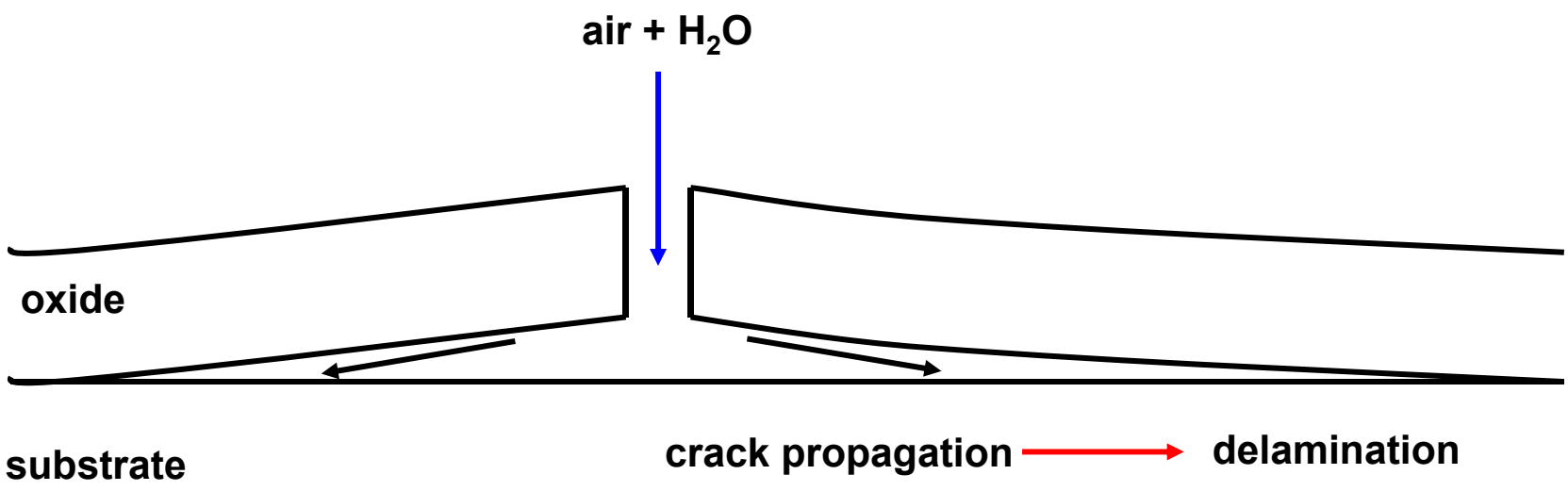
Effect of Water Vapor on Cracking and Spalling of α-Al_2O_3 Scales



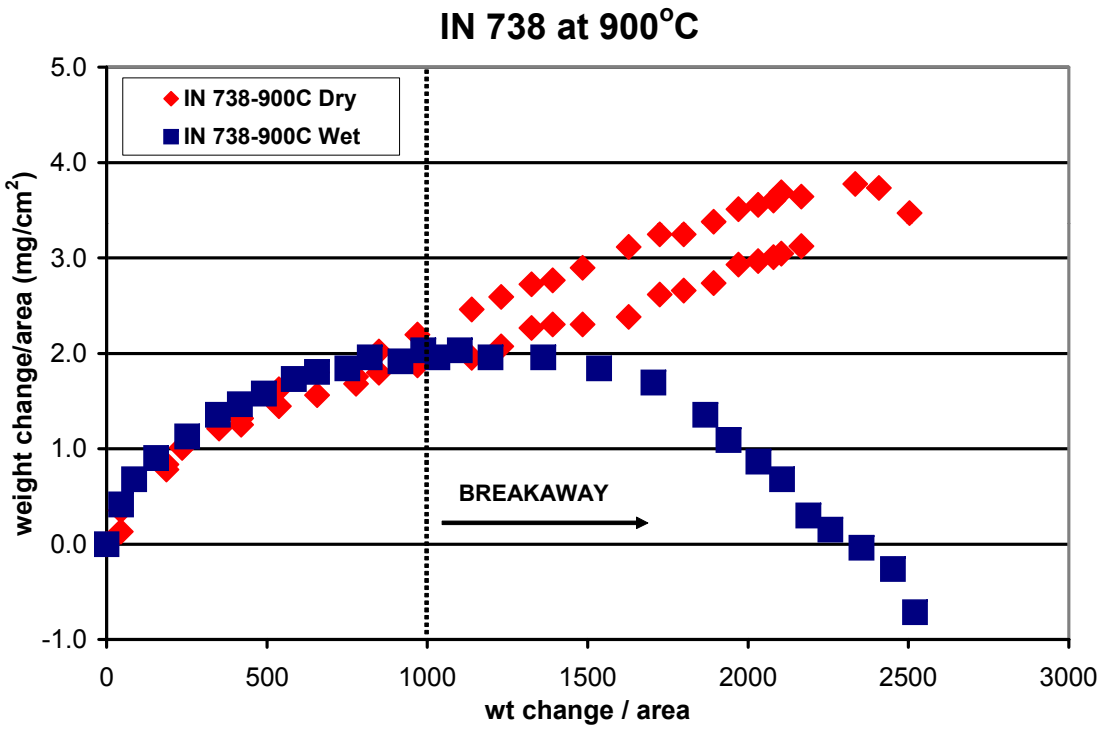
- The presence of water vapor in the oxidizing gas mixture causes the α-Al_2O_3 scales to crack and spall more profusely than in dry gases

Mechanism: Stress Corrosion Cracking

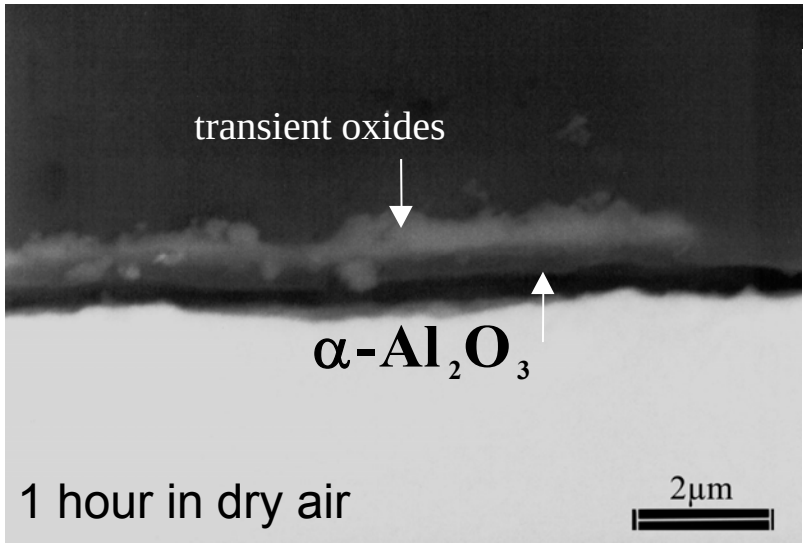
• Although cyclically oxidized low S superalloys do not spall as much as regular S superalloys, water vapor has access to the oxide/substrate interface in both cases.
• Low S superalloys have increased spallation resistance because of a higher Al_2O_3/substrate interfacial toughness.
• A crack that forms propagates until it is large enough to result in failure. Water vapor has access to the oxide/substrate interface through cracks in the oxide and, combined with the stress, can cause spalling of the scale by interfacial stress corrosion cracking.

