Materials for Oxy-Fuel Turbomachine Conditions

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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.

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 gases containing 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.

Specific Objectives Phase II

1. Evaluating the performance of thermal barrier coatings in environments which are rich in steam and CO_2.

Outline

Phase I Results

Degradation of Superalloys and Metallic Coatings

Phase II Results

Degradation of Thermal Barrier Coatings

Mechanisms of Degradation Induced by H_2O and CO_2

Phase I Results

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%)

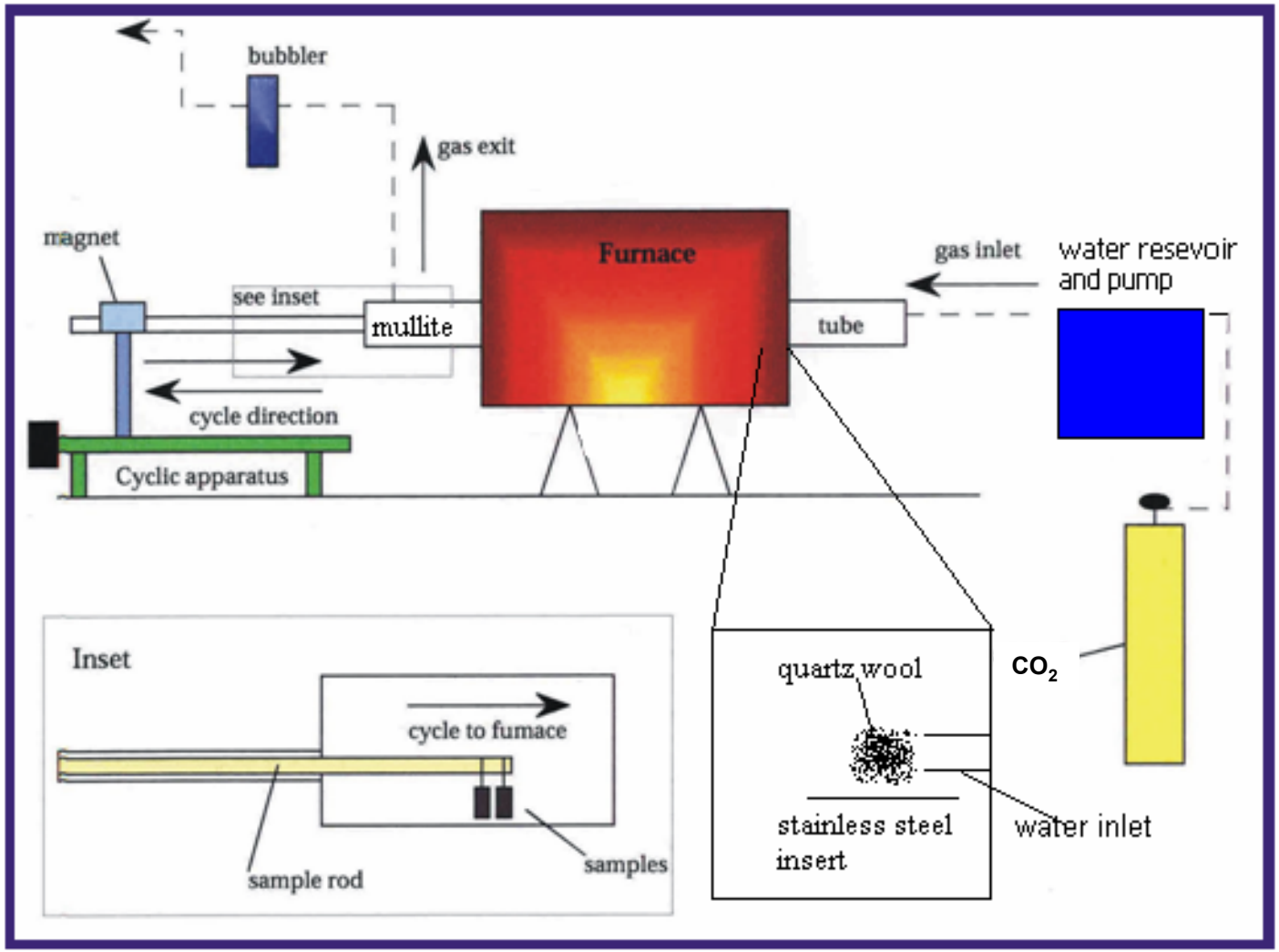
coating	Ni	Co	Cr	Al	Y	Pt
NiCoCrAlY	Bal.	22.5	16.5	13.5	0.5	-
Pt-modified Aluminide †	42	-	-	23	-	35

† 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.

Task 4: Oxidation of Alloys and Coatings

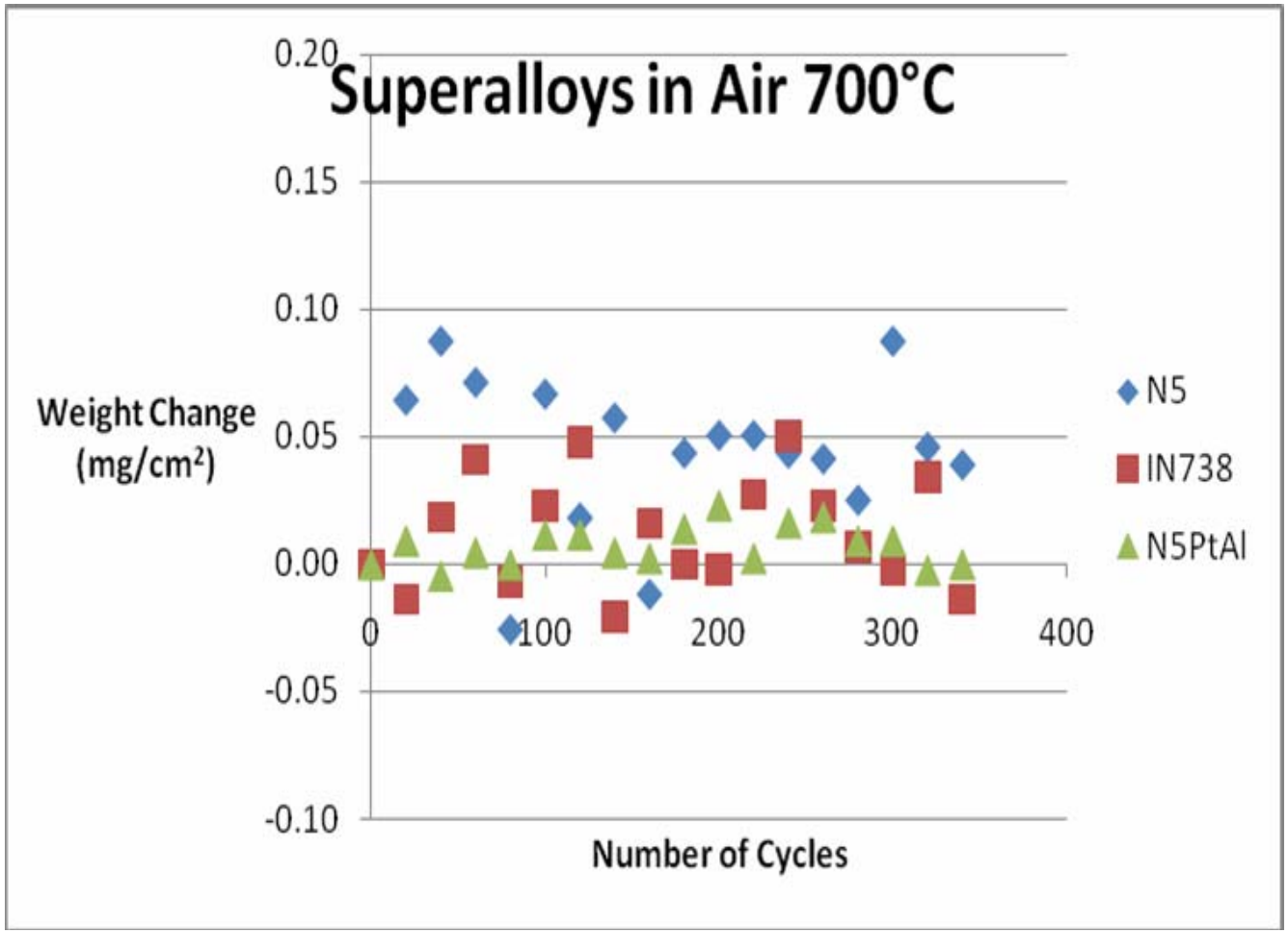
Equilibrium Gas Compositions for Input Gas of 85% H_2O-15% CO_2

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}

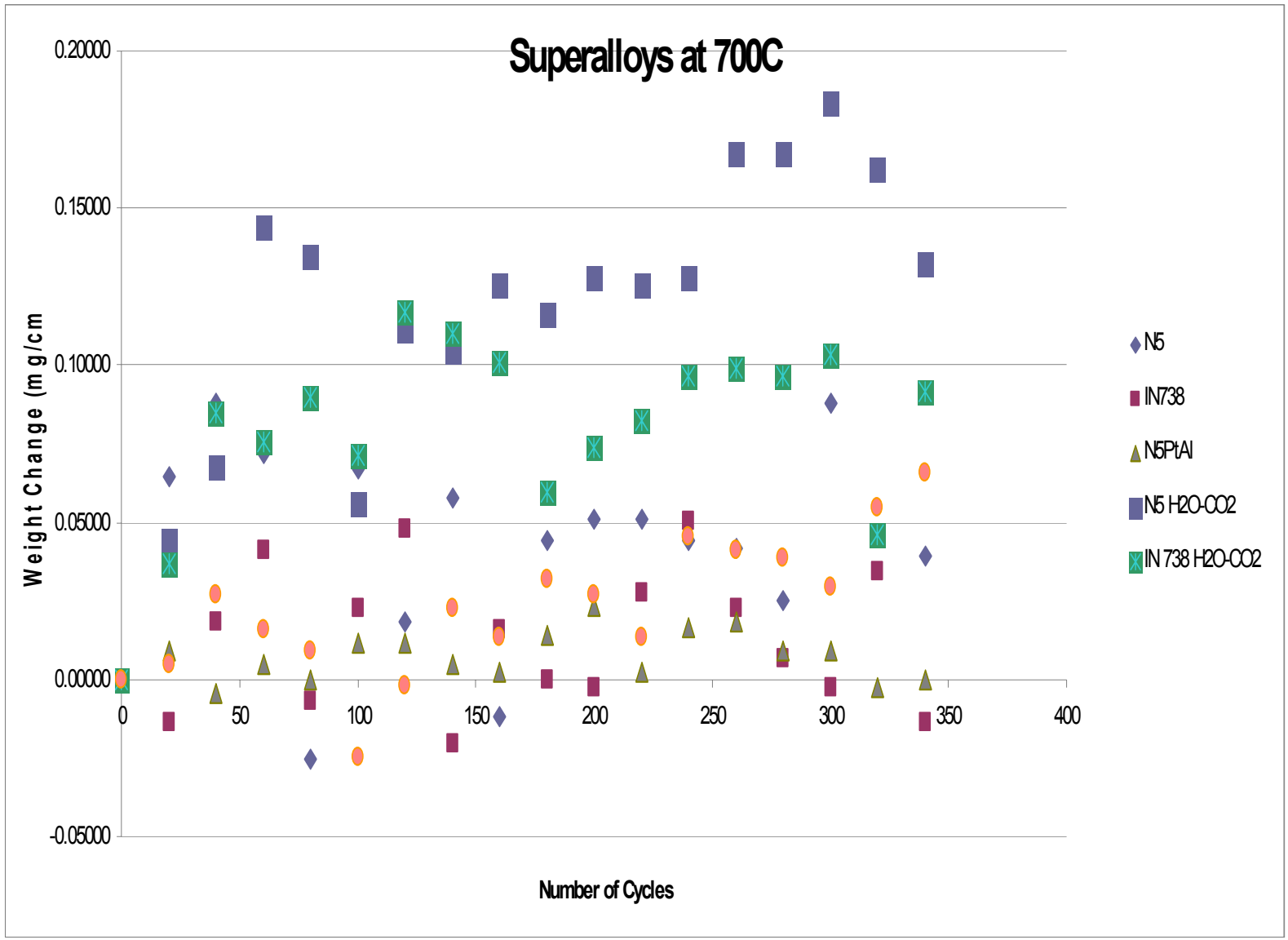
Task 4: Oxidation of Alloys and Coatings

Air Exposures at 700°C



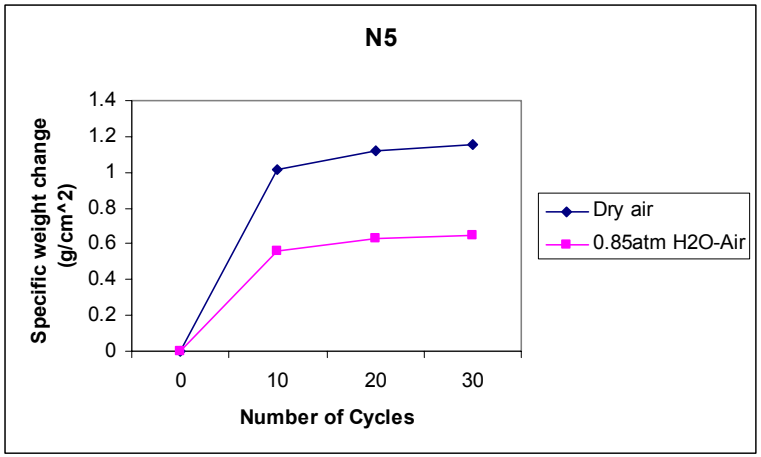
Task 4: Oxidation of Alloys and Coatings

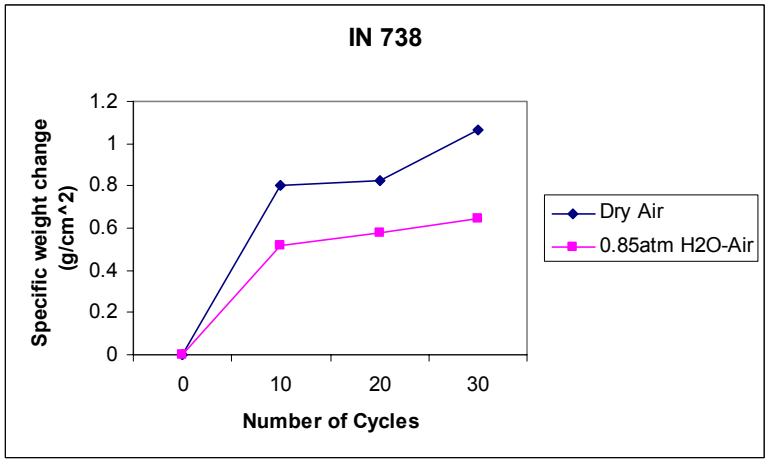
Exposures in H_2O-CO_2 at 700°C

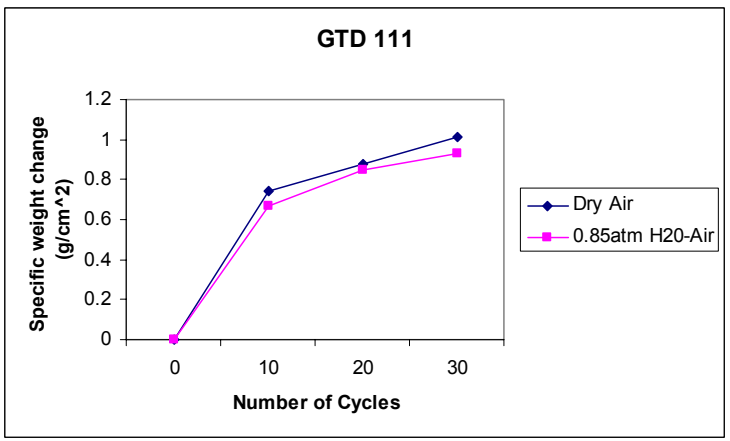


Task 4: Oxidation of Alloys and Coatings

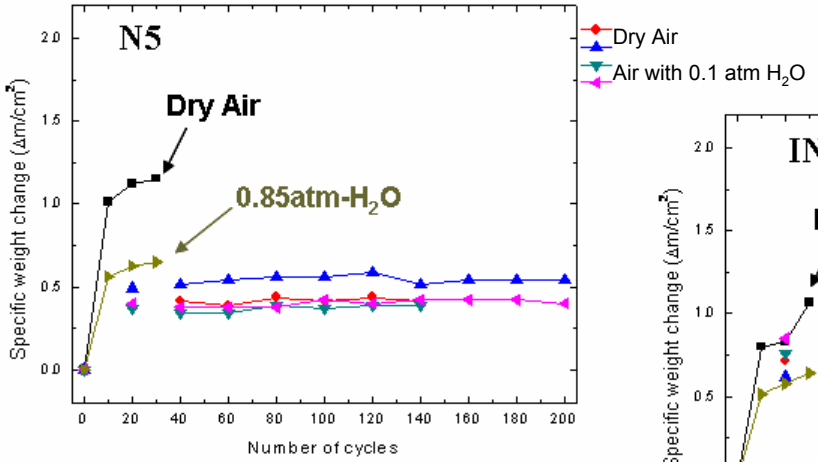
Exposures at 900°C

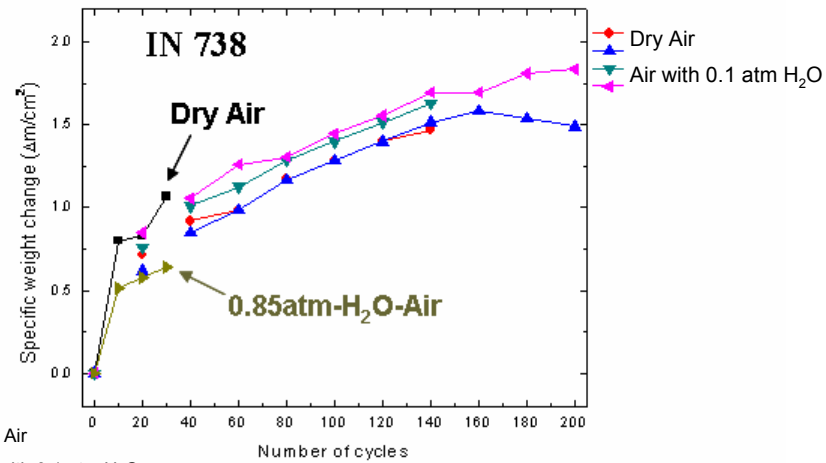


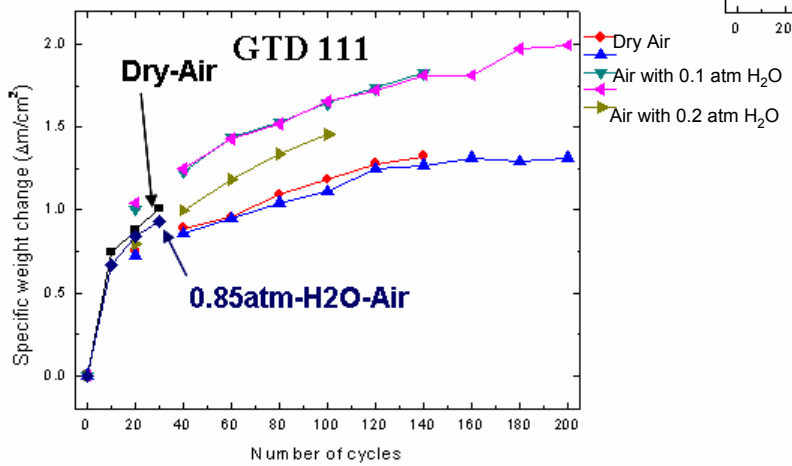




Task 4: Oxidation of Alloys and Coatings



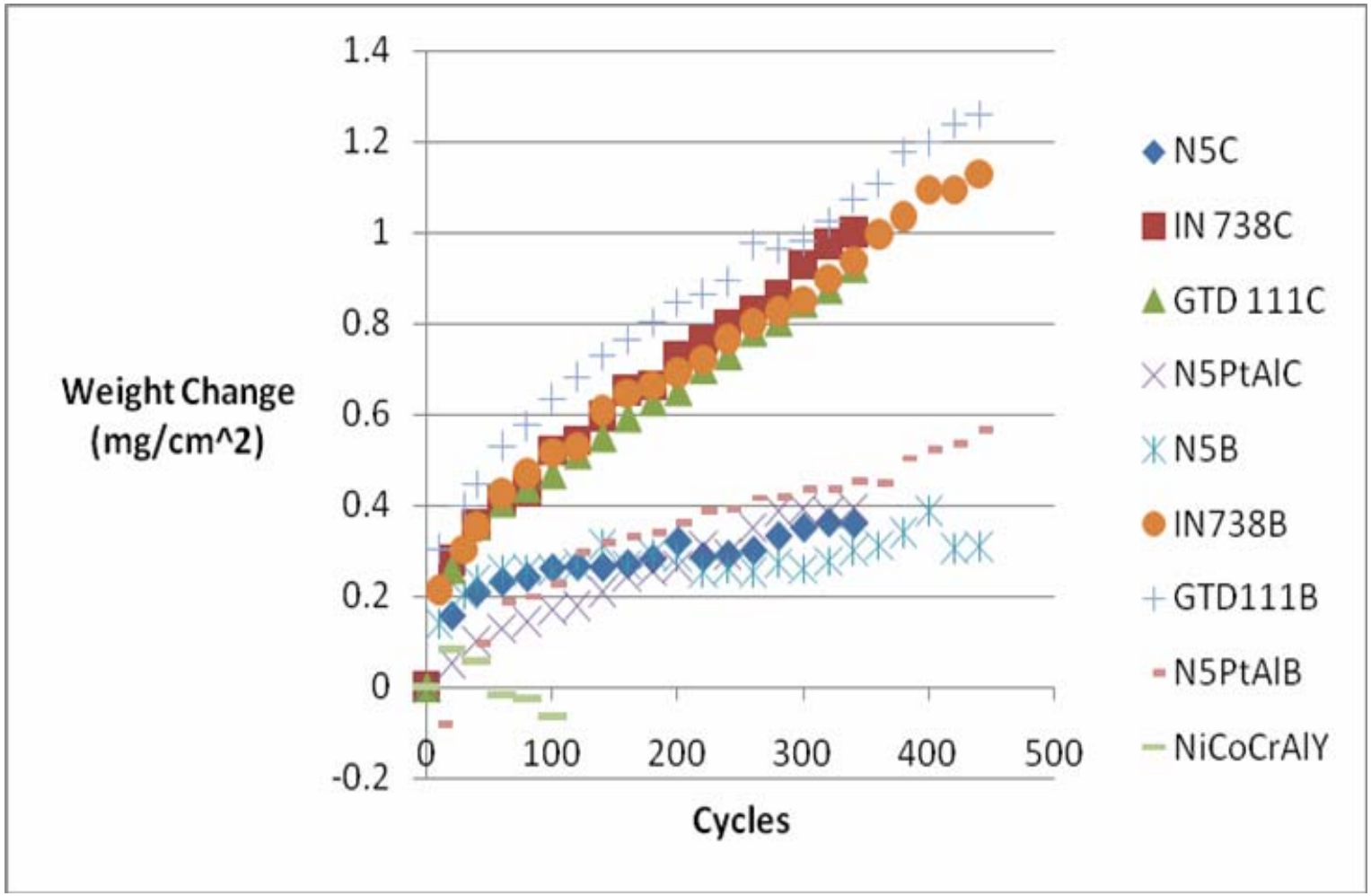




Exposures at 900°C

Task 4: Oxidation of Alloys and Coatings

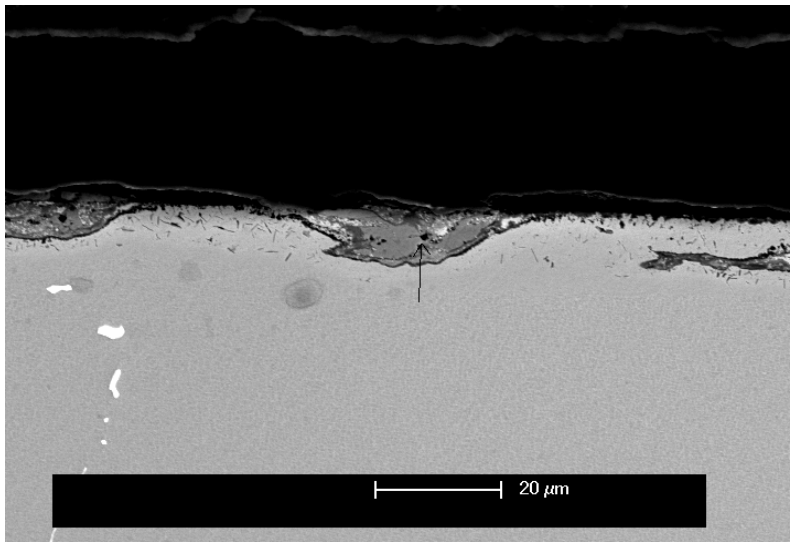
Superalloys and Coatings in 85% H_2O-15%CO_2 – 900°C



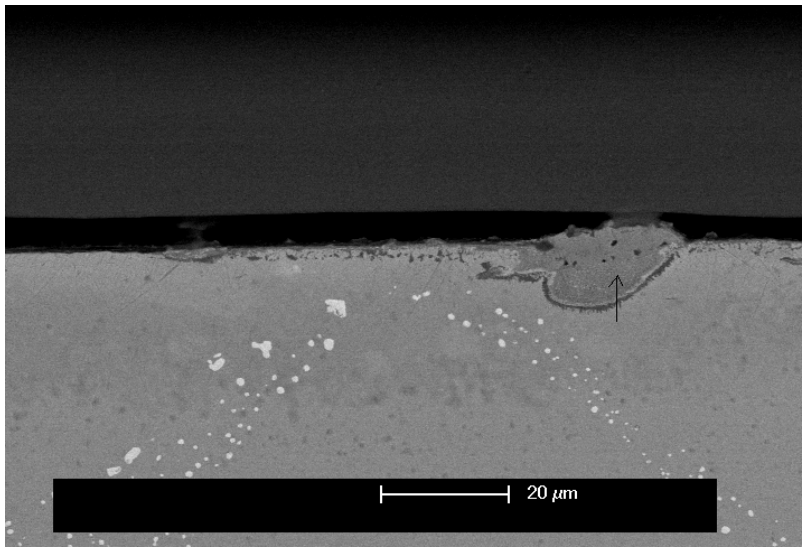
Task 4: Oxidation of Alloys and Coatings