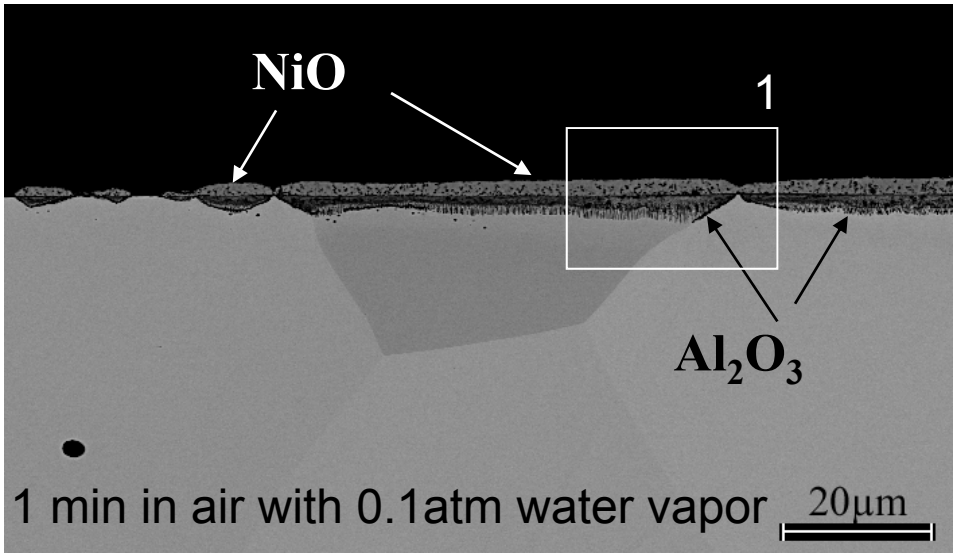


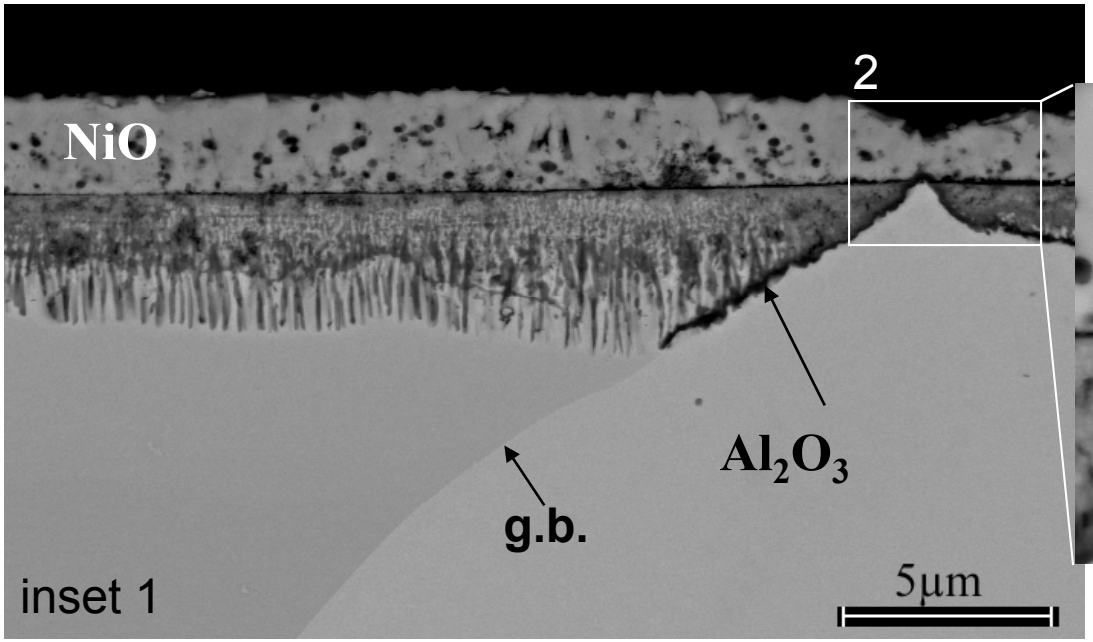
Cyclic Oxidation of IN-738 at 900°C

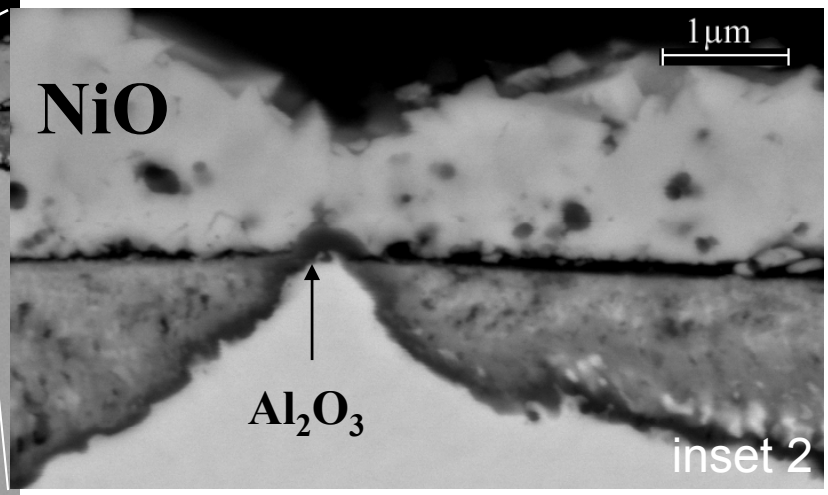


Selective Oxidation Ni-8Cr-6Al oxidized @ 1100°C



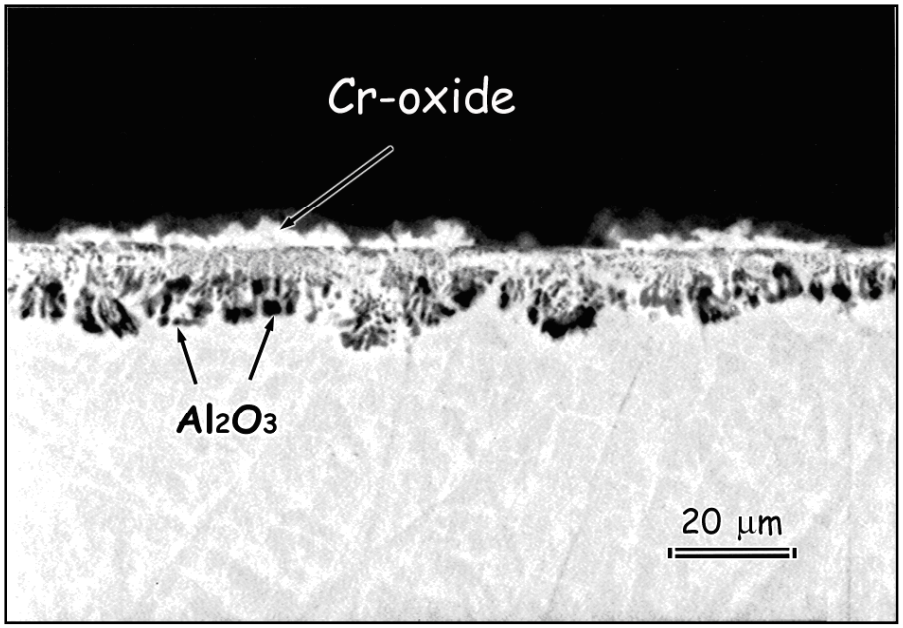


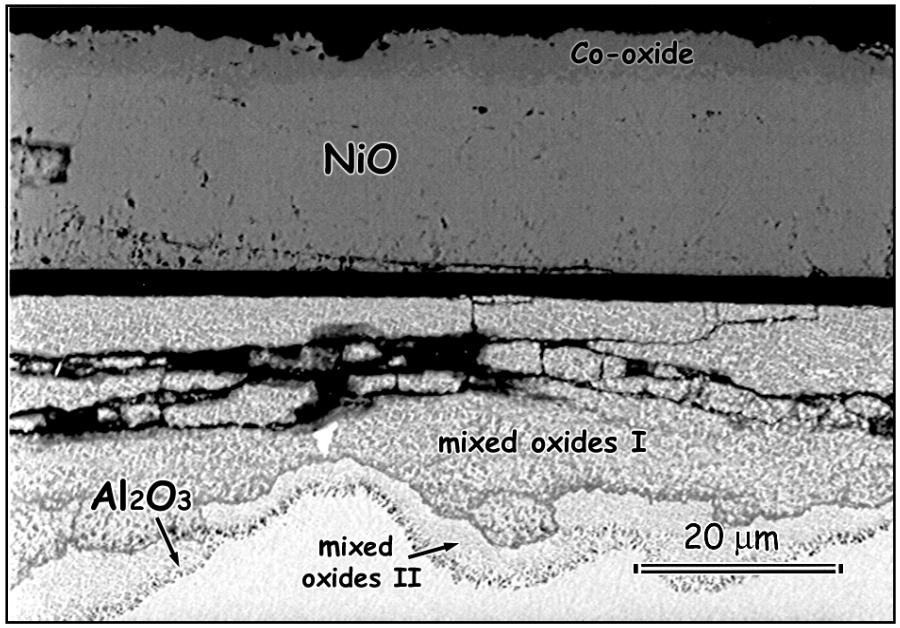




Cyclic Oxidation at 700°C

PWA 1484

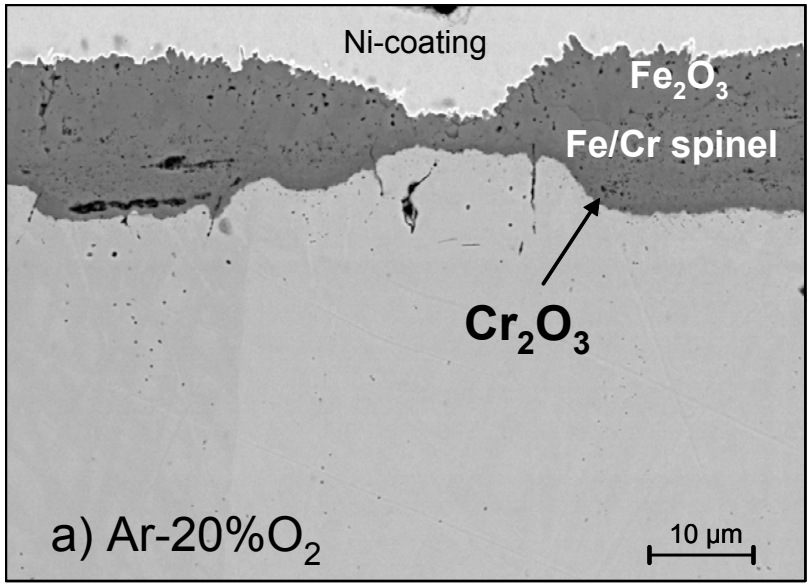


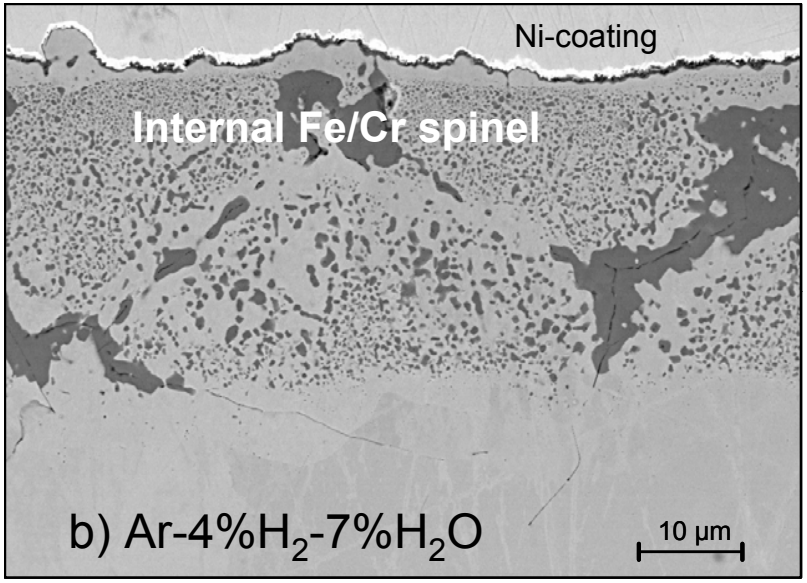


Dry Air

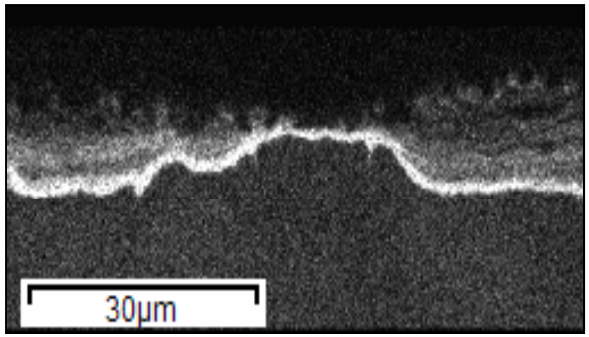
Air + 10% H_2O

Oxidation of Fe-10Cr at 900°C





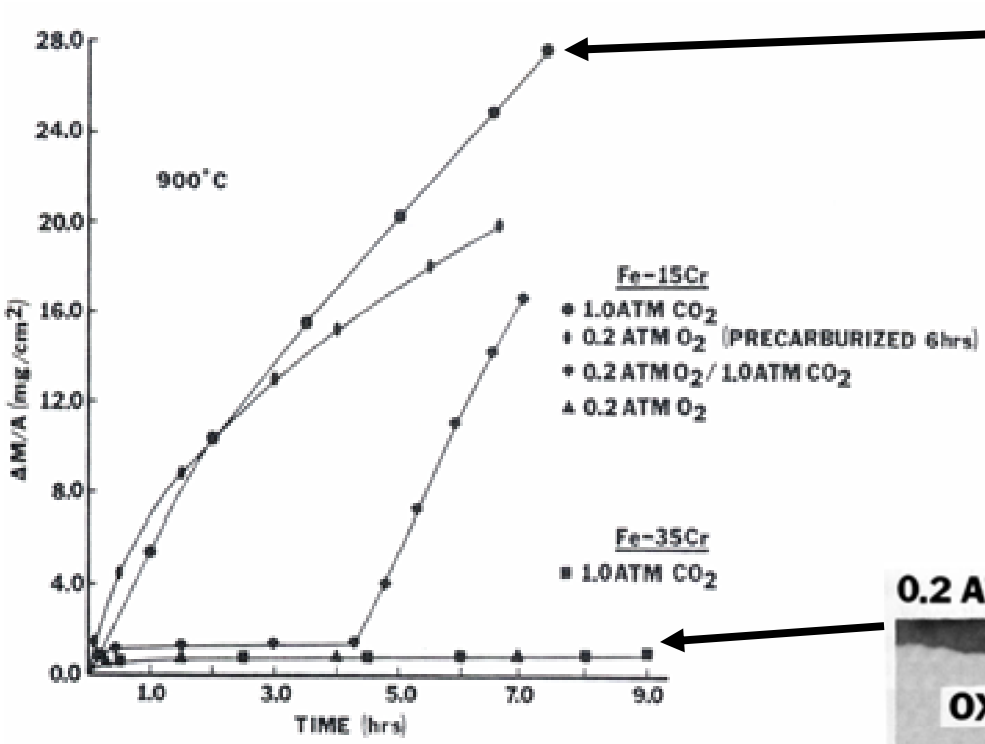
$p_{O2} \approx 10^{-15}$ atm

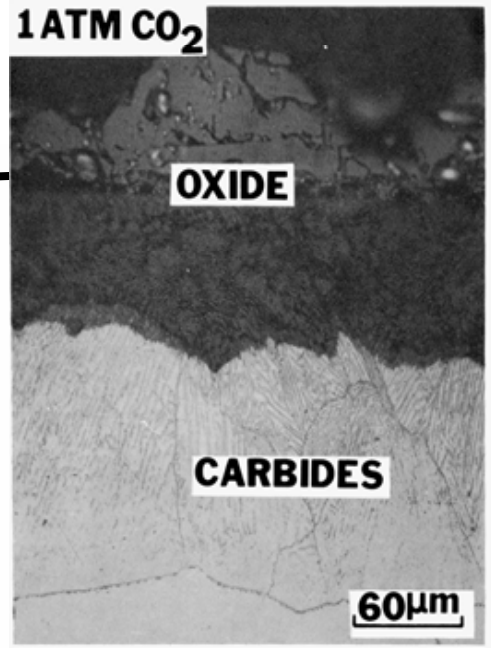


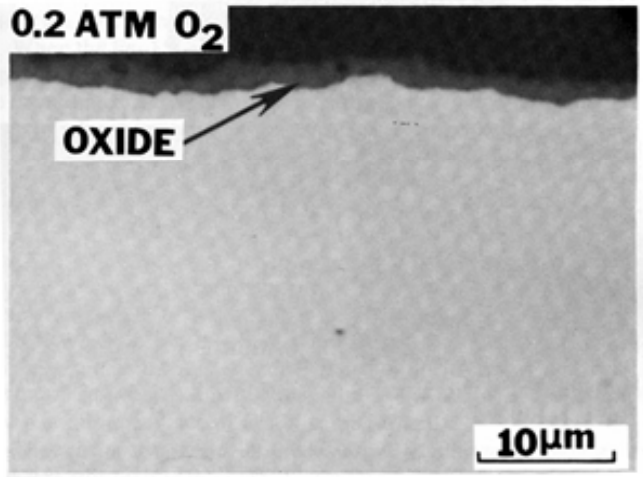
Cr Map

E. Essuman, G.H. Meier), J. Żurek, M. Hänsel, L. Singheiser, W.J. Quadakkers "Enhanced internal oxidation as trigger for breakaway oxidation of FeCr-alloys in water vapor containing gases", Scripta Mat., 57, 845 (2007).

Effect of CO_2 on Selective Oxidation





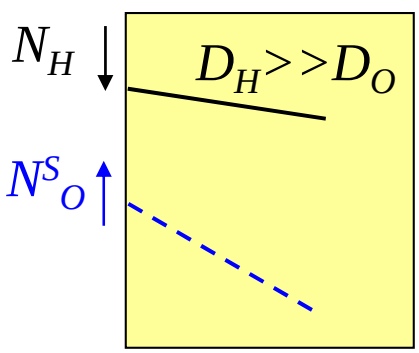


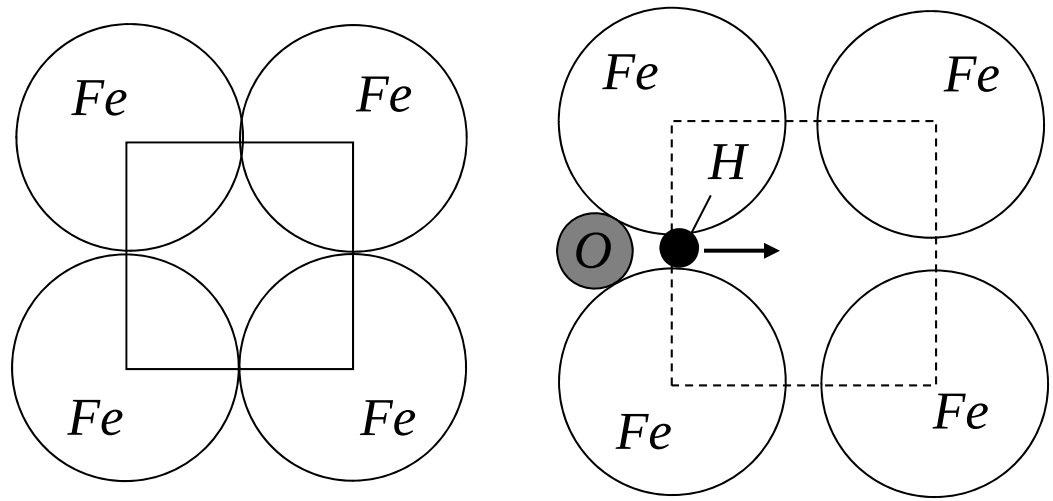
Proposed mechanism of enhanced internal oxidation of Cr in $(H_2)H_2O$-containing gases

$$N_{Cr}^{(1)} > \left[\frac{\pi g^*}{3} N_O^{(S)} \frac{D_O V_m}{\tilde{D}_{Fe-Cr} V_{CrO_{1.5}}} \right]^{1/2}$$