Exposures at 900°C

Dry Air



Air – 85% H_2O

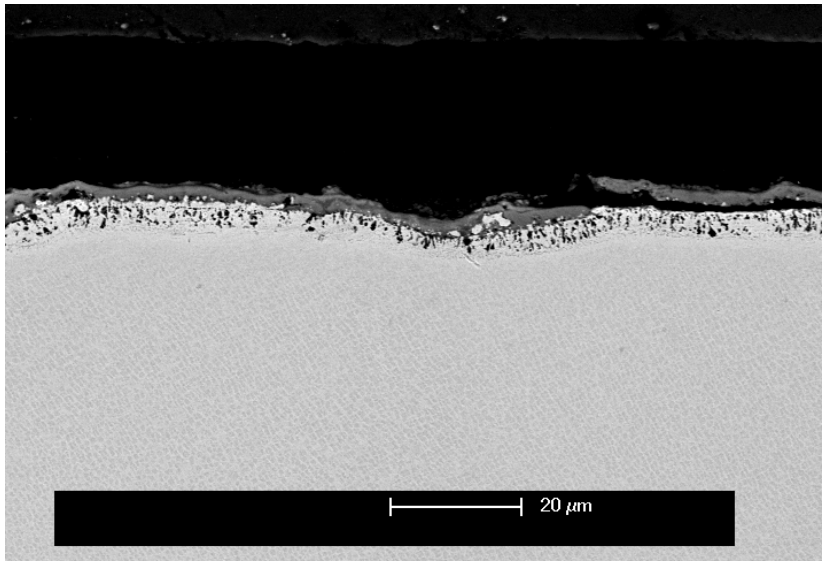


Rene N5

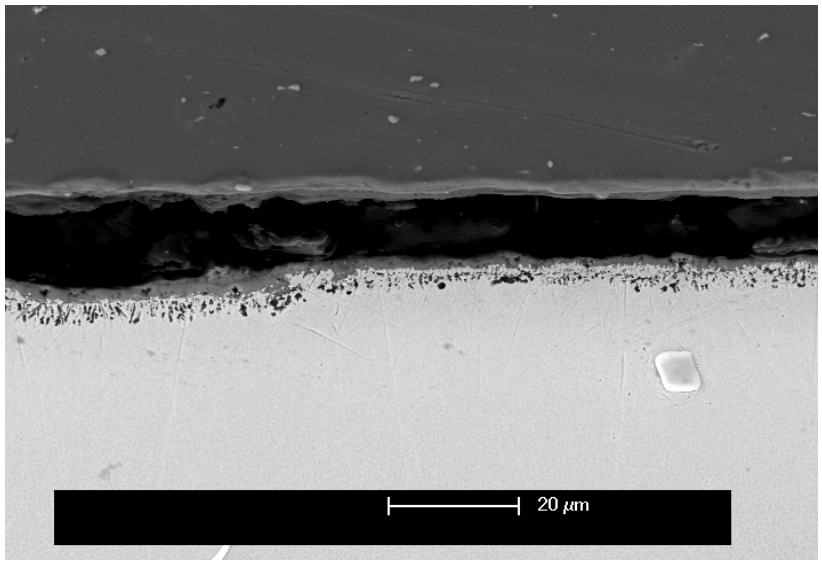
Task 4: Oxidation of Alloys and Coatings

Exposures at 900°C

Dry Air



Air – 85% H_2O



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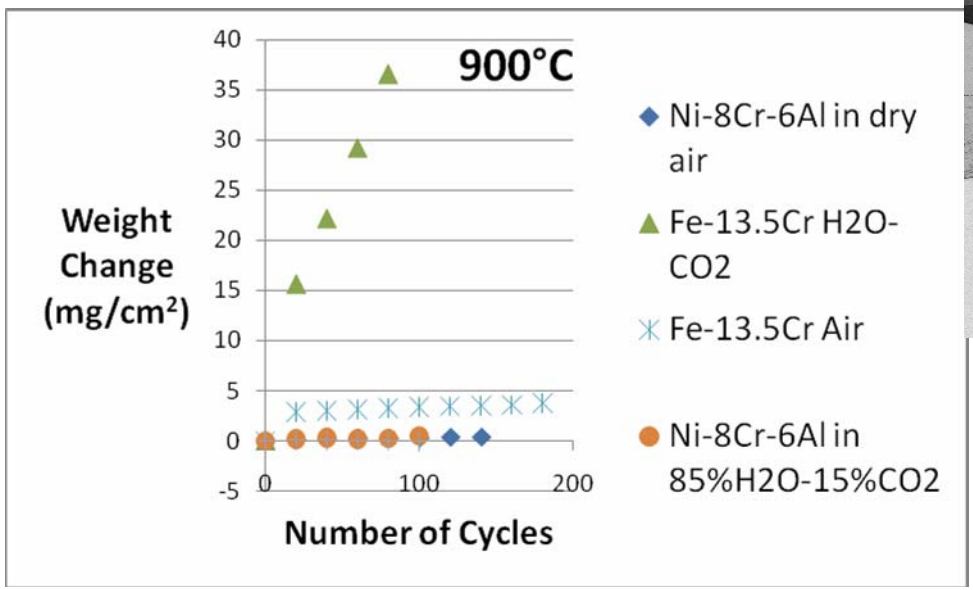
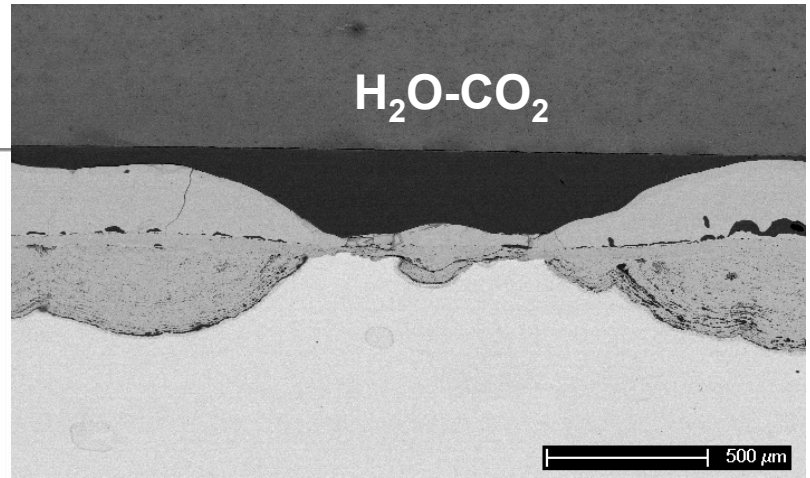
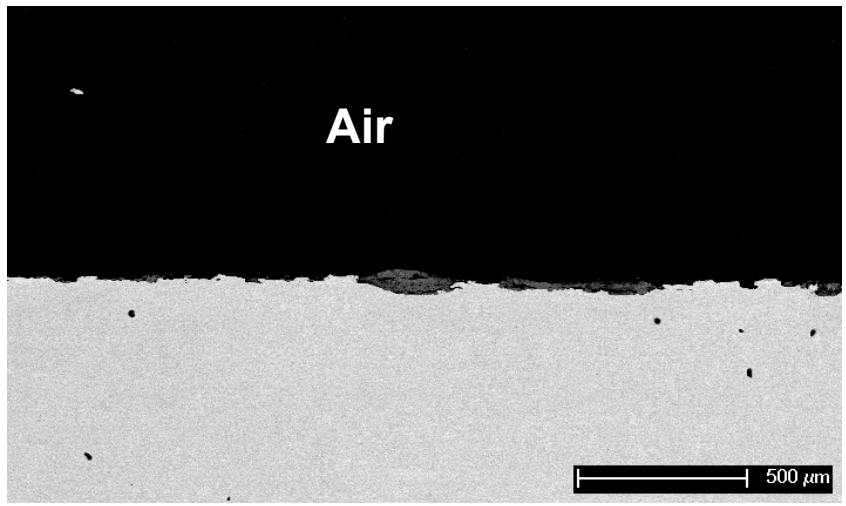
Task 4: Oxidation of Alloys and Coatings

Model Alloys



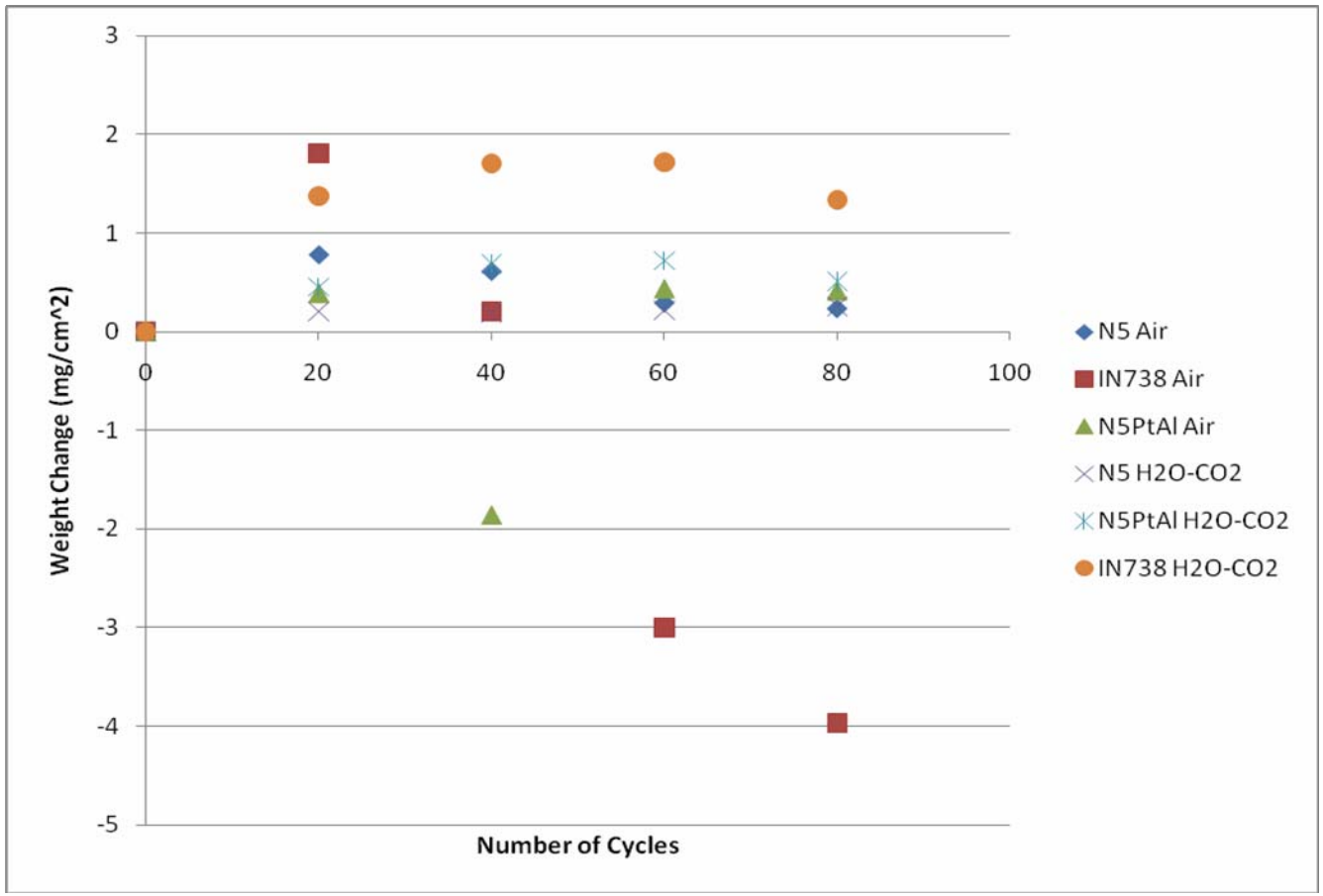
Fe-13.5%Cr





Task 4: Oxidation of Alloys and Coatings

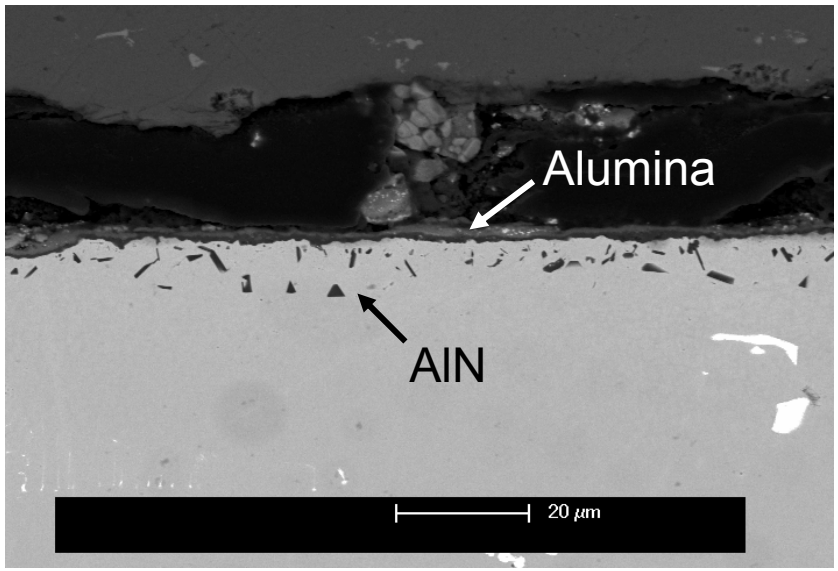
Exposures at 1100°C



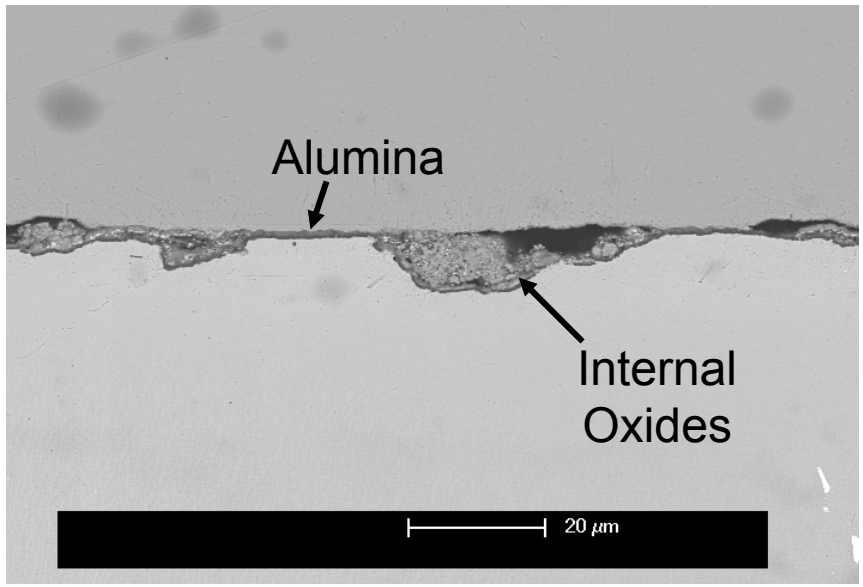
Task 4: Oxidation of Alloys and Coatings

Exposures at 1100°C

Dry Air



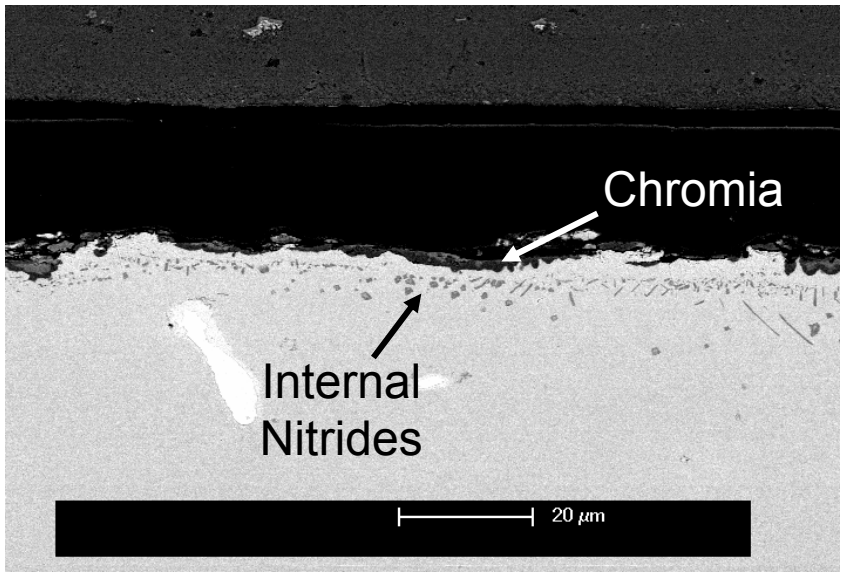
85%H_2O – 15%CO_2

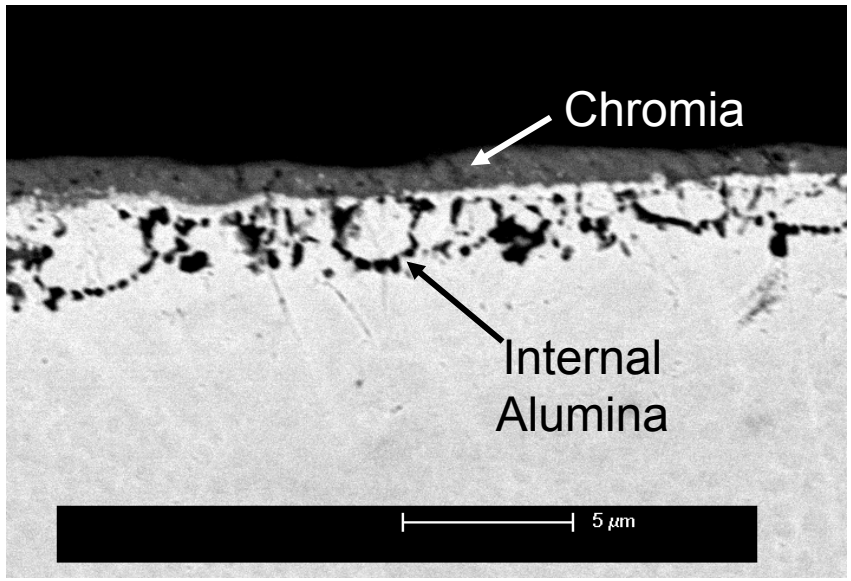


Rene N5

Task 4: Oxidation of Alloys and Coatings

Exposures at 1100°C





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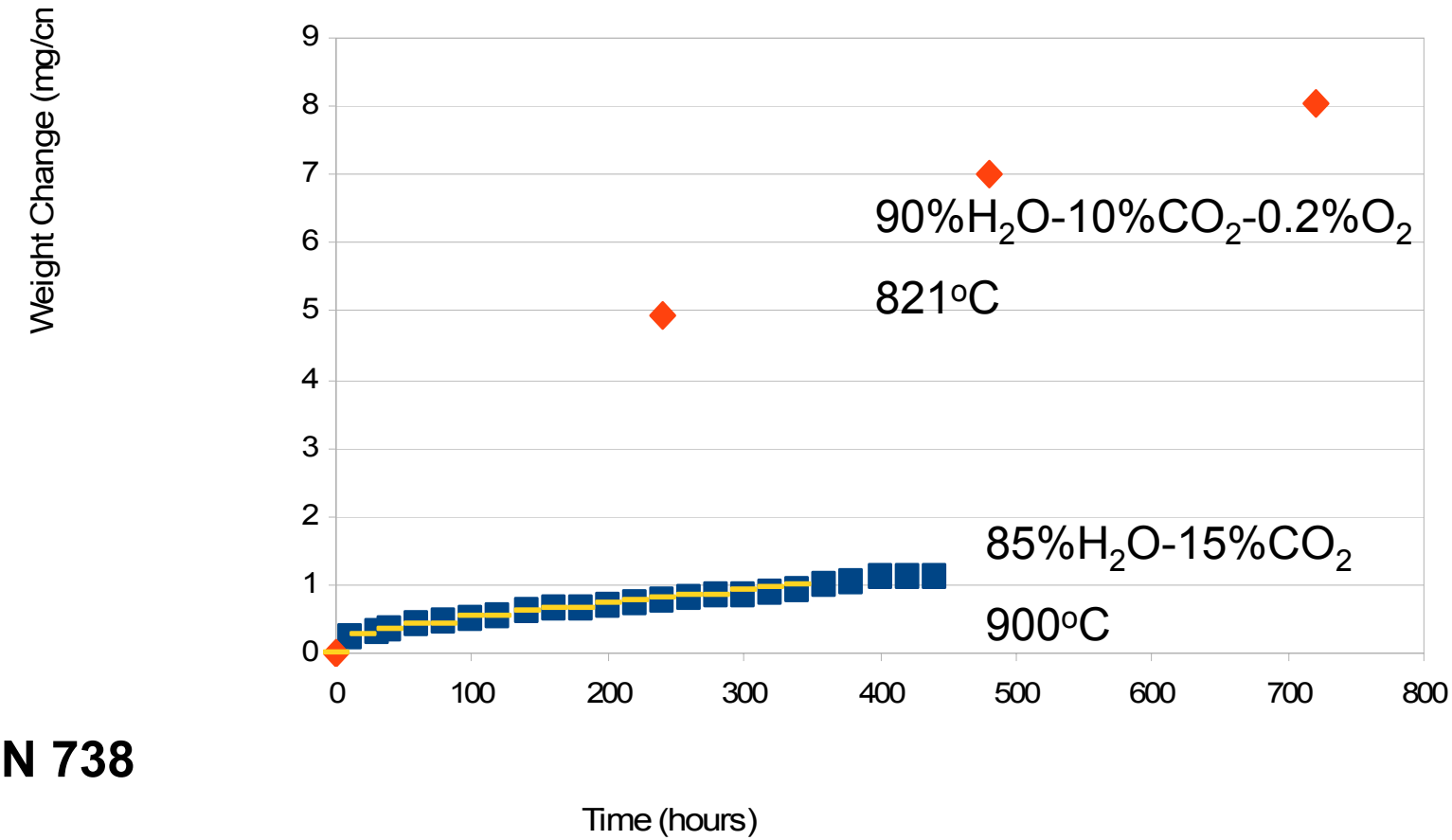
Task V Excess Oxygen Effects

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



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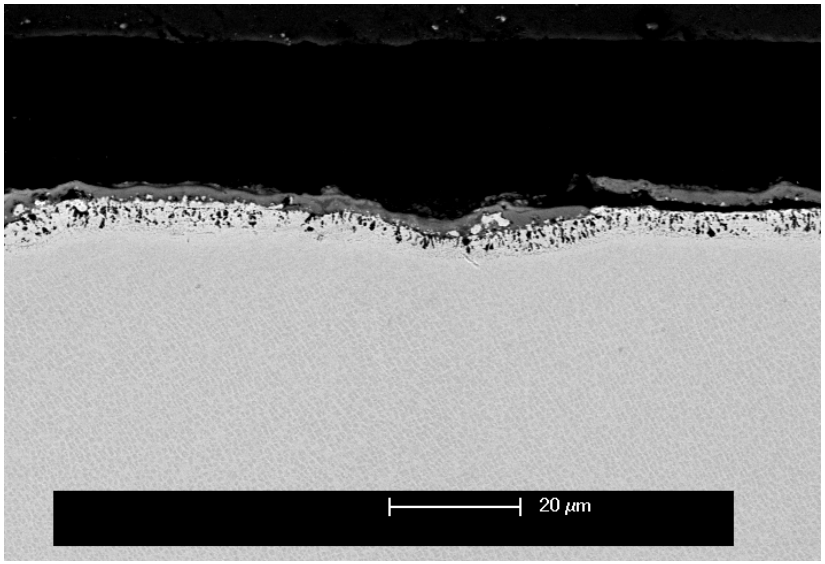
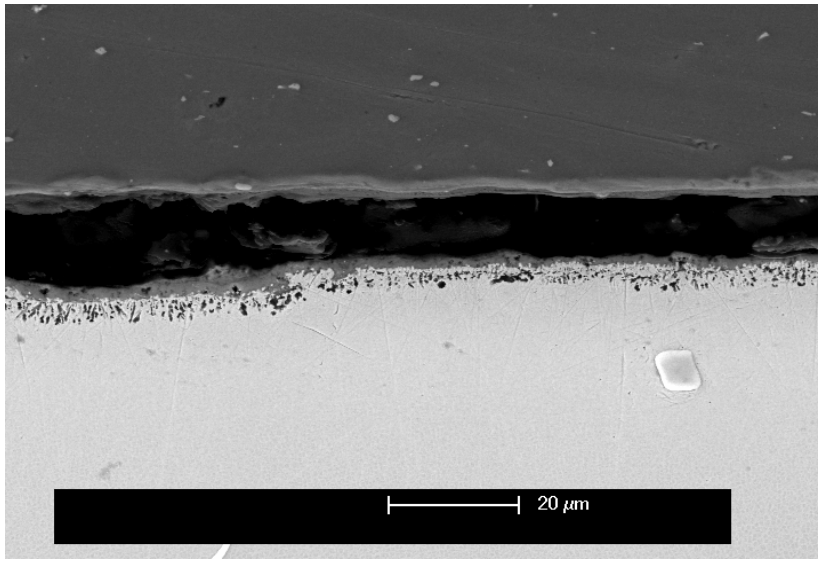
Excess-O_2 results provided by G. Holcomb, NETL-Albany

Task V Excess Oxygen Effects

Dry Air **900°C** **85% H_2O-15%Air**





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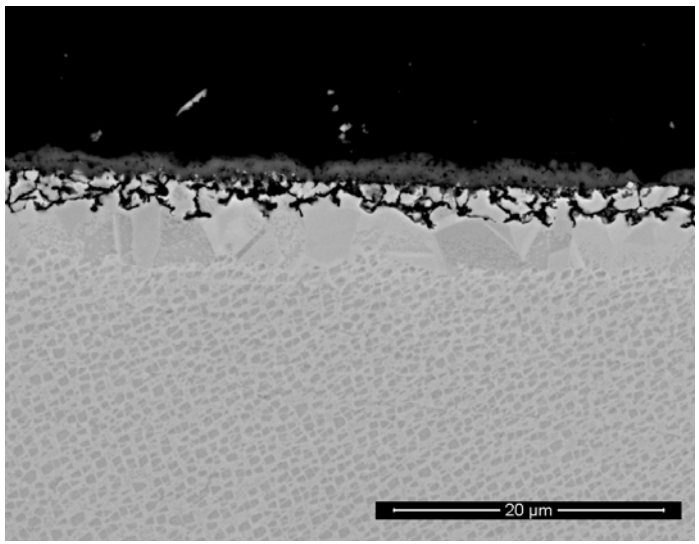


821°C

90%H_2O-10%CO_2-0.2%O_2

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.

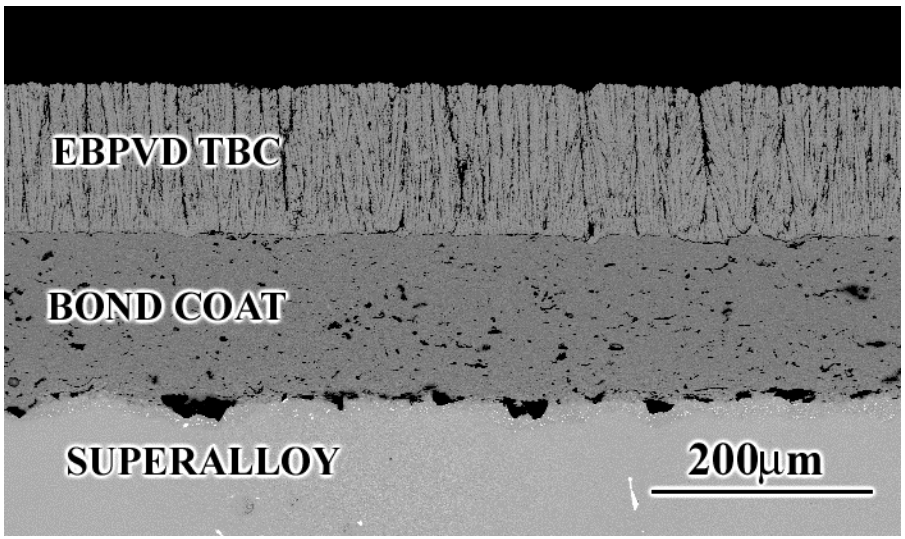
Task IV: Alloys and Coatings with sufficient Cr/Al concentrations are no more severely degraded in H_2O/CO_2 than in dry air.