$$H_2O(g) = 2\underline{H} + \underline{O}$$

$$N_o^S = K_1 \frac{p_{H_2O}}{N_H^2}$$

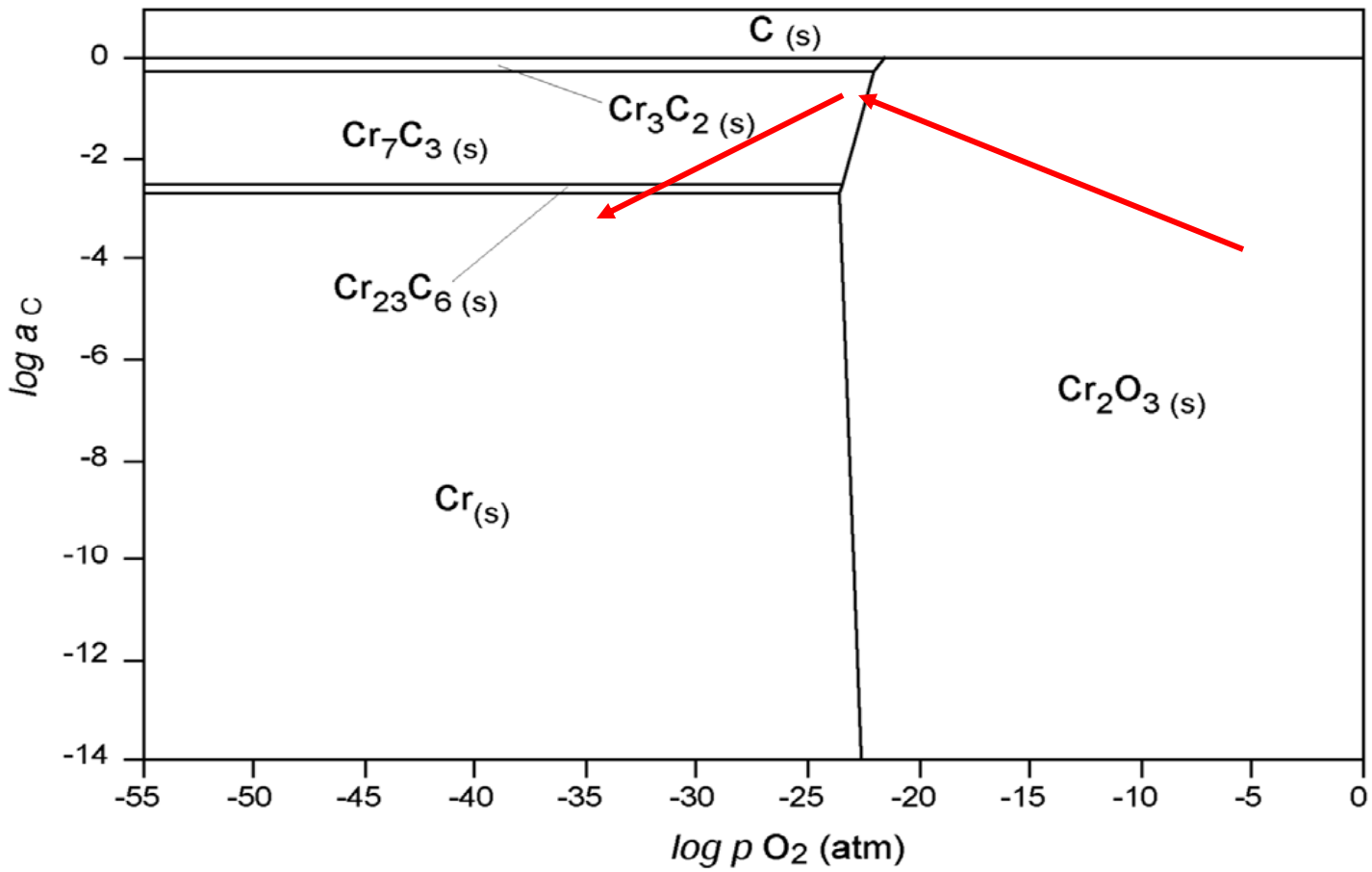




Hydrogen increases oxygen solubility and/or diffusivity in metal

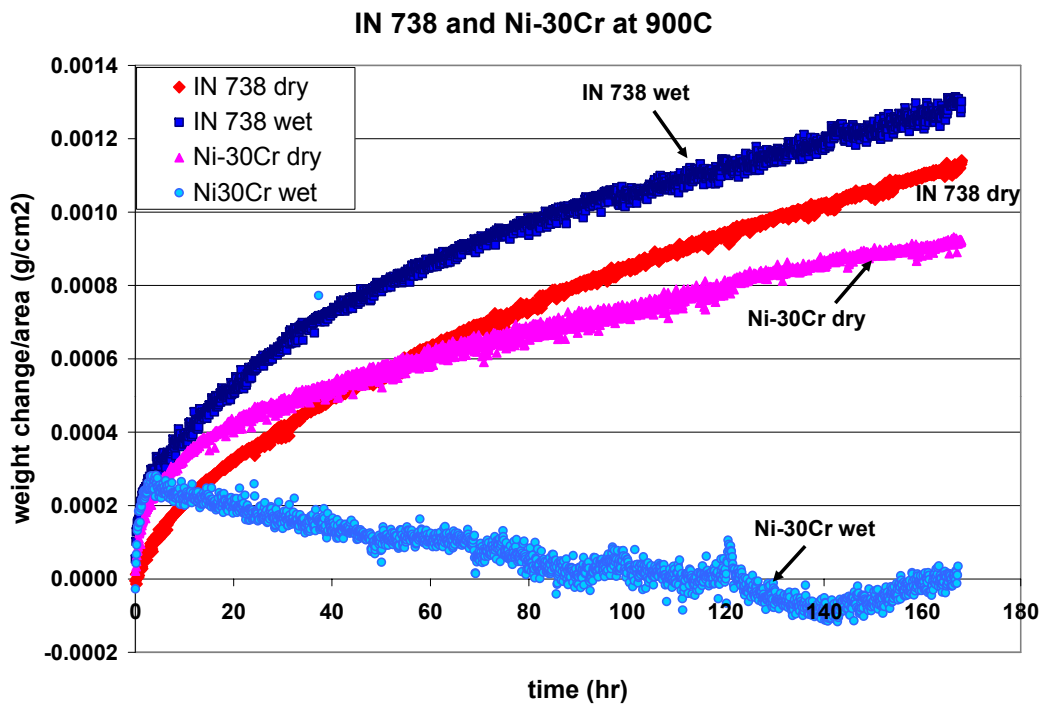
Proposed Mechanism for Effect of CO_2 on Selective Oxidation

$$CO_2(g) = O(Ox) + CO(g) \quad a_C\uparrow$$



Isothermal Stability Diagram for the Cr-C-O System at 1250K

Evaporation Effects



$$Cr_2O_3 + 1.5O_2 + 2H_2O = 2CrO_2(OH)_2$$

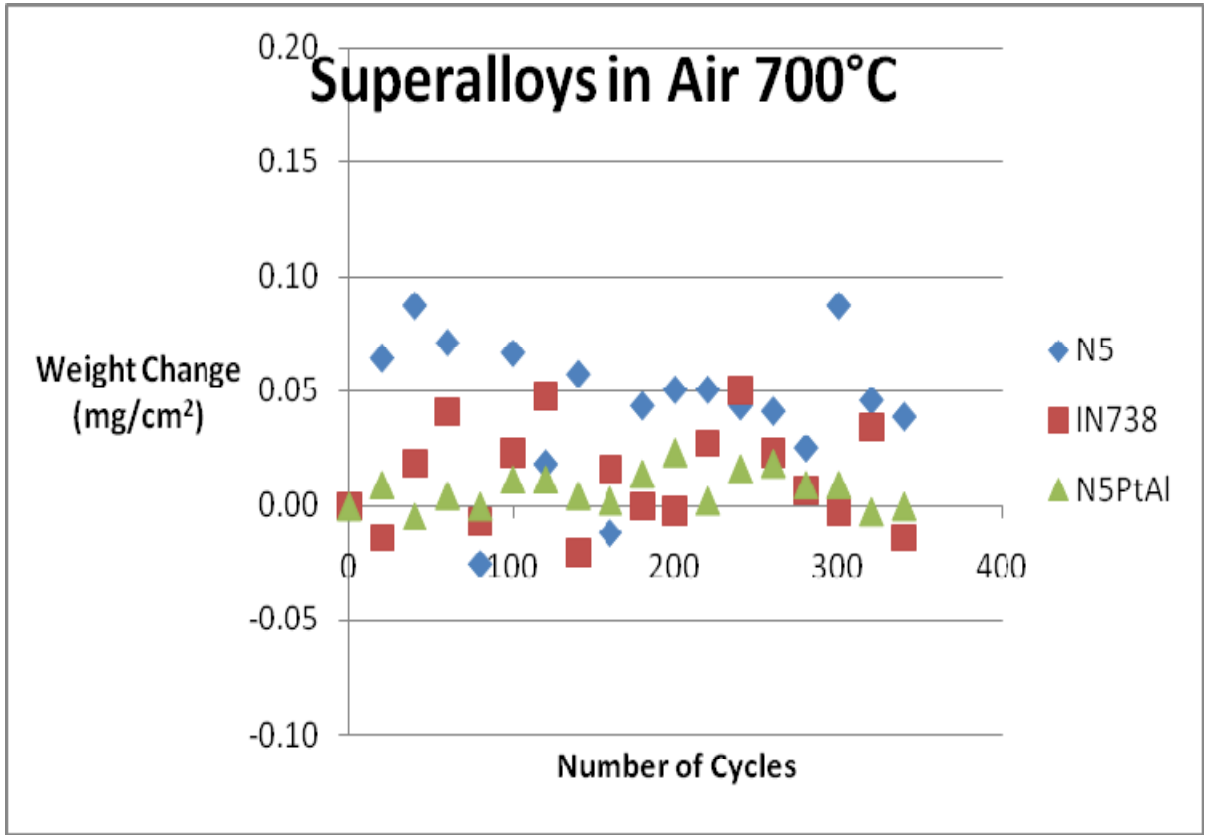
Task 4: Oxidation of Alloys and Coatings

Equilibrium Gas Compositions for Input Gas of 85% H_2O-15% CO_2

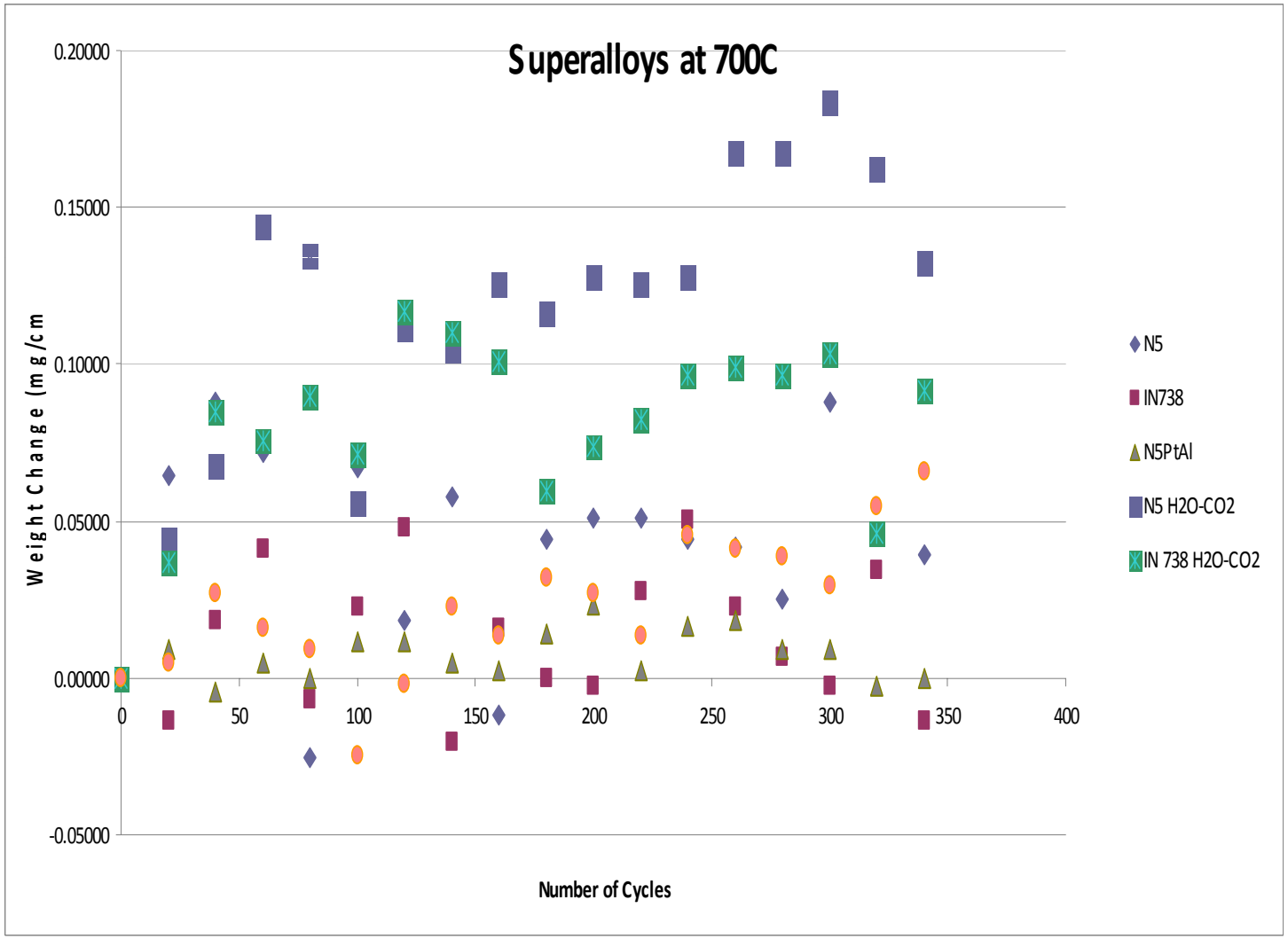
Partial Pressures (atm)

Temperature (°C)	700	900	1100
H_2O	≈0.85	≈0.85	≈0.85
CO_2	≈0.15	≈0.15	≈0.15
H_2	1.2×10^{-7}	3.9×10^{-6}	4.5×10^{-5}
CO	1.4×10^{-8}	8.9×10^{-7}	1.7×10^{-5}
O_2	6.9×10^{-8}	2.4×10^{-6}	3.1×10^{-5}