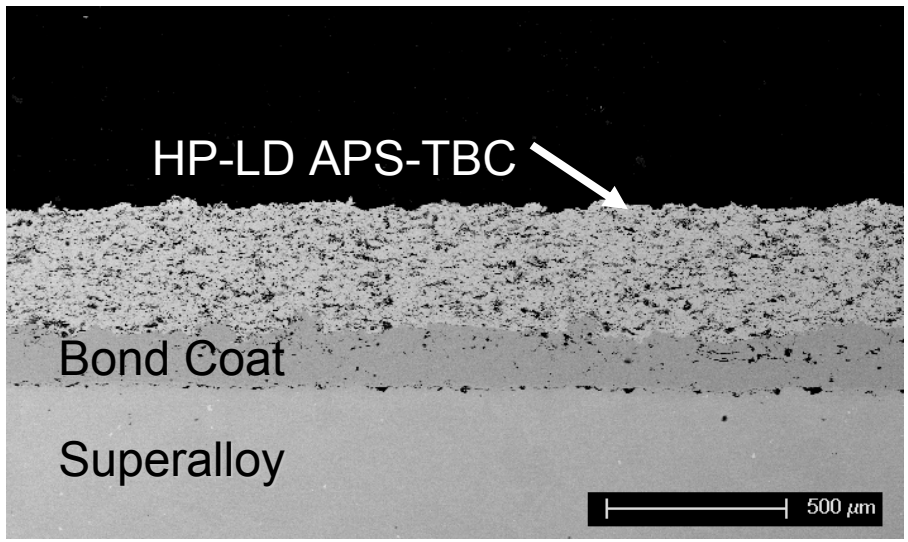
Alloys which are borderline chromia/alumina-formers are severely degraded in H_2O/CO_2 atmospheres.

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

Phase II Results

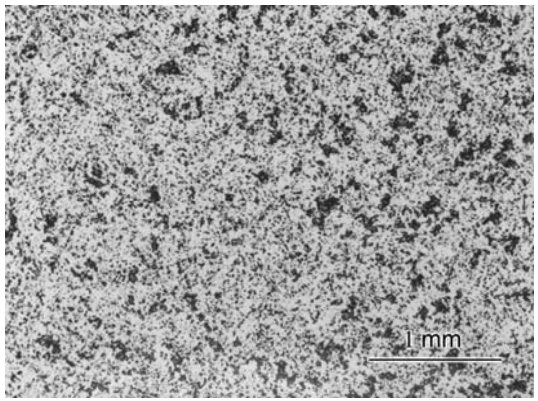
As-Fabricated TBCs

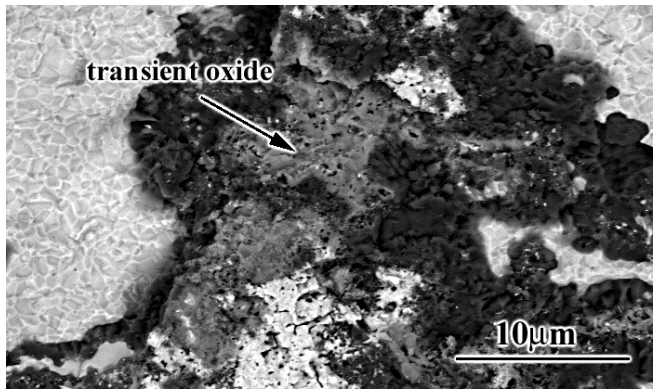




Fracture Surfaces EBPVD TBCs

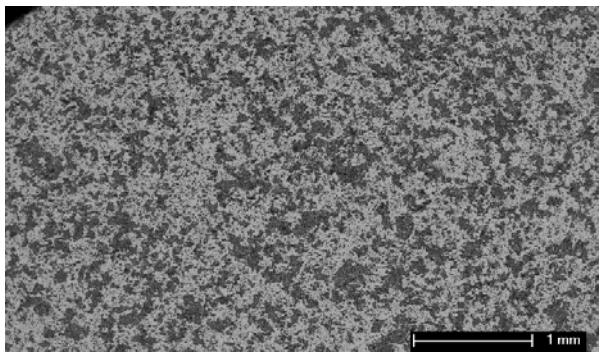
Exposures at 1100°C

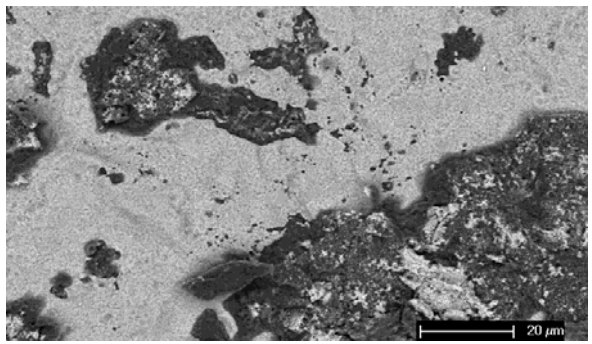




Laboratory Air

100 Cycles

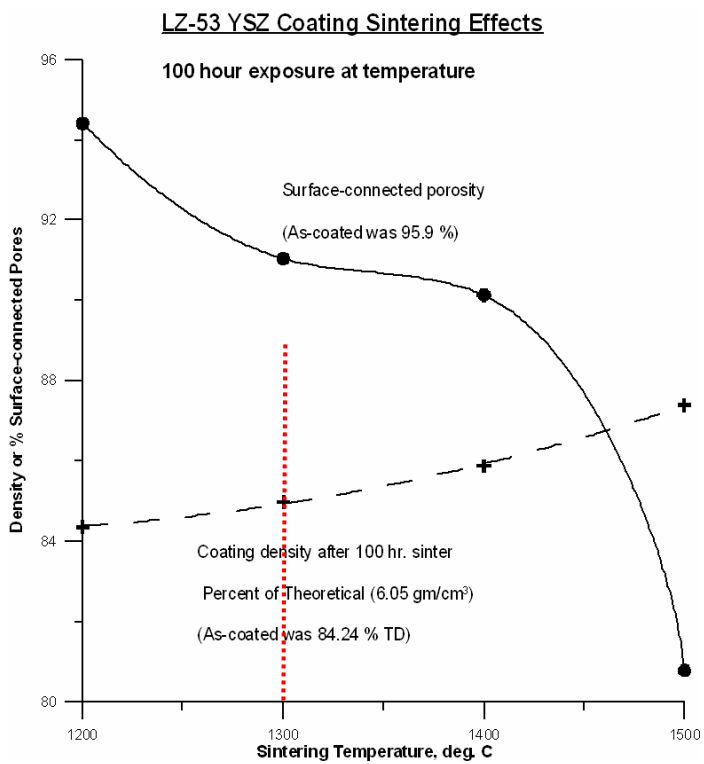




85% H_2O – 15%CO_2

80 Cycles

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

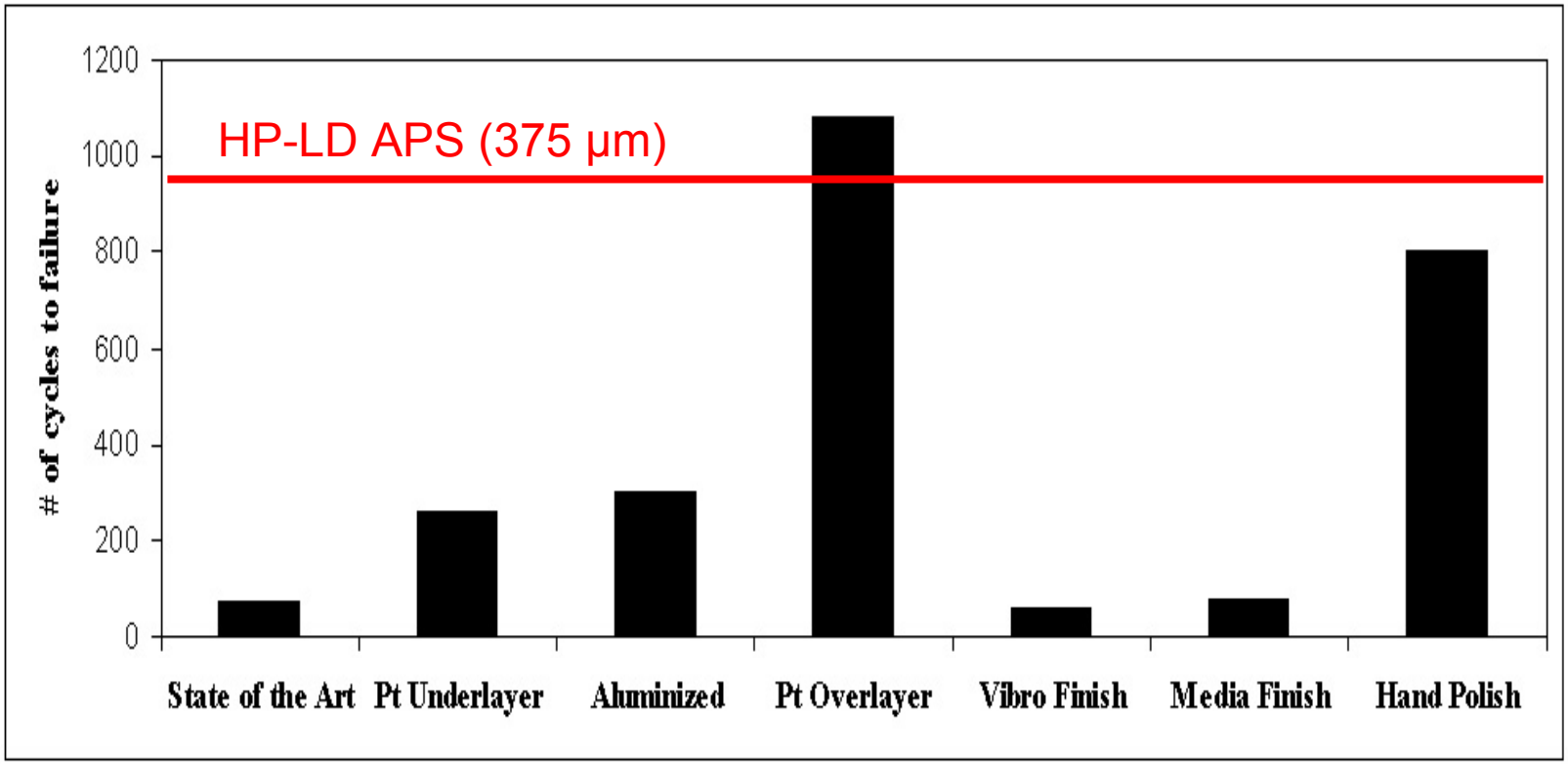
Pt-Aluminide Bond Coat 1000 cycles

No measurable transformation to monoclinic phase at 1300°C.

As-sprayed κ < 1 w/m K.

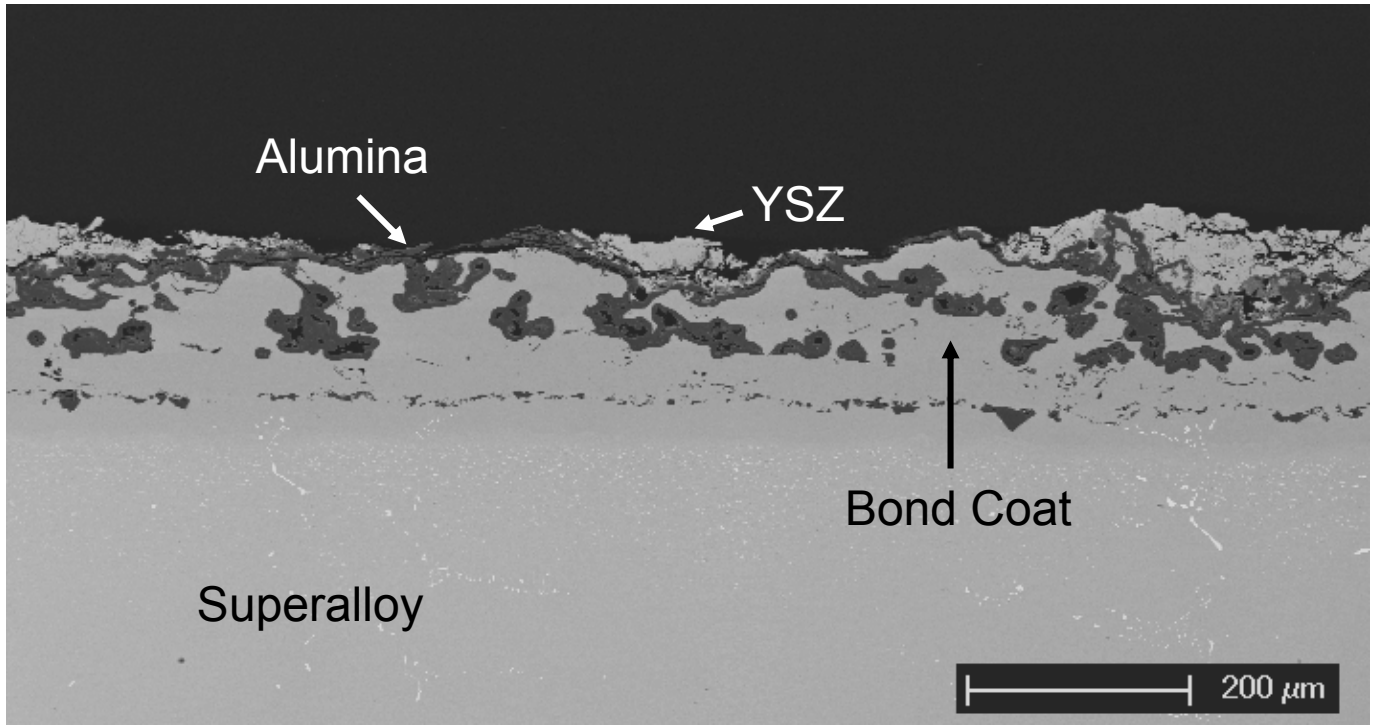
M. A. Helminiak, et al, Surface Coatings & Tech., 204, 793 (2009).

FCT Failure Times at 1100°C for EBPVD TBCs (150 µm thick) with Modified NiCoCrAlY Bond Coats on N5



N. M. Yanar, F. S. Pettit, and G. H. Meier, Metallurgical and Materials Trans. A, 37A, 1563 (2006).

Typical Failure Mode for HP-LD TBC in Laboratory Air at 1100°C



375 μm HP-LD APS TBC on Mar M509:

Failed in 220 cycles in Lab Air

Still in test after 160 cycles in 85%H_2O-15%CO_2

Summary

- Oxyfuel Environments are no more severe than Air for highly-resistant superalloys, metallic coatings and TBCs.
- Oxyfuel Environments disrupt the selective oxidation process for borderline alloys.

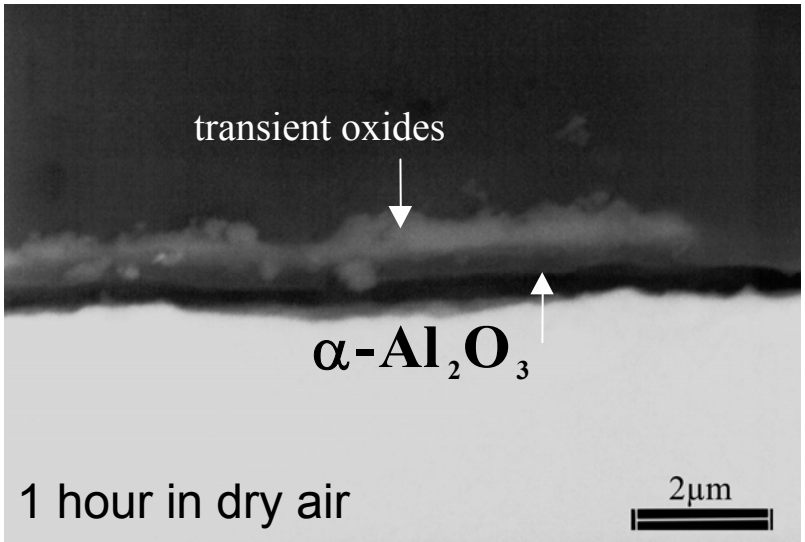
This may be an issue for components in the later stages of design life.

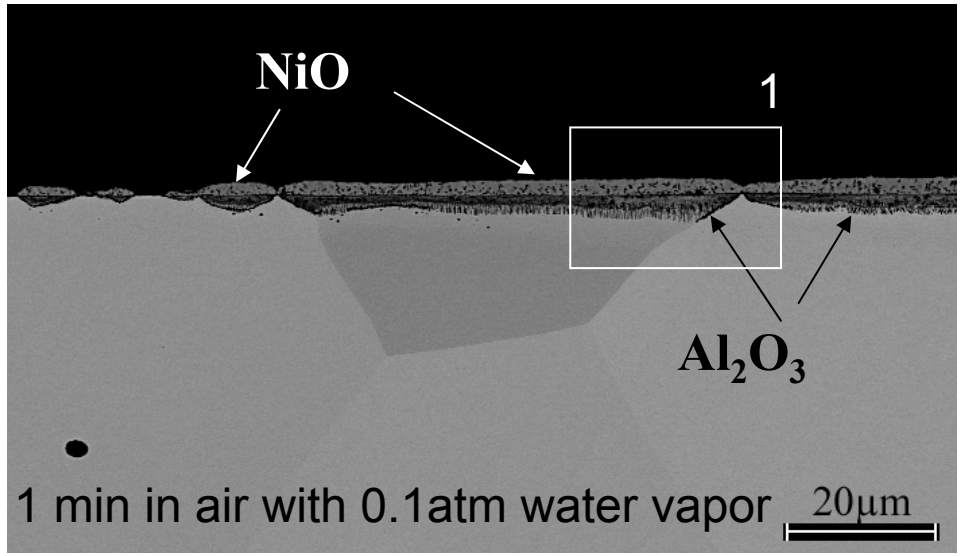
Water Vapor Effects on High Temperature Oxidation

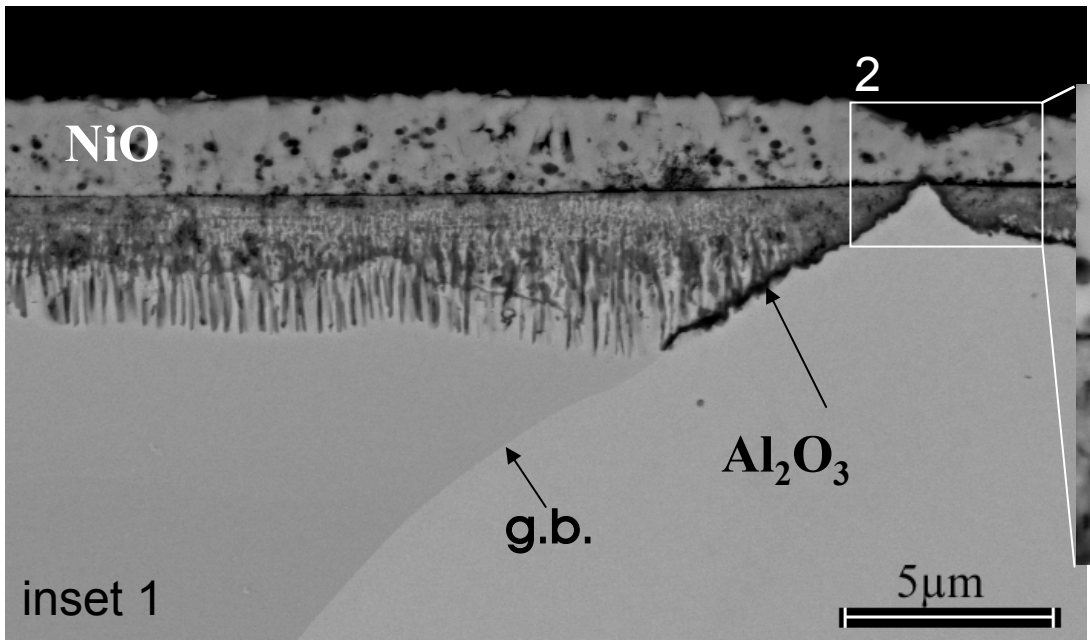
- **The effects depend on the alloy system.**
- **In the case of Al_2O_3- and Cr_2O_3-formers, water vapor affects the oxidation resistance adversely.**

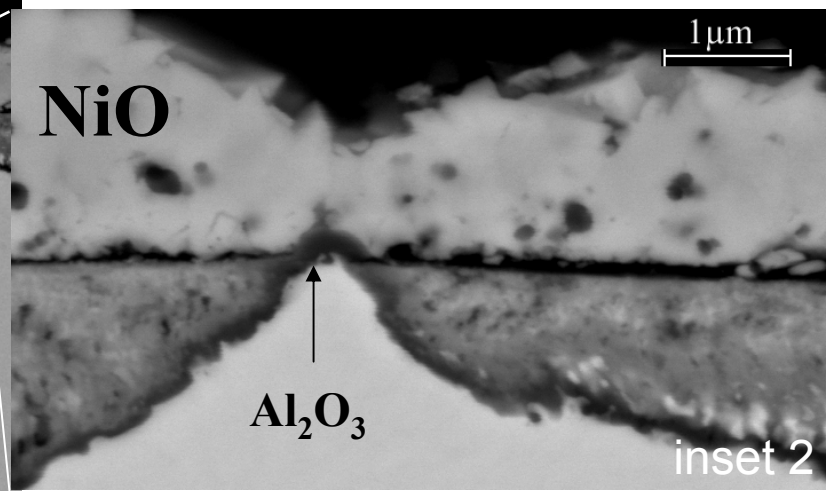
  - **Selective oxidation is often disrupted.**
  - **Transient oxidation is often accelerated**
  - **Evaporation of oxide films is accelerated (chromia, silica)**
  - **Adherence of alumina is degraded (Chromia adherence is often improved)**

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



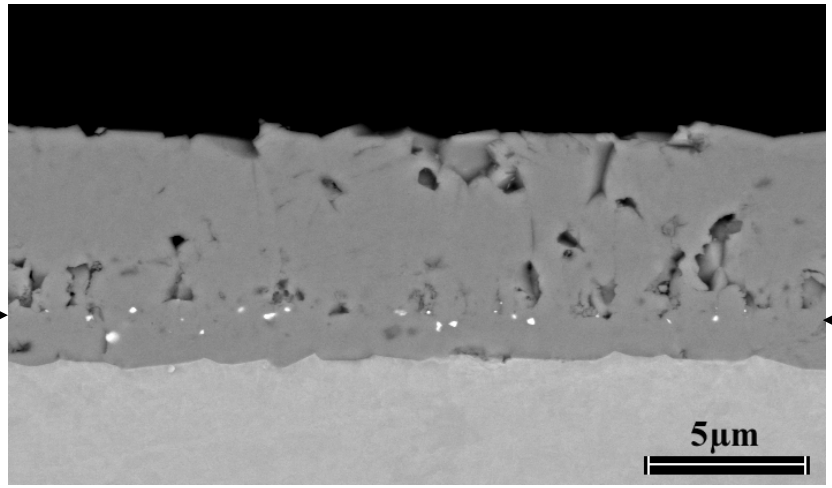




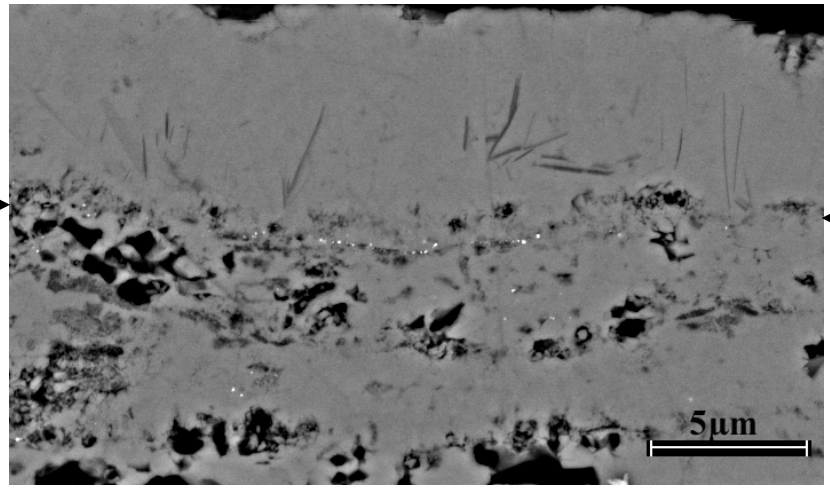


Effect of H_2O on Transient Oxidation

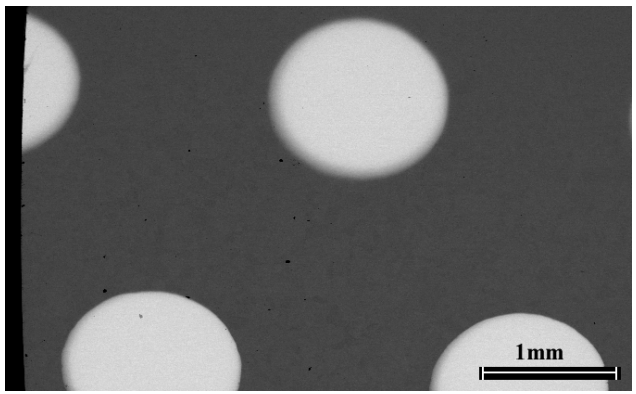
Ni specimens exposed for 1hr@1100°C showing position of Pt markers in the scale (see arrows);



dry air



air with water vapor (0.1atm)



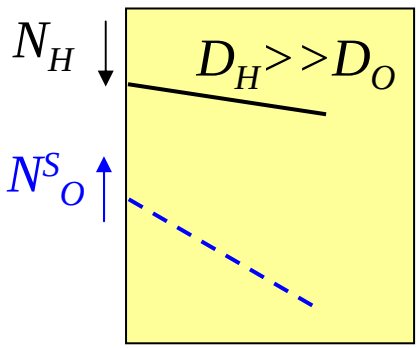
Pt mesh deposited in dots of 1mm diameter by sputtering

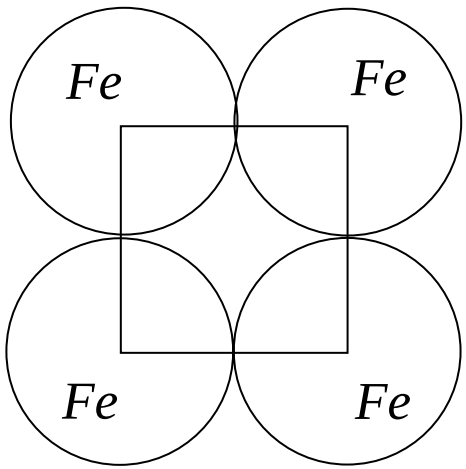
Proposed mechanism of enhanced internal oxidation of Cr in $(H_2)H_2O$-containing gases