Task 4: Oxidation of Alloys and Coatings

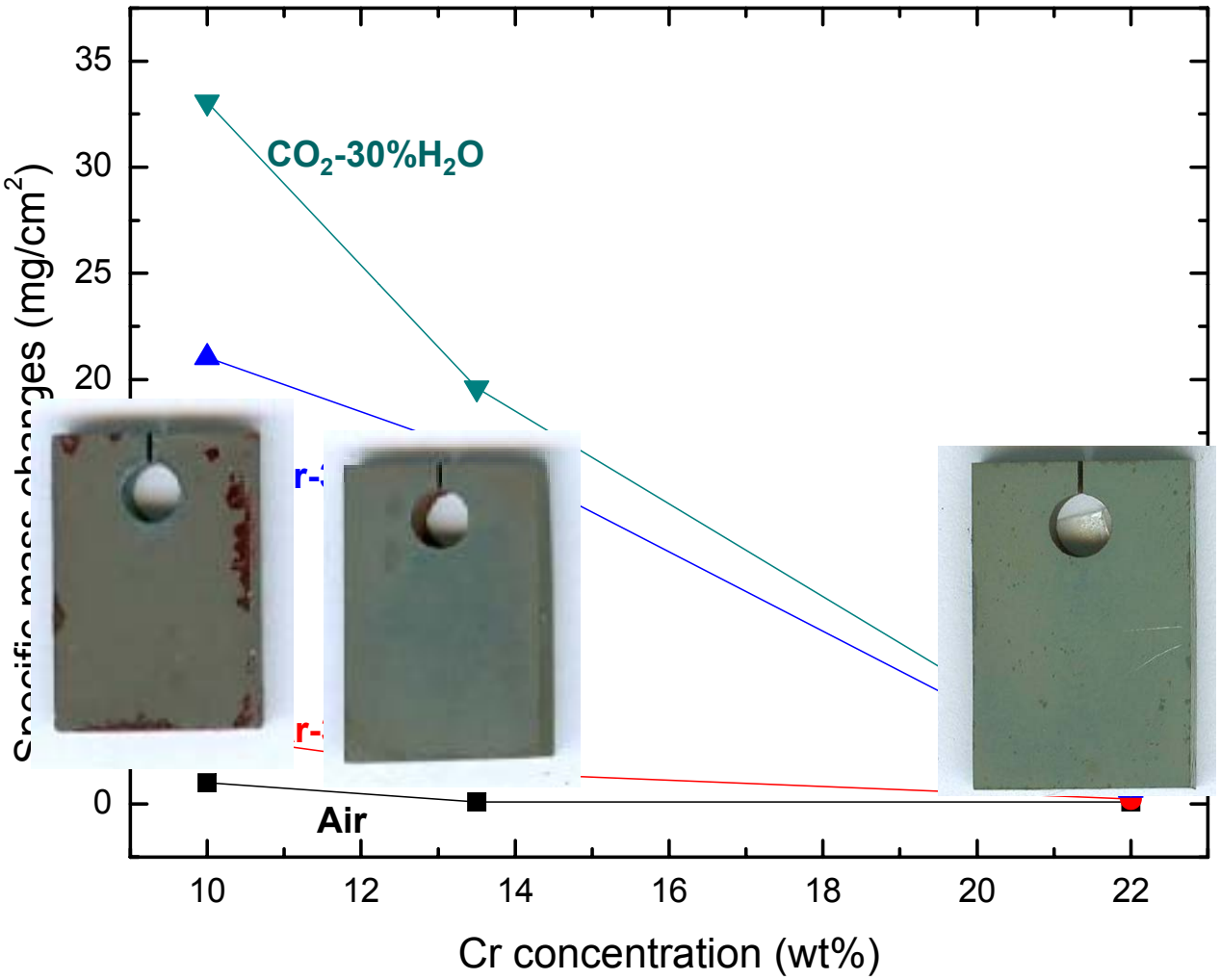


Task 4: Oxidation of Alloys and Coatings



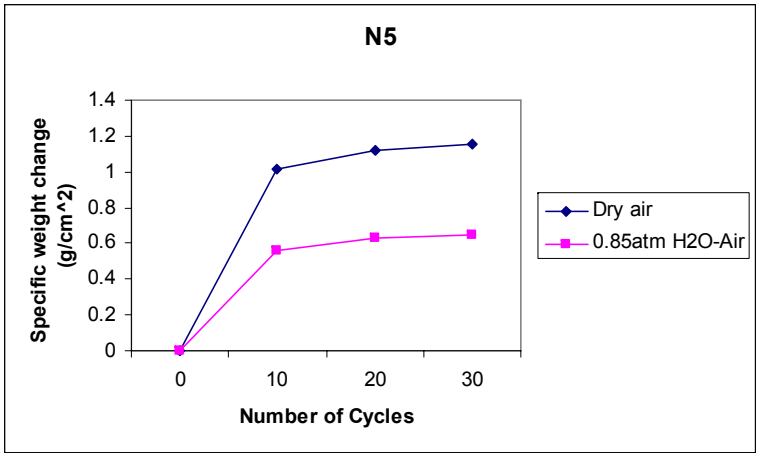
Task 4: Oxidation of Alloys and Coatings

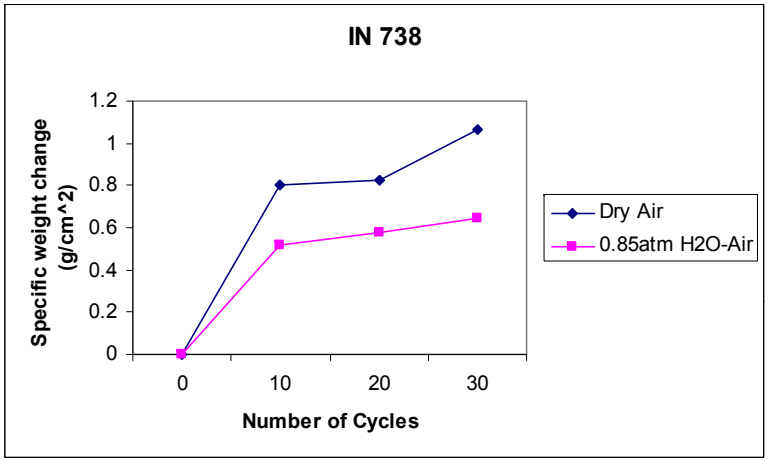
Fe-Cr model alloys - 4 day isothermal exposure at 650°C

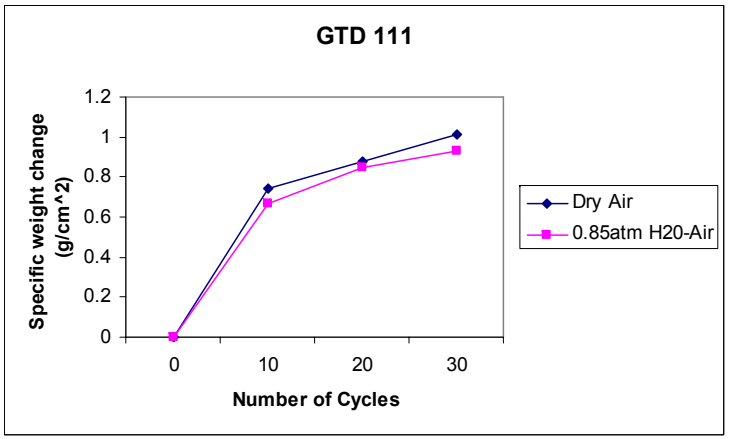


Task 4: Oxidation of Alloys and Coatings

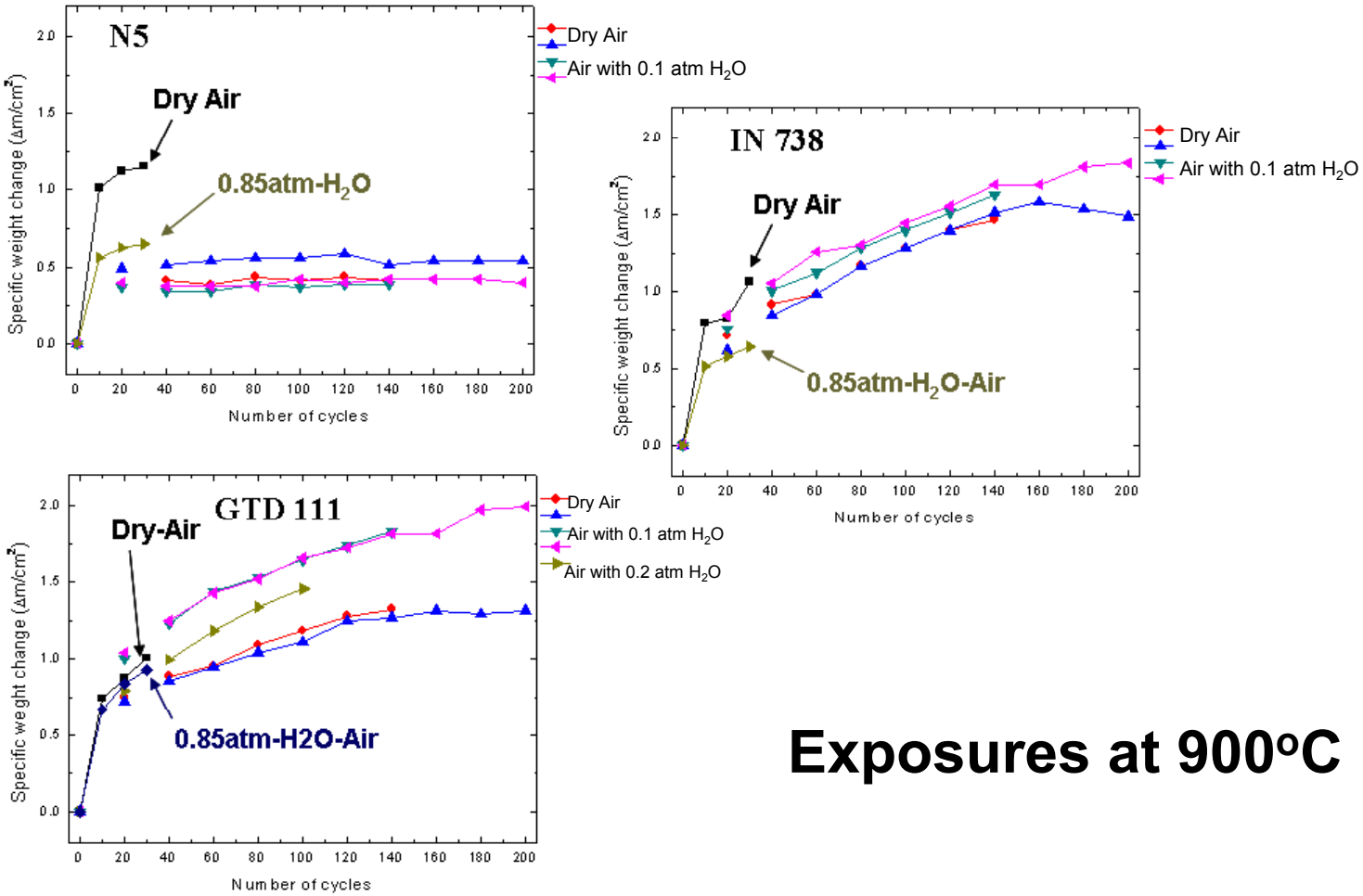
Exposures at 900°C







Task 4: Oxidation of Alloys and Coatings



Exposures at 900°C

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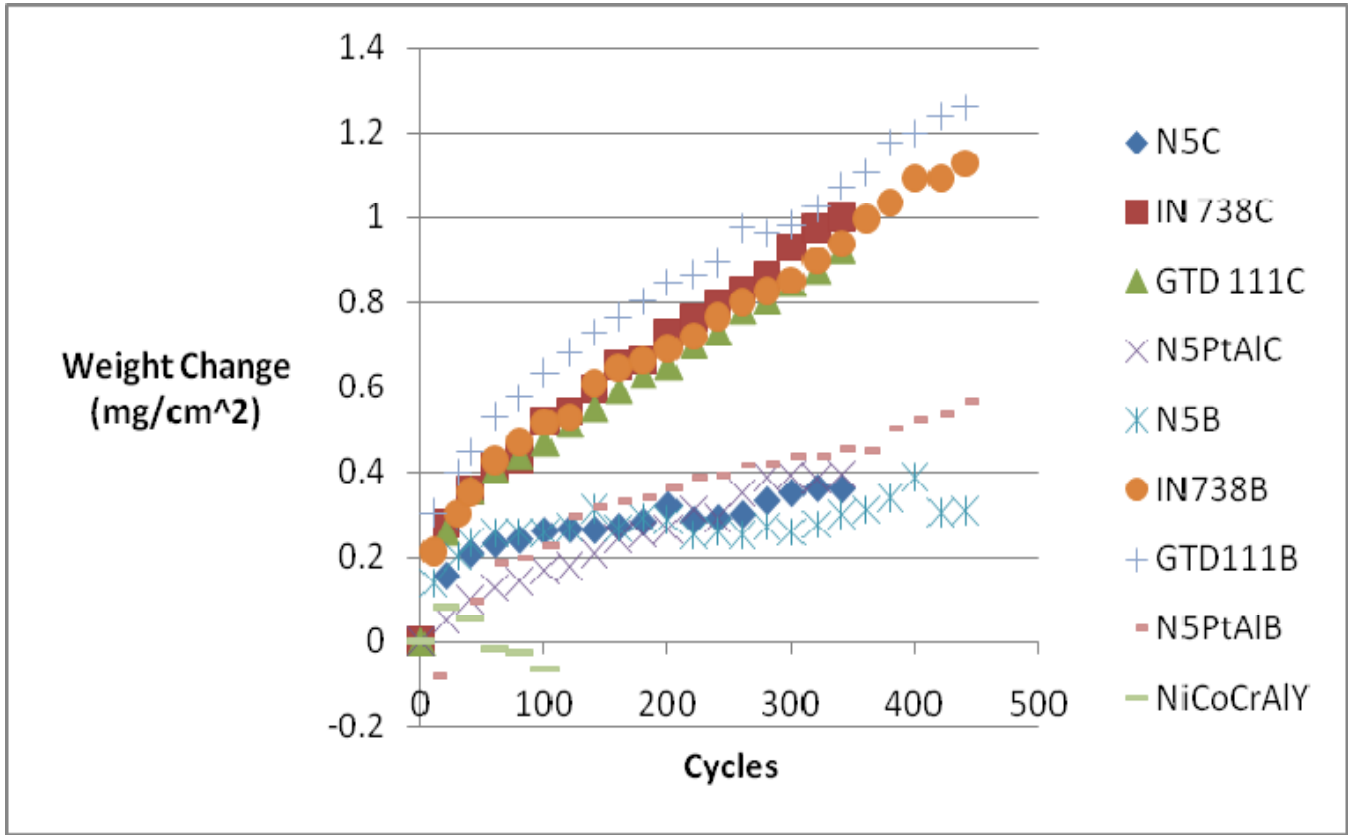
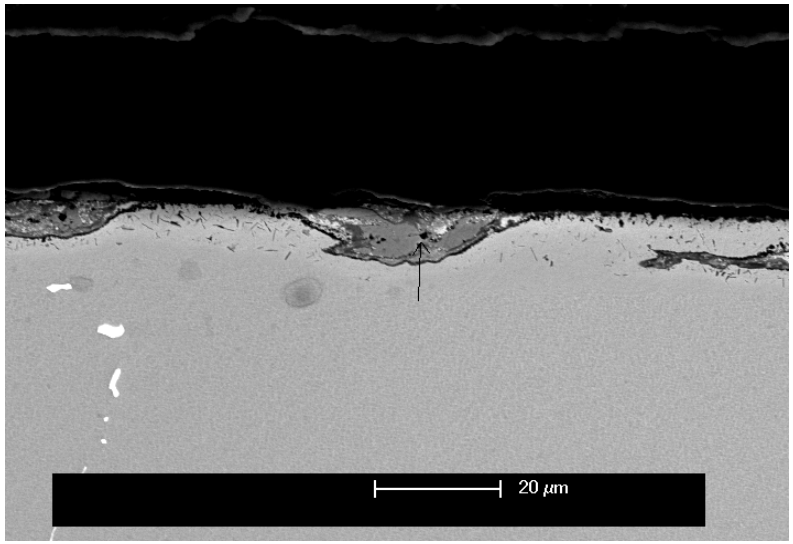
Task 4: Oxidation of Alloys and Coatings