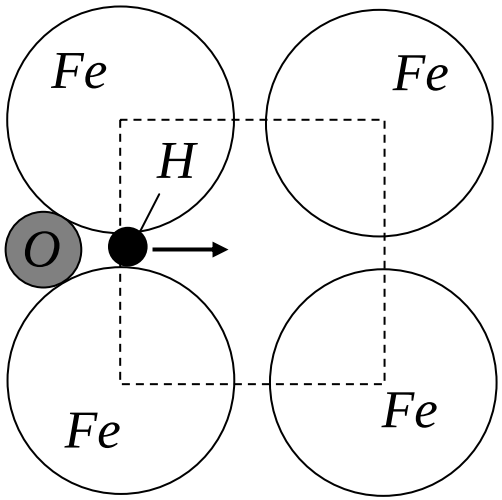
$$N_{Cr}^{(1)} > \left[\frac{\pi g^*}{3} N_O^{(S)} \frac{D_O V_m}{\tilde{D}_{Fe-Cr} V_{CrO_{1.5}}} \right]^{1/2}$$

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

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



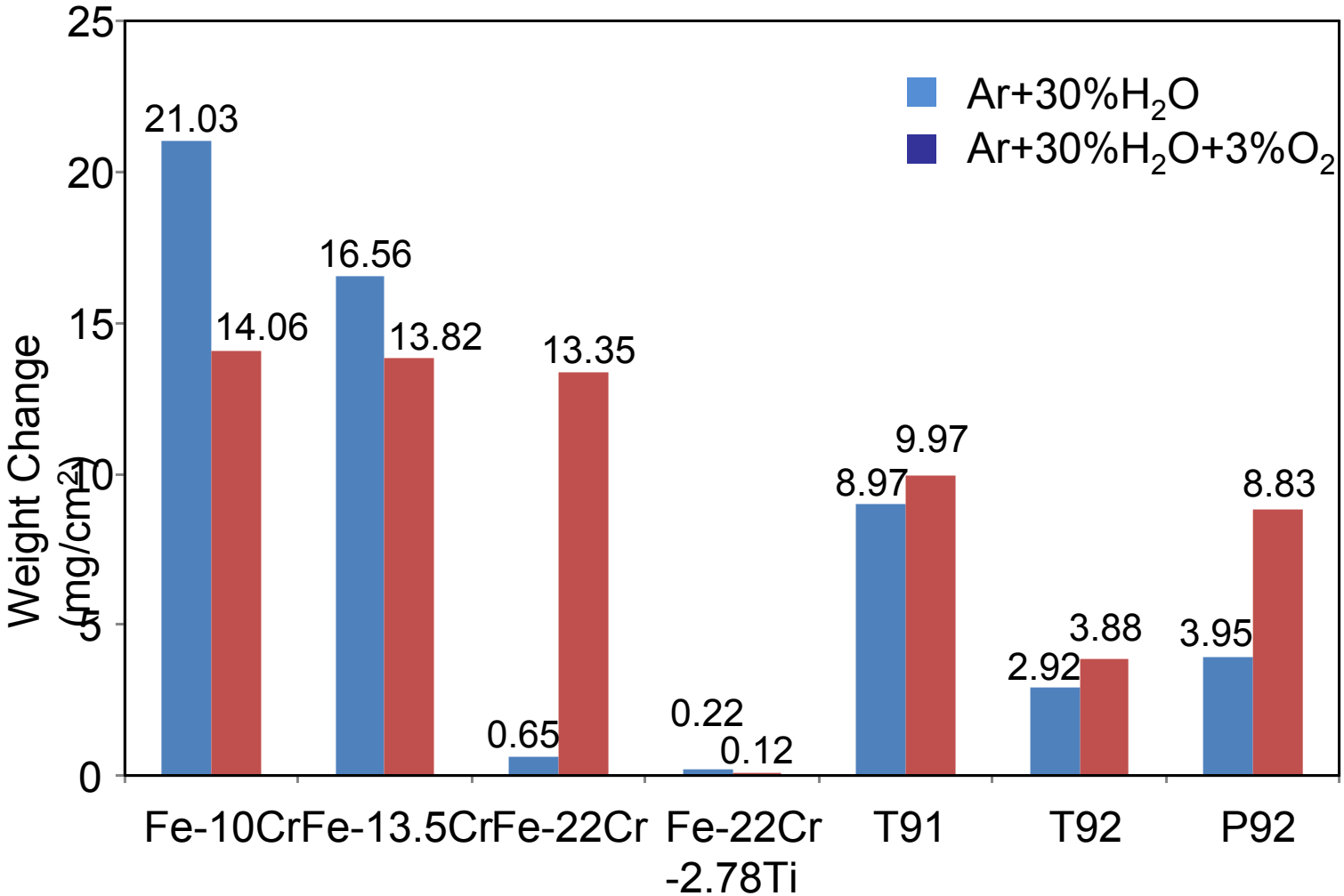




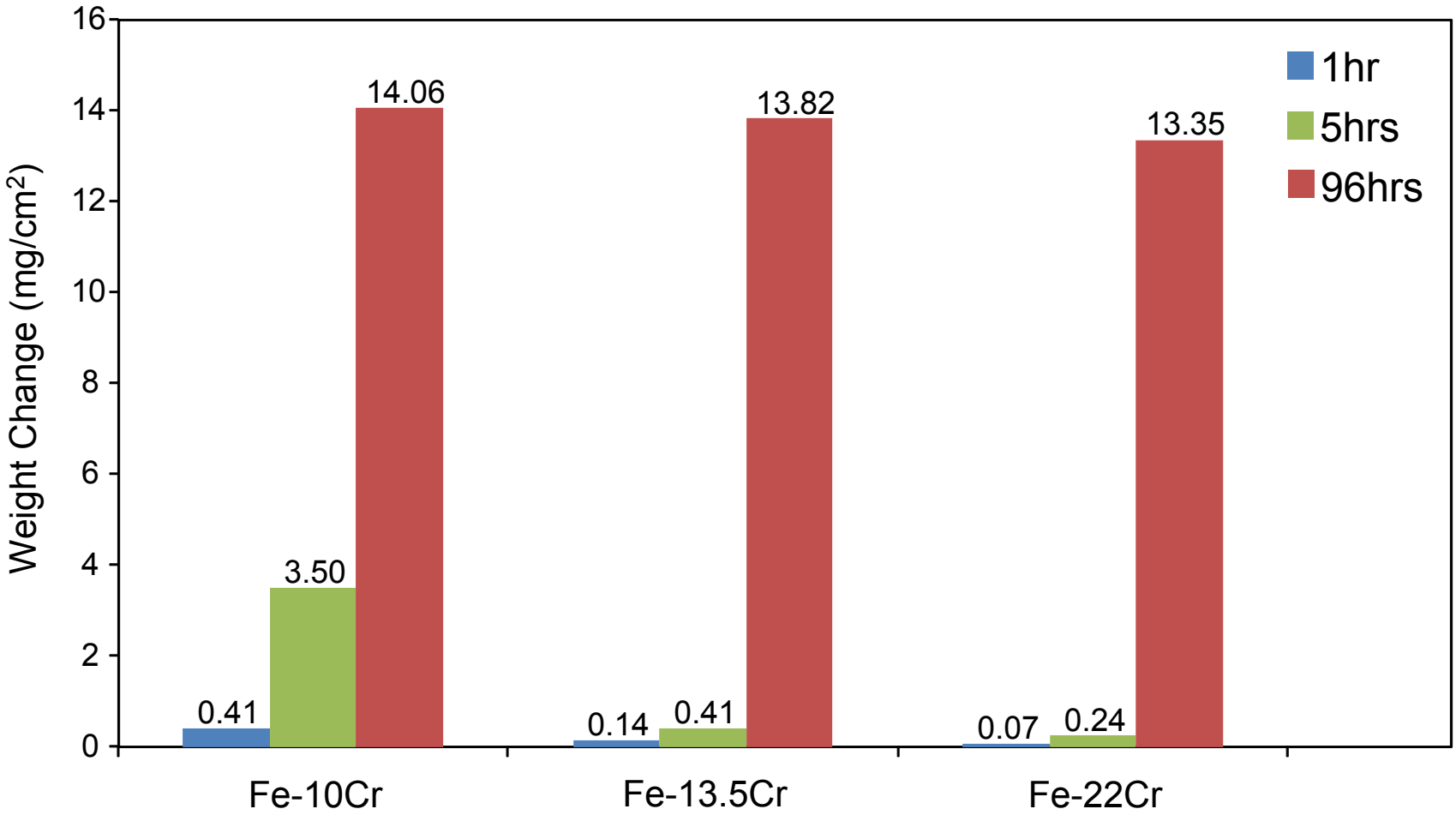
Hydrogen increases oxygen solubility and/or diffusivity in metal

E. Essuman, G.H. Meier), J. Żurek, M. Hänsel, L. Singheiser, W.J. Quadakkers Scripta Mat., 57, 845 (2007).

Isothermal Oxidation at 650°C for 4 days



Isothermal Oxidation at 650°C in Ar+30%H_2O+3%O_2

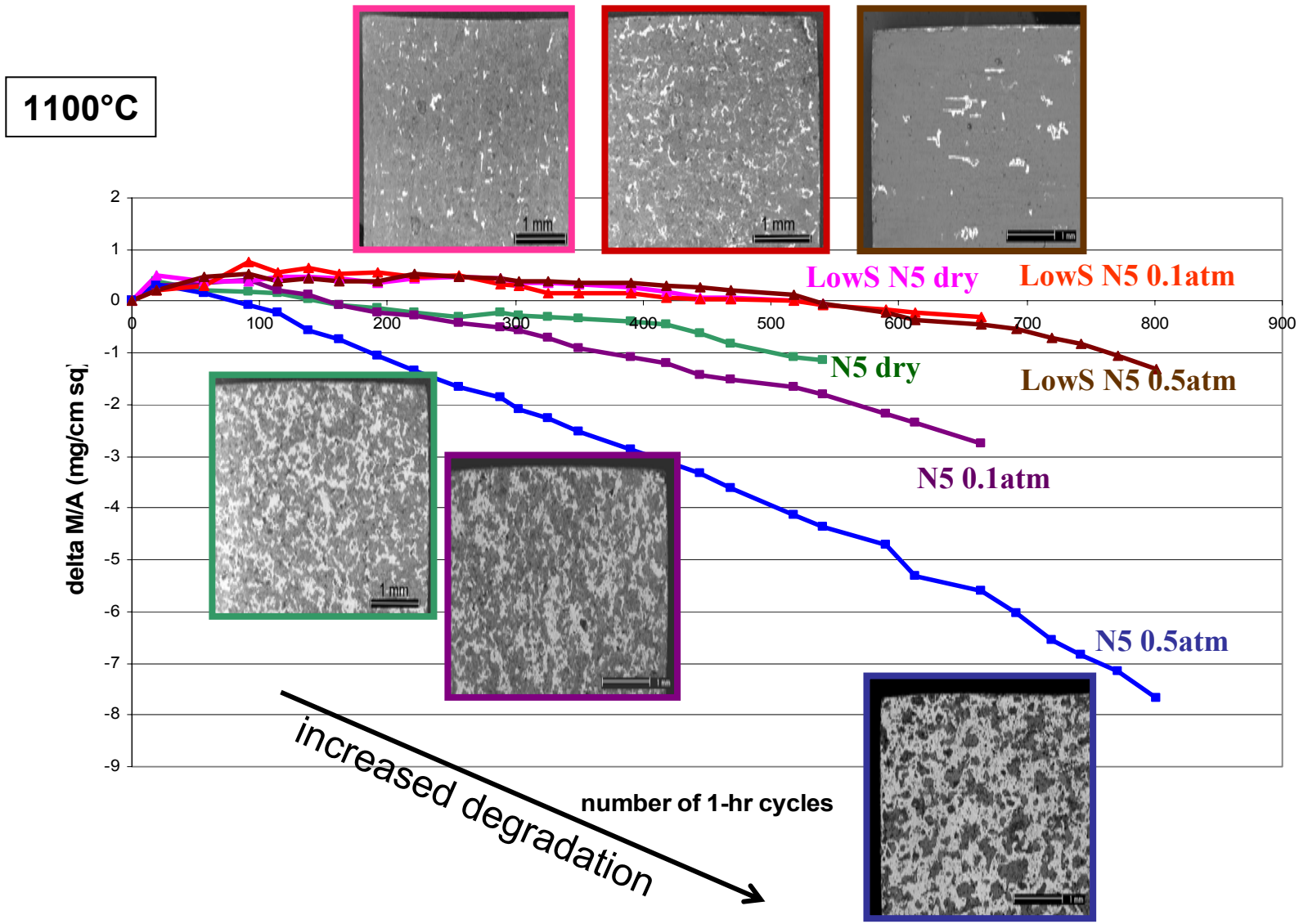


Summary

- The reason for the detrimental effect of the excess O_2 (even Fe-22Cr forms Fe-rich scales) is believed to be the result of accelerated reactive evaporation of the chromia scale according to the reaction

$$\frac{1}{2}Cr_2O_3(s) + H_2O(g) + \frac{3}{4}O_2(g) = CrO_2(OH)_2(g)$$

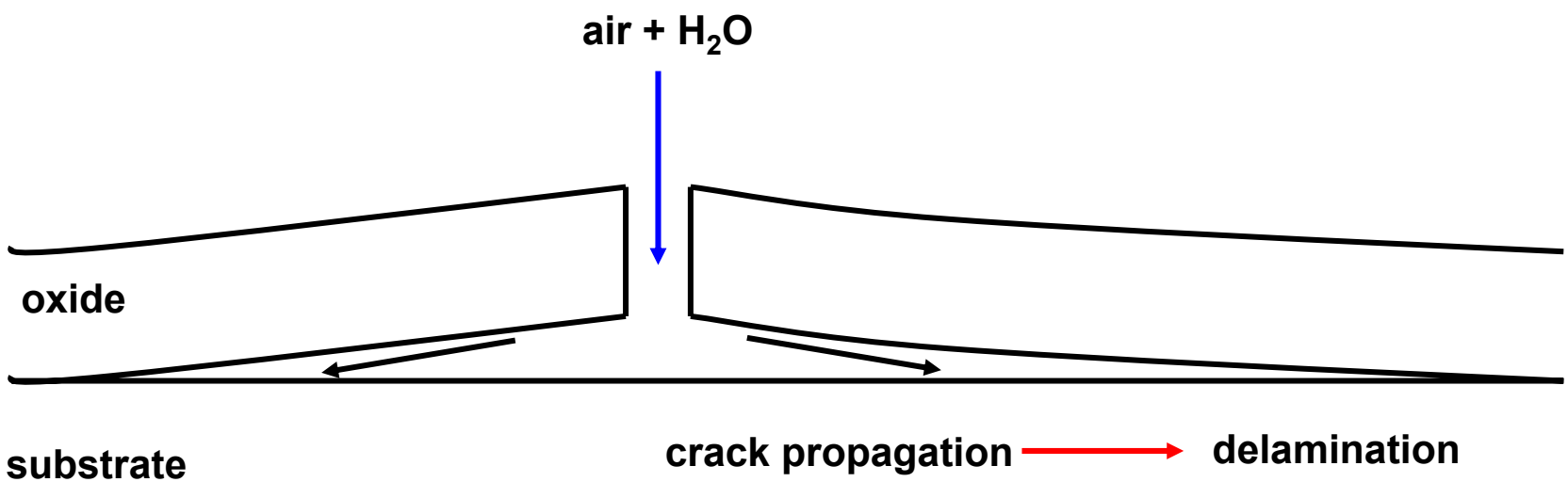
Effect of Water Vapor on Cracking and Spalling of α-Al_2O_3 Scales



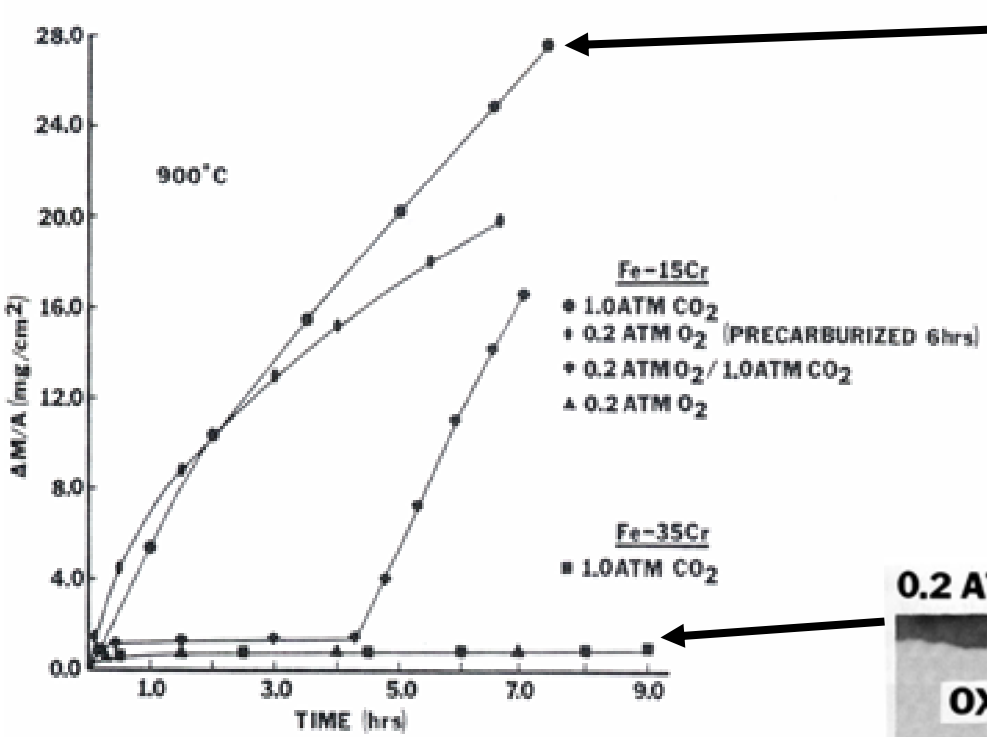
- The presence of water vapor in the oxidizing gas mixture causes the α-Al_2O_3 scales to crack and spall more profusely than in dry gases

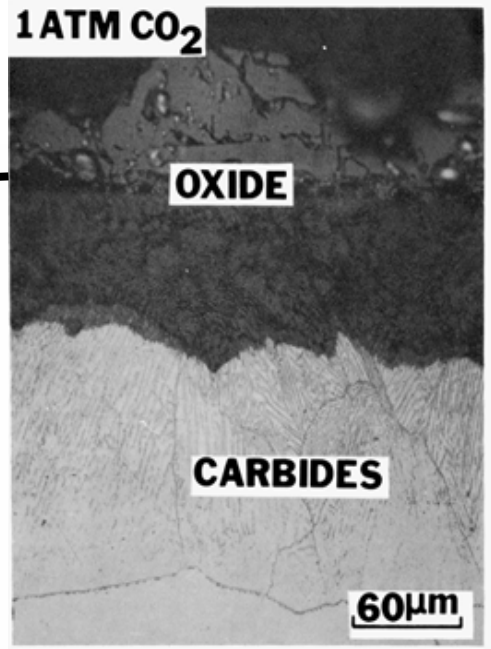
Mechanism: Stress Corrosion Cracking

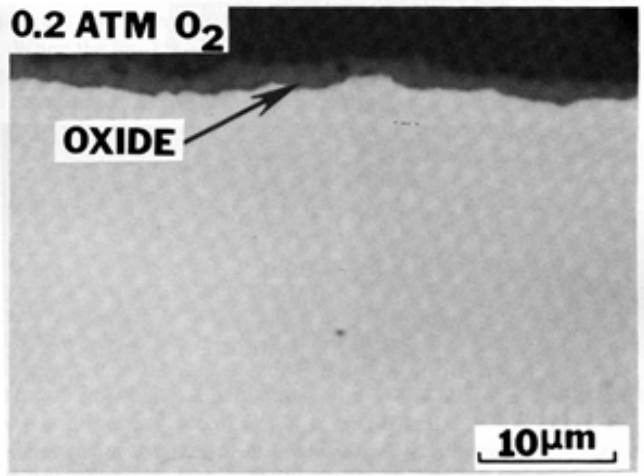
- Although cyclically oxidized low S superalloys do not spall as much as regular S superalloys, water vapor has access to the oxide/substrate interface in both cases.
- Low S superalloys have increased spallation resistance because of a higher Al_2O_3/substrate interfacial toughness.
- A crack that forms 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.



Effect of CO_2 on Selective Oxidation

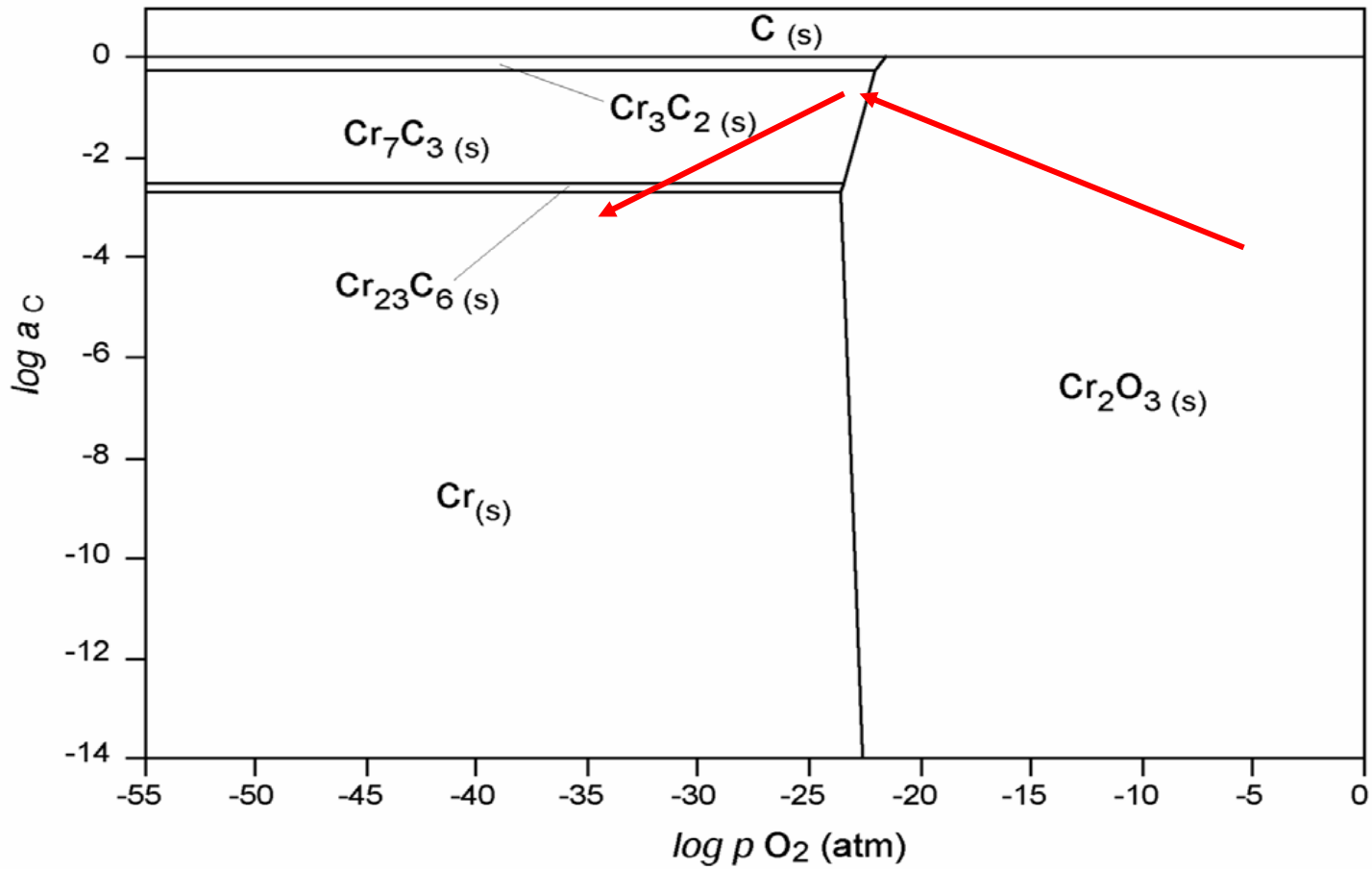






Proposed Mechanism for Effect of CO_2 on Selective Oxidation

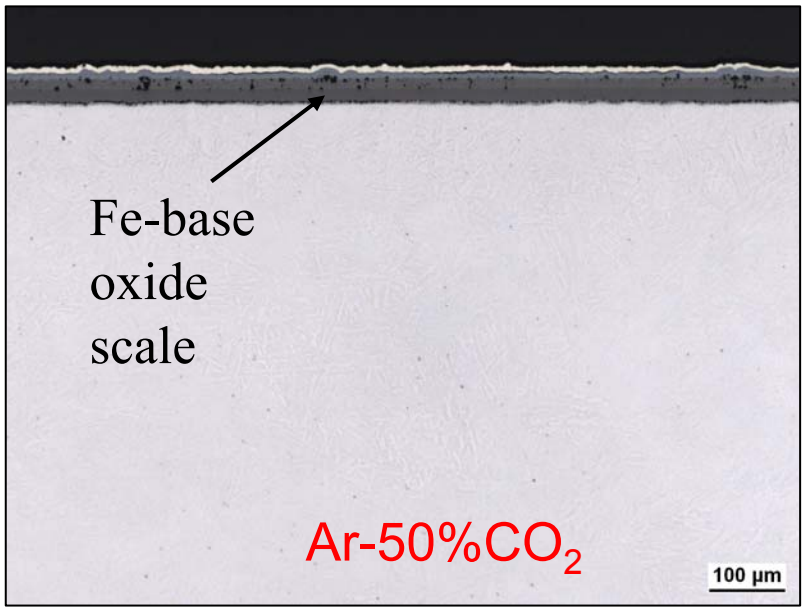
$$CO_2(g) = O(Ox) + CO(g) \quad a_C\uparrow$$

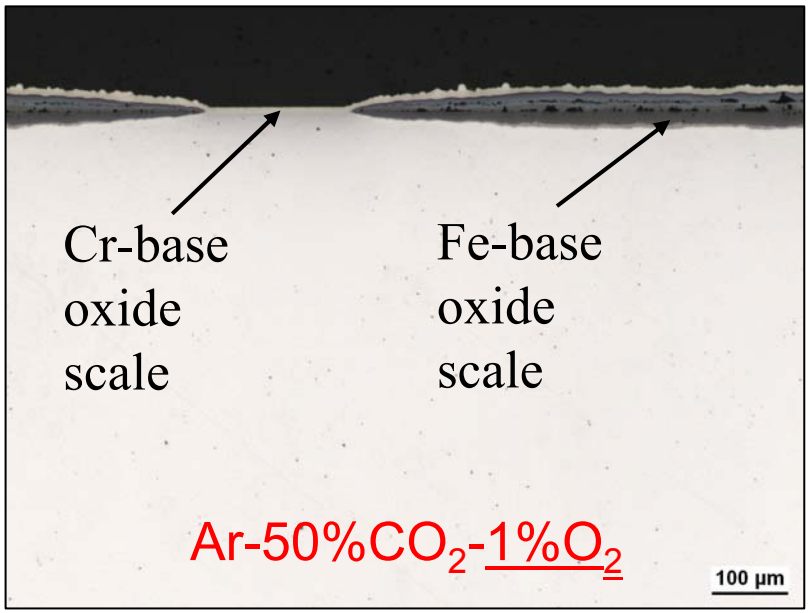