Superalloys and Coatings in 85% H_2O-15%CO_2 – 900°C

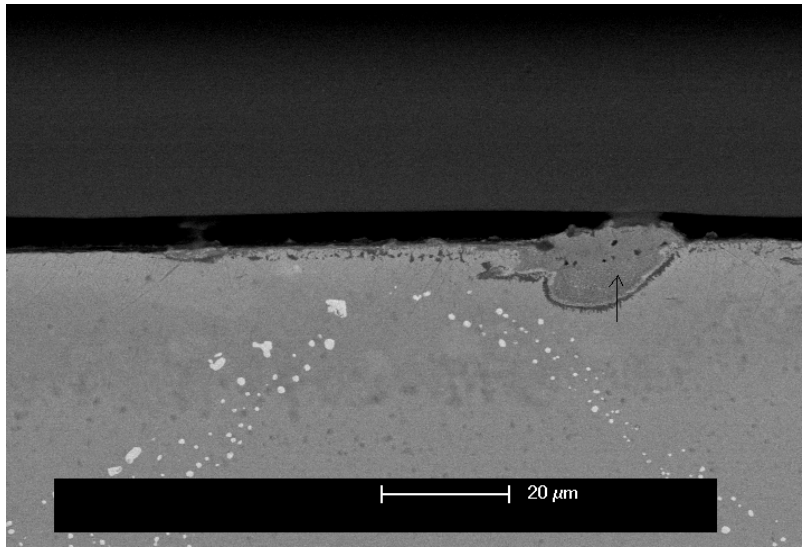


Task 4: Oxidation of Alloys and Coatings

Dry Air



Air – 85% H_2O



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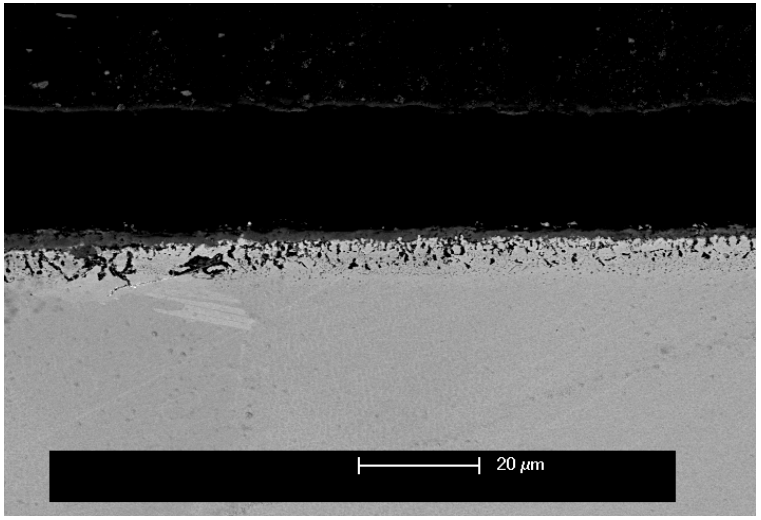
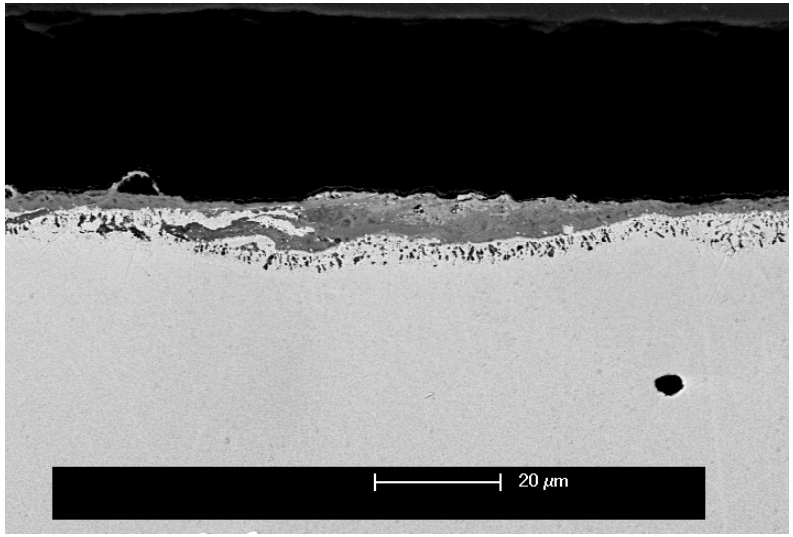
Task 4: Oxidation of Alloys and Coatings

Dry Air



Air – 85% H_2O



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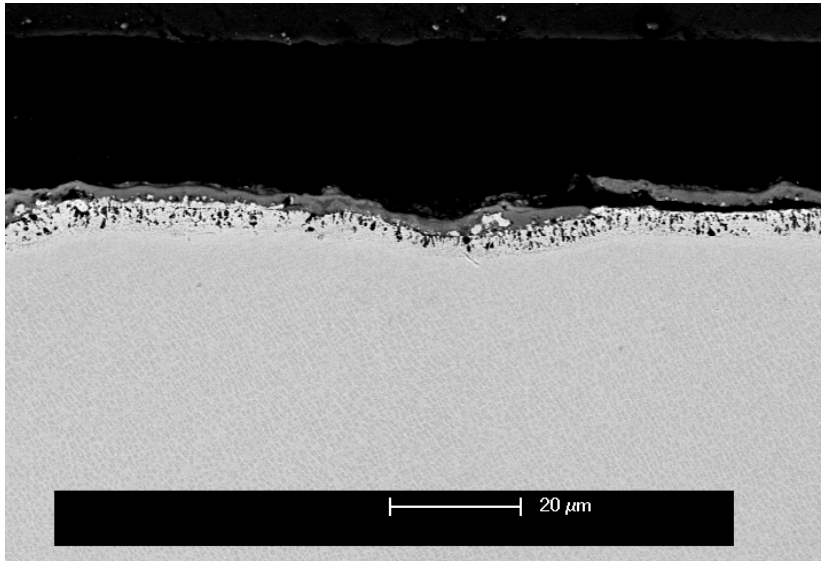
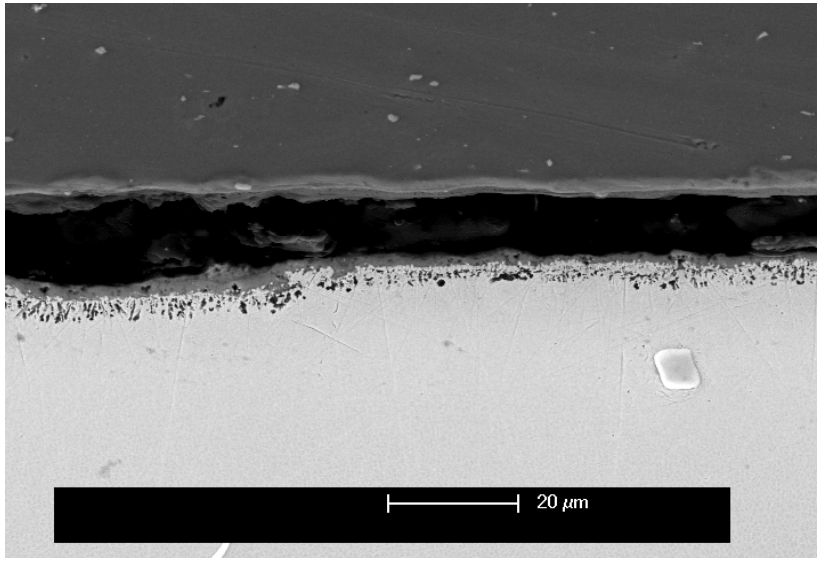
Task 4: Oxidation of Alloys and Coatings

Dry Air



Air – 85% H_2O



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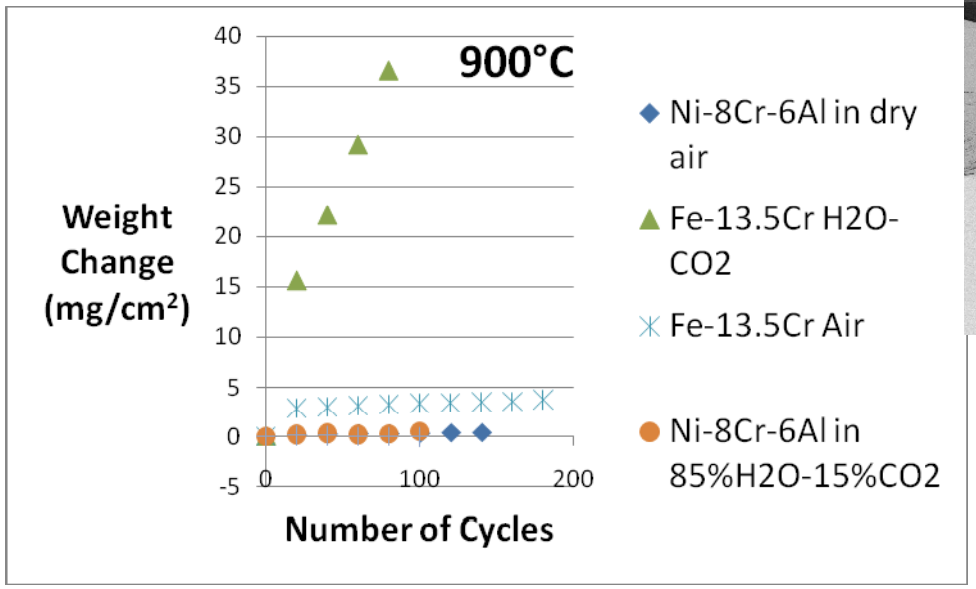
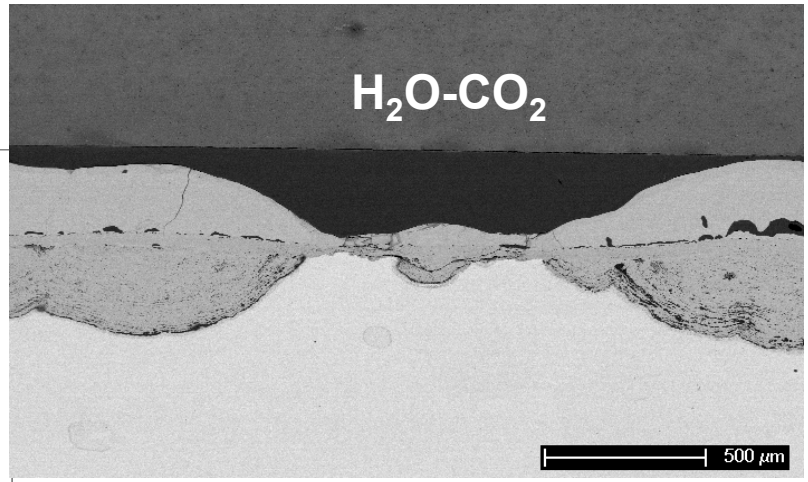
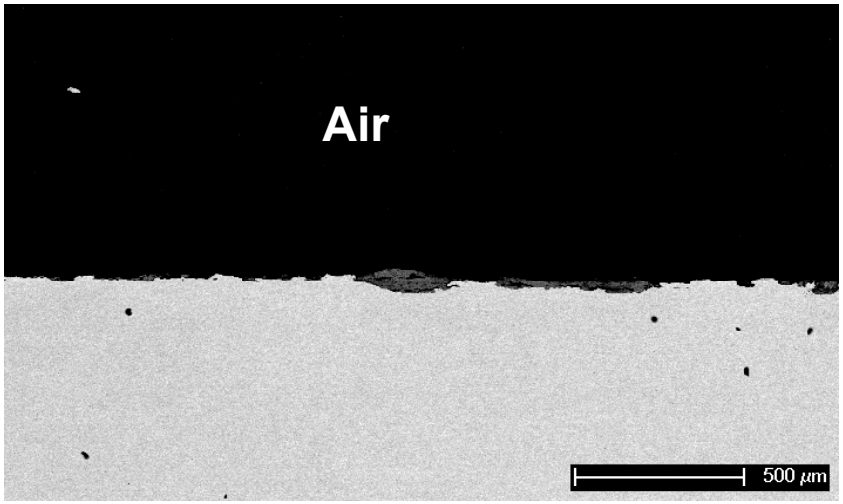
Task 4: Oxidation of Alloys and Coatings

Model Alloys

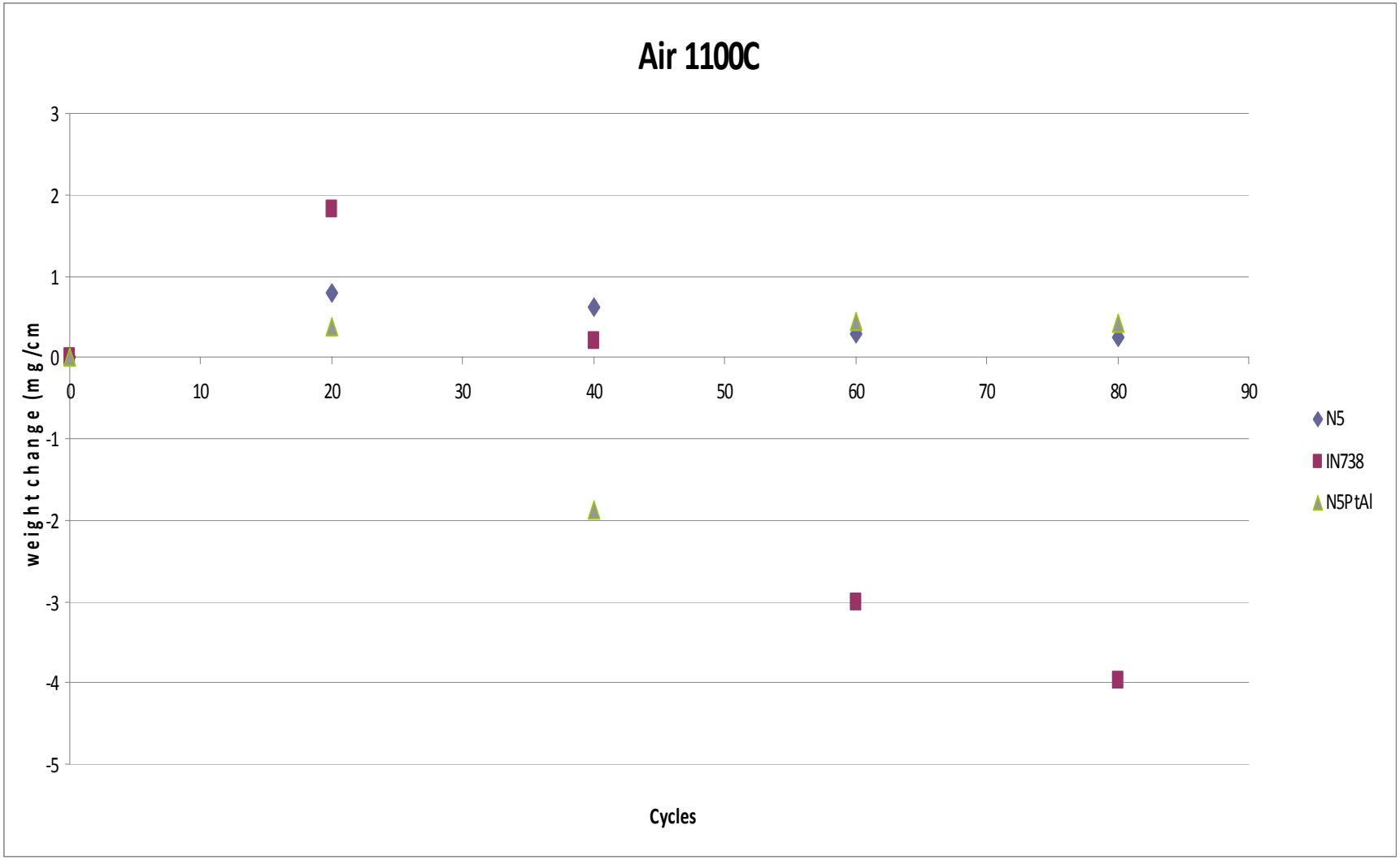


Fe-13.5%Cr





Task 4: Oxidation of Alloys and Coatings



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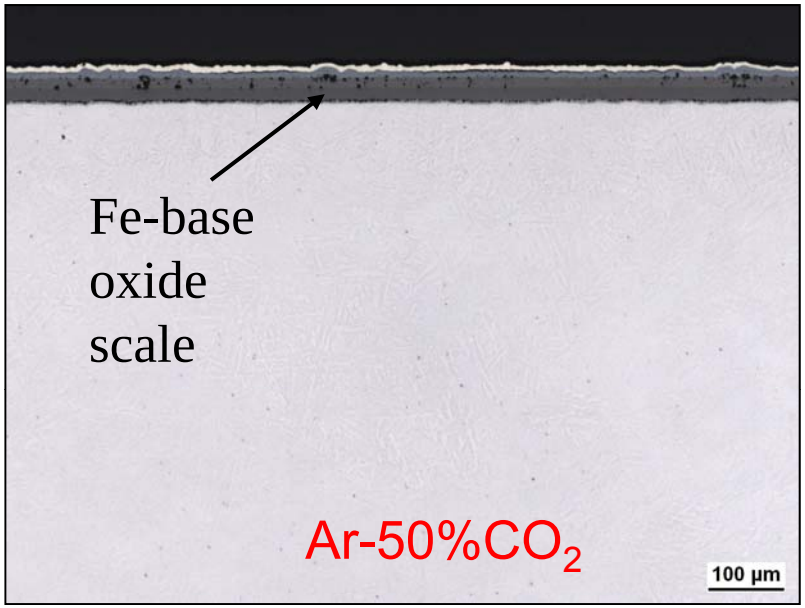
Task V Excess Oxygen Effects

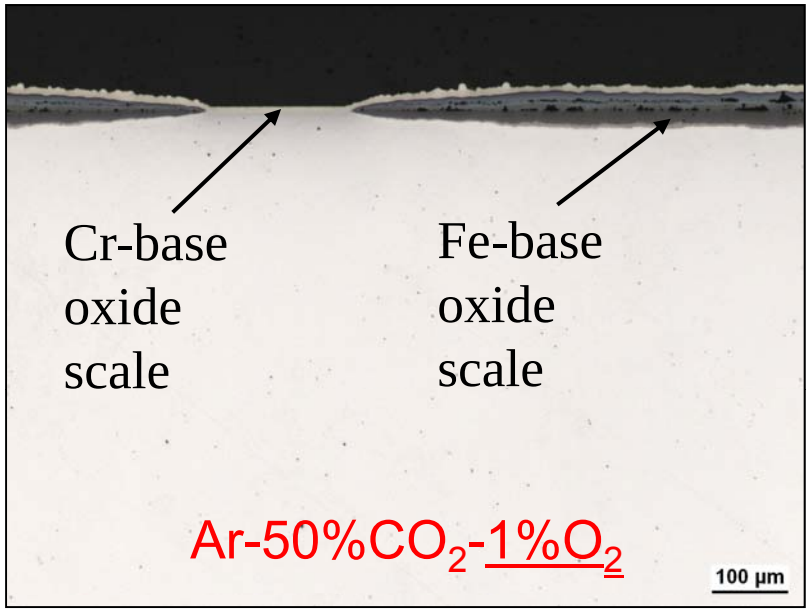
Equilibrium Gas Compositions for Input Gas of 80% H_2O-15% CO_2-5%O_2

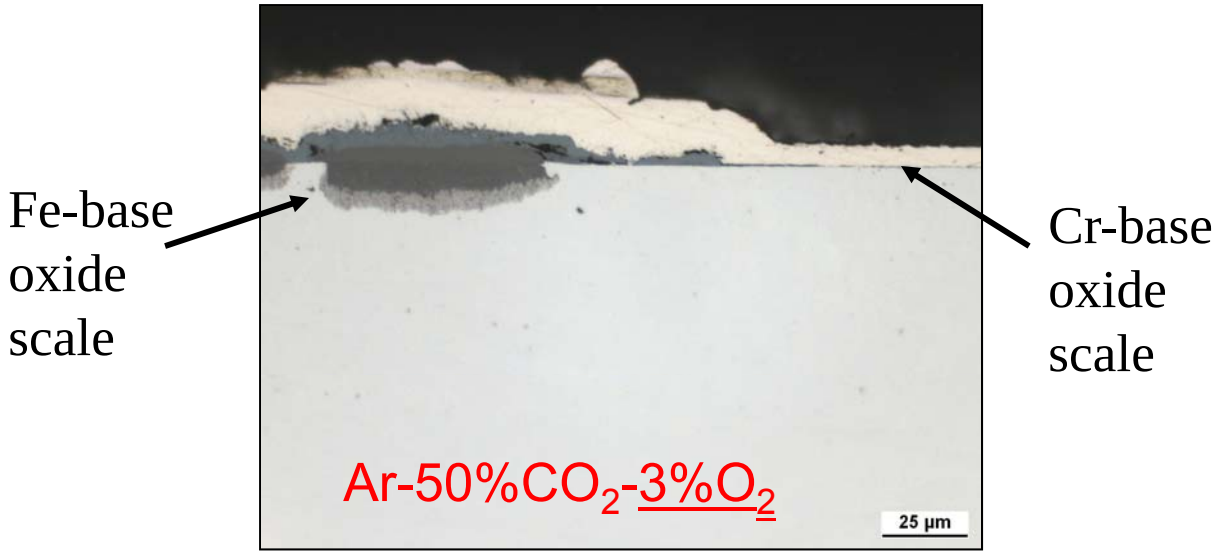
Temperature (°C)	700	900	1100
H_2O	~0.80	~0.80	~0.80
CO_2	~0.15	~0.15	~0.15
H_2	1.4×10^{-10}	2.5×10^{-8}	1.1×10^{-6}
CO	1.6×10^{-11}	6.2×10^{-9}	4.1×10^{-7}
O_2	~0.05	~0.05	~0.05

Task V Excess Oxygen Effects

Fe-9%Cr







Task V Excess Oxygen Effects

Effect of CO_2 On Selective Oxidation of Cr

$$N_{Cr}^{(1)} > \left[\frac{\pi g^*}{3} N_O^{(S)} \frac{D_O V_m}{\tilde{D}_{Fe-Cr} V_{CrO_{1.5}}} \right]^{1/2} + N_{Cr}(\text{Carbide})$$

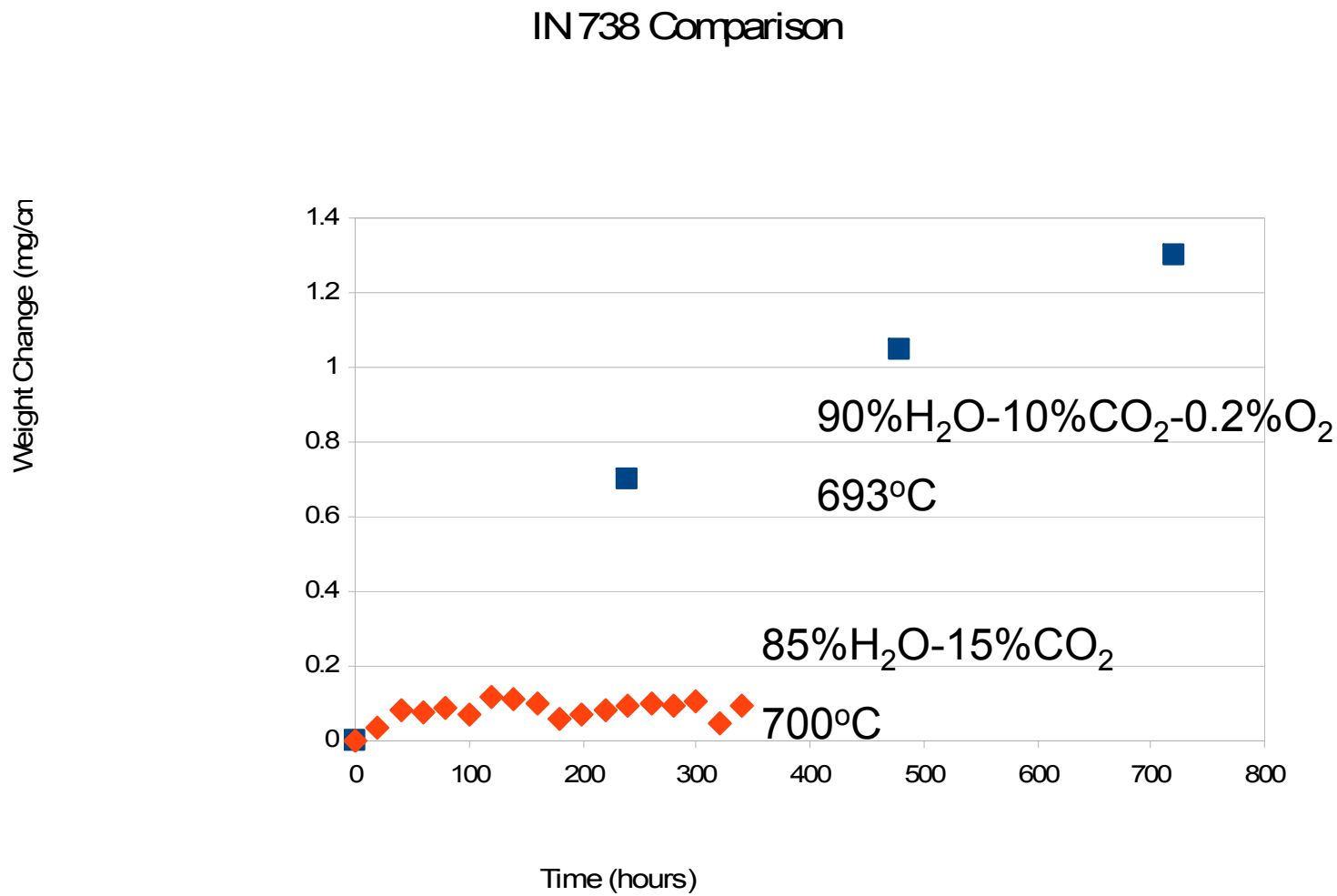
$CO_2(g) = O(Ox) + CO(g)$

↑

$O_2(g)$

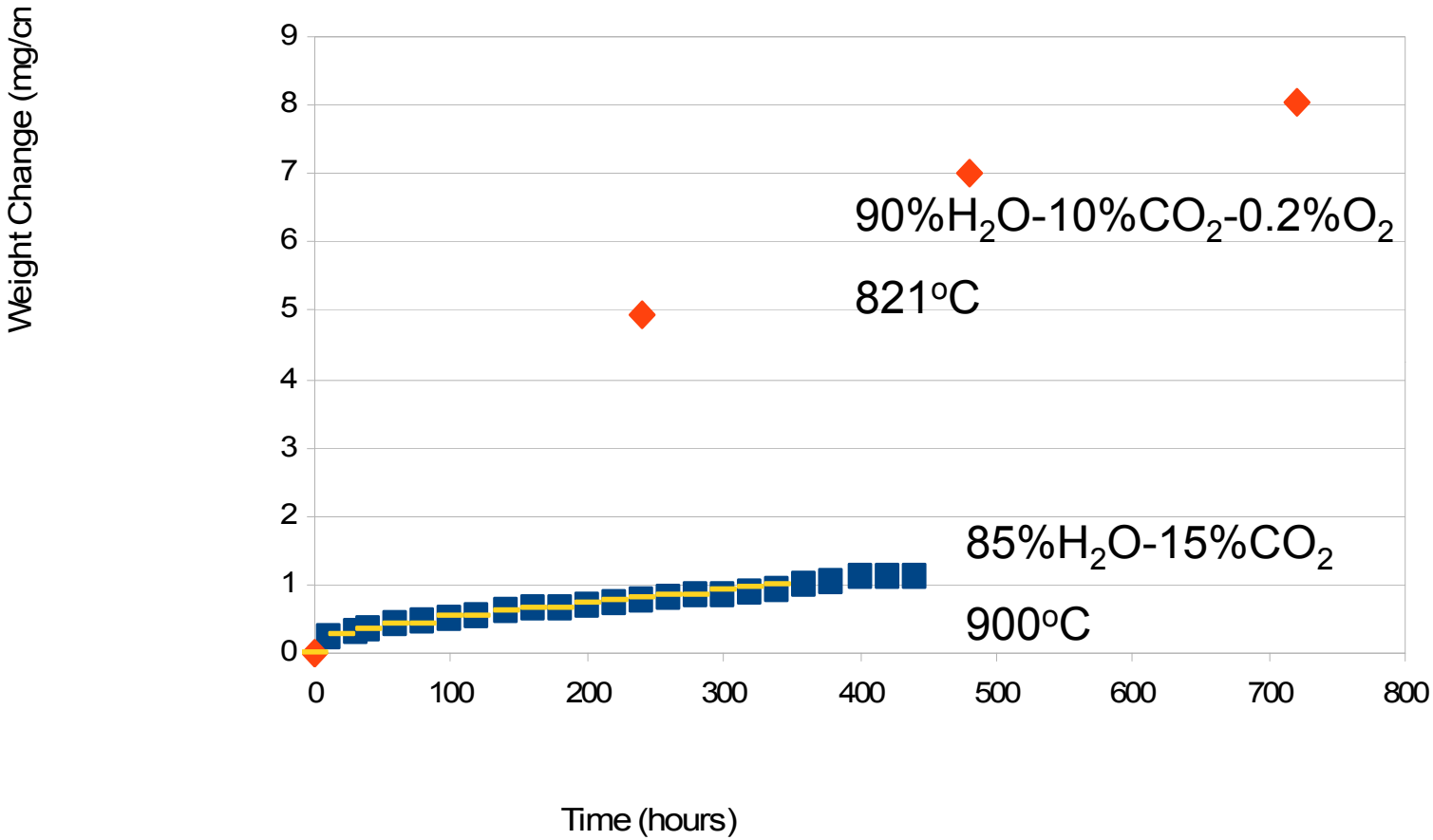
The presence of excess O_2 provides a source of oxygen in addition to the CO_2 molecules and decreases $N_{Cr(}$(Carbide).

Task V Excess Oxygen Effects



Excess-O_2 results provided by
G. Holcomb, NETL-Albany

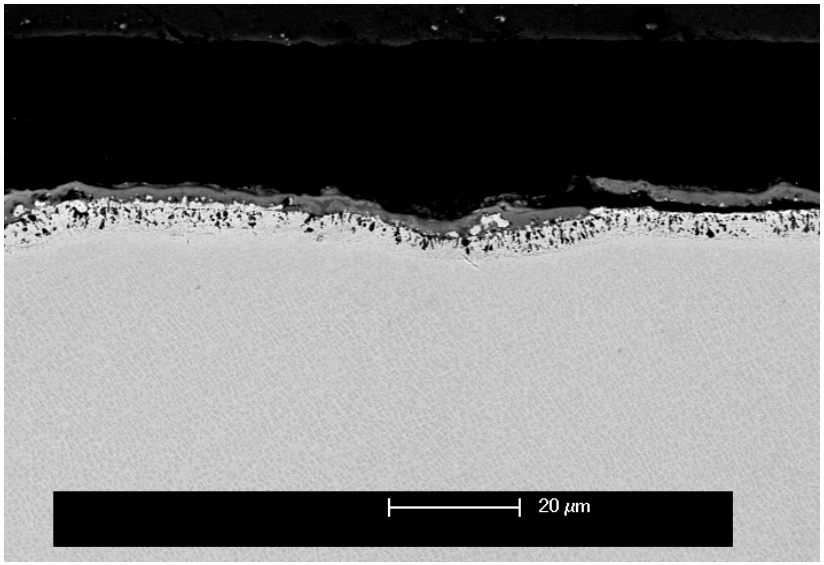
Task V Excess Oxygen Effects

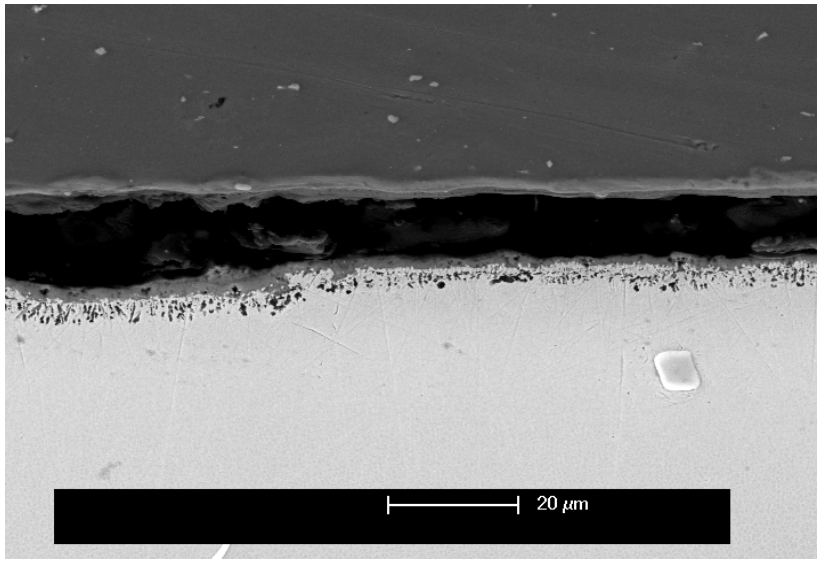


Excess-O_2 results provided by G. Holcomb, NETL-Albany

Task V Excess Oxygen Effects

Dry Air **900°C** **85% H_2O-15%Air**





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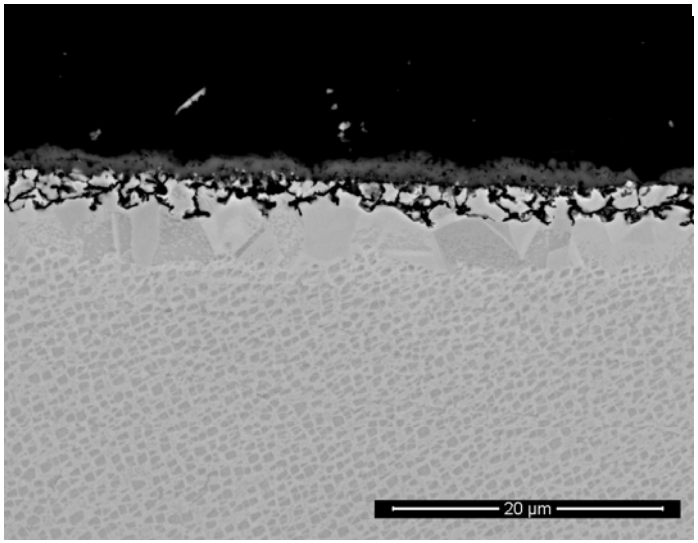

821°C

90%H_2O-10%CO_2-0.2%O_2

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Summary: Tasks I - V

Task I: Alloys and Coatings have been acquired

Task II: Exposure Apparatus has been modified.

Task III: Background literature results have been analyzed.

Task IV: Alloys and Coatings with sufficient Cr/Al concentrations are no more severely degraded in H_2O/CO_2 than in dry air.

Alloys which are borderline chromia/alumina-formers are severely degraded in H_2O/CO_2 atmospheres.

CO_2 effects are associated with carburization.

H_2O effects are associated with enhanced internal oxidation.

Task V: Excess oxygen tends to alleviate the detrimental carburization effects for exposures in CO_2.

The effects of excess oxygen in H_2O base atmospheres are not well-defined and require further study.

Project Status

		Quarter											
Task	**Description**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
I	**Preparation of Test Specimens**												
II	**Modification of Equipment**												
III	**Establish Baseline for Comparison**												
IV	**Testing in 85% H_2O – 15% CO_2**												
V	**Testing in 80% H_2O – 15% CO_2- 5% O_2**												
VI	**Determine Effects of Contaminants**												
VII	**Influence of H_2O – CO_2 Gases on TBC's**												

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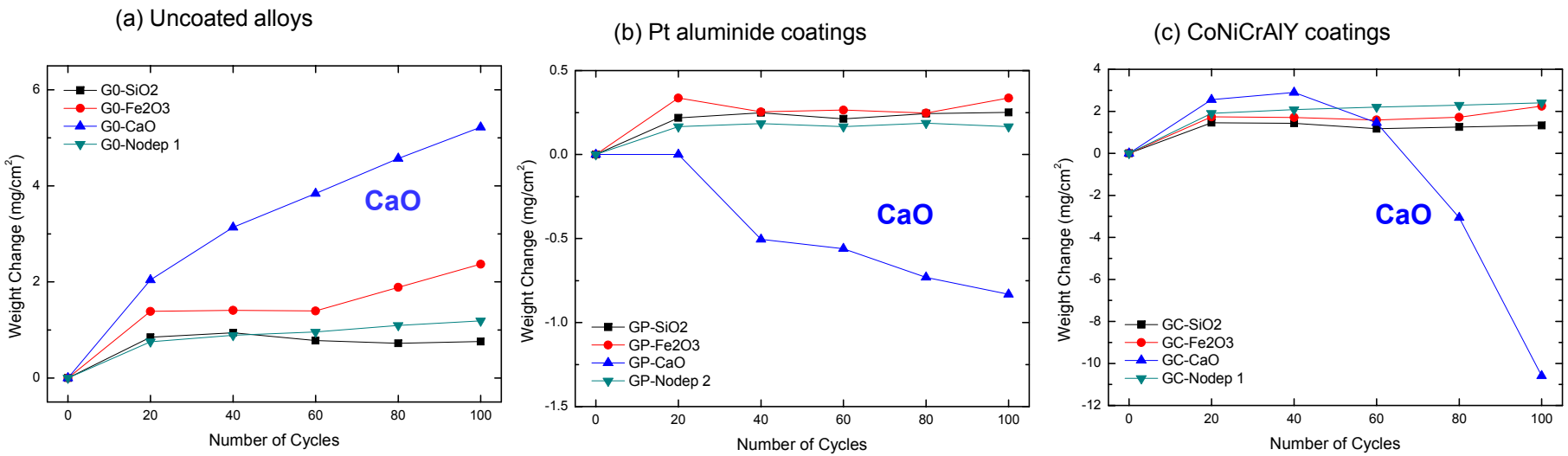
Work to be Performed in Next Six Months

- Continue Task V study of Excess Oxygen Effects
- Task VI Study of Contaminant Effects
- Begin Task VII Evaluation of TBC Degradation

Task VI Contaminant Effects

Effect of Deposits of CaO, Fe_2O_3, and SiO_2 on Coated and Uncoated GTD-111at 900°C in Air



Task VII Degradation of TBCs in H_2O-CO_2 Atmospheres

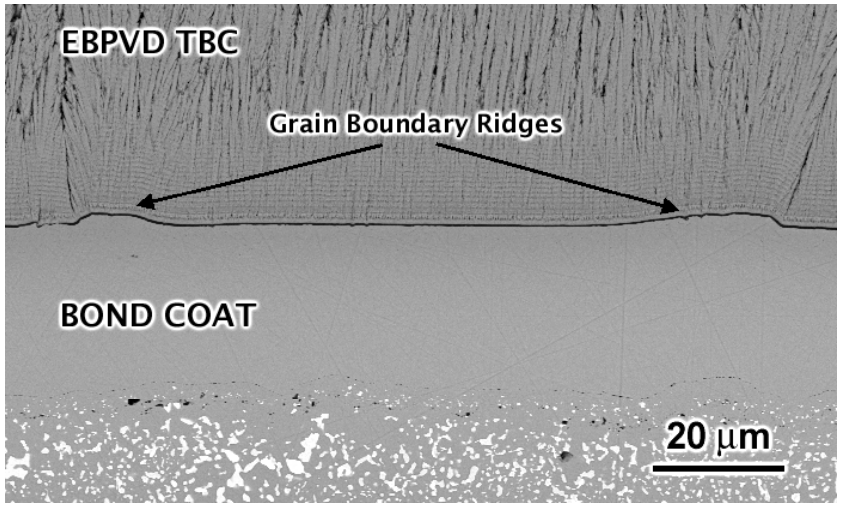
Substrate: **GTD-111**

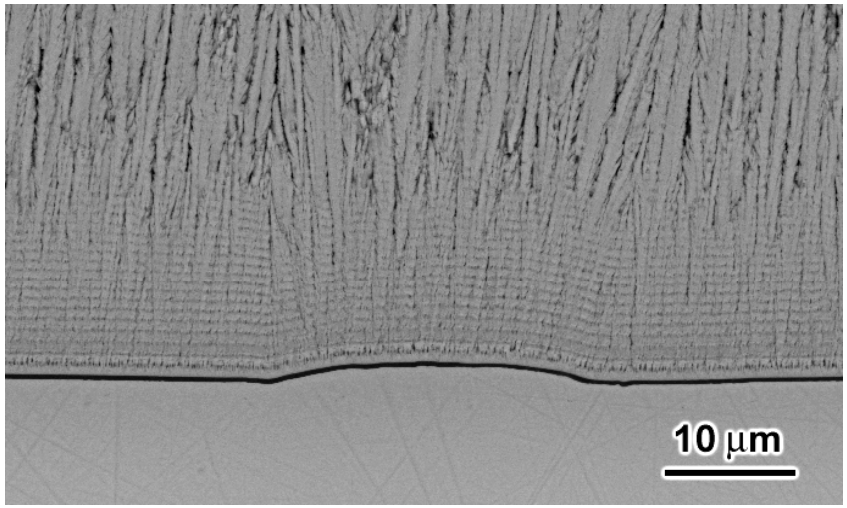
Bond Coat: **Ar-shrouded Plasma Sprayed NiCoCrAlY**

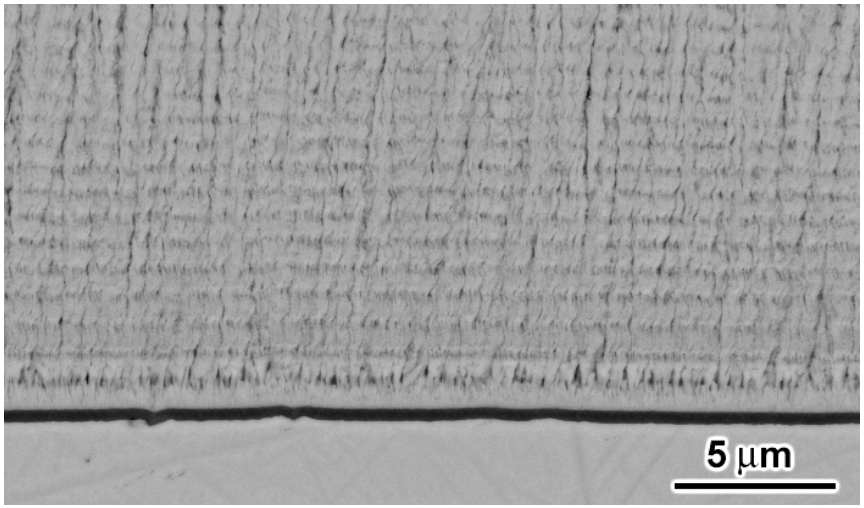
Topcoats: **EBPVD YSZ**

Air Plasma Sprayed YSZ

As Processed EBPVD TBC on Pt-Aluminide Bond Coat

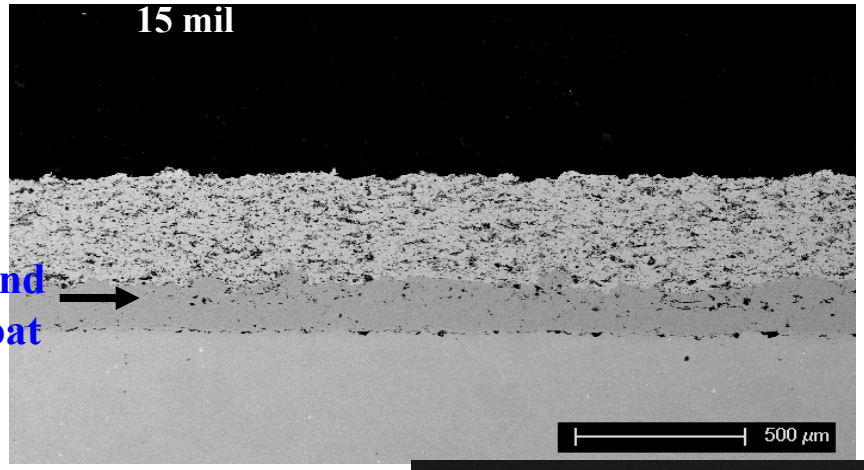


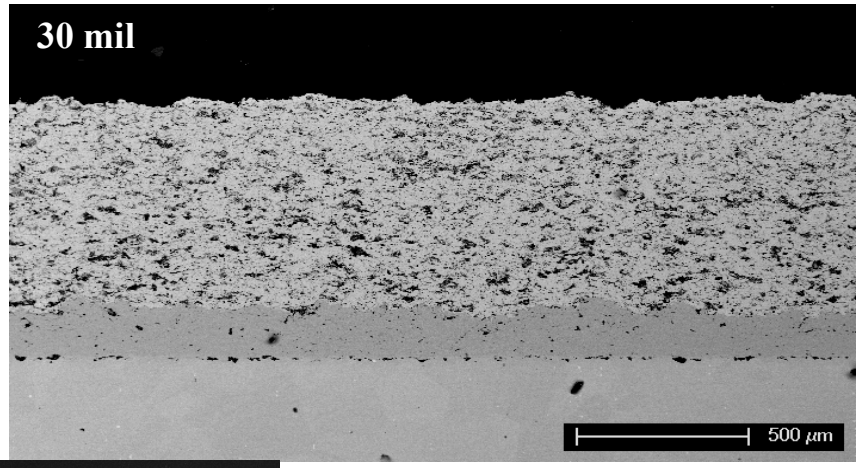


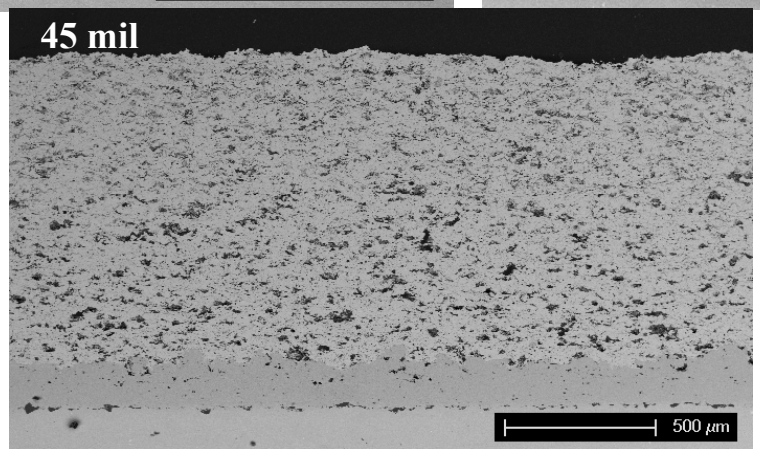


- *Very flat interface away from the grain boundary ridges*
- *Dense TBC with parallel rows of pores close to TGO*

As-Processed High-Purity Low-Density TBCs on NiCoCrAlY Bond Coat





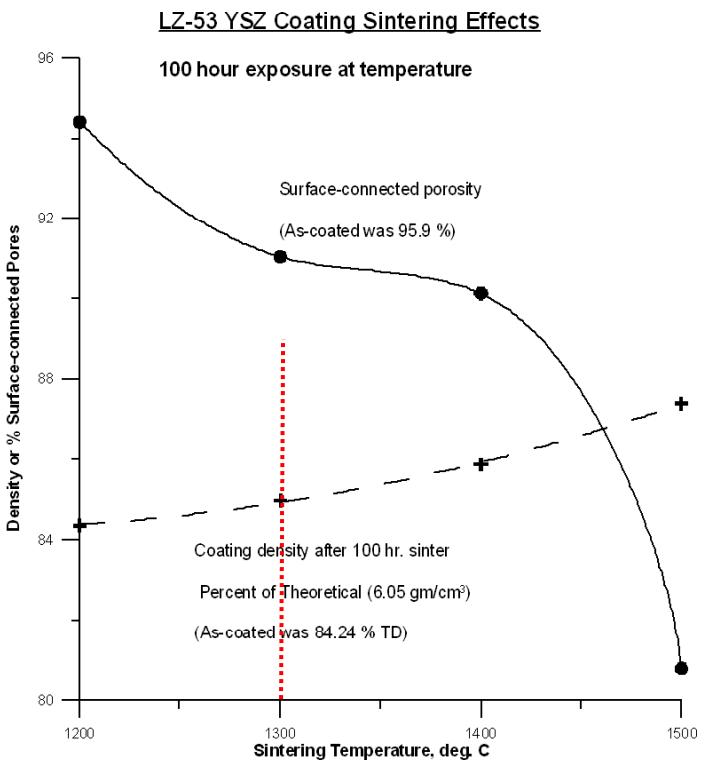


15 mil ≈ 375 µm

30 mil ≈ 750 µm

45 mil ≈ 1125µm = 1.125 mm

High-Purity Low-Density APS-TBC



Cycle Lifetimes w/ Exposure at 1100C		
Substrate	TBC Thickness (mils)	Cycles to Failure
IN718	15 (375μm)	300
IN718	30 (750μm)	150
IN718	45 (1,125μm)	60
HA188	15	840
HA188	45	330
N5	15	940
N5	45	520

Failure Times for SOA 125μm EBPVD TBCs

NiCoCrAlY Bond Coat – 100cycles

Pt-Aluminide Bond Coat 1000 cycles

No measurable transformation to monoclinic phase at 1300°C.

As-sprayed κ < 1 w/m K.

M. A. Helminiak, Surface Coatings & Tech., in press.

Surface photographs of 7YSZ TBC specimens

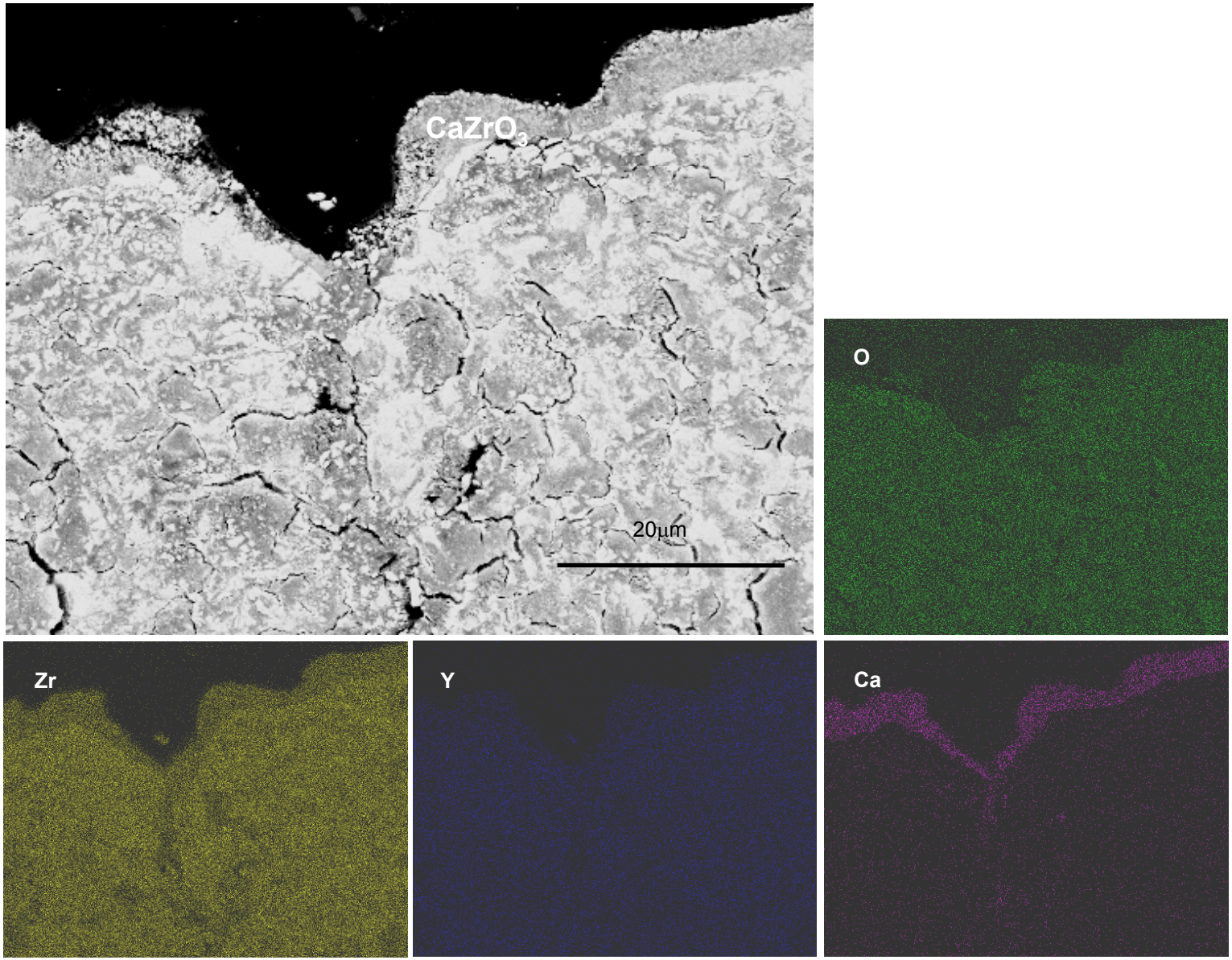
: isothermally exposed in dry air up to 200 hours with and without CaO deposits

Grey – ZrO_2 under reducing conditions during the plasma-spray process.

White - ZrO_2 via oxygen saturation during exposure

Elemental mapping showing the formation of Ca zirconates

: APS 7YSZ TBC – isothermally exposed for 200 hours at 950°C with CaO deposits



Questions ?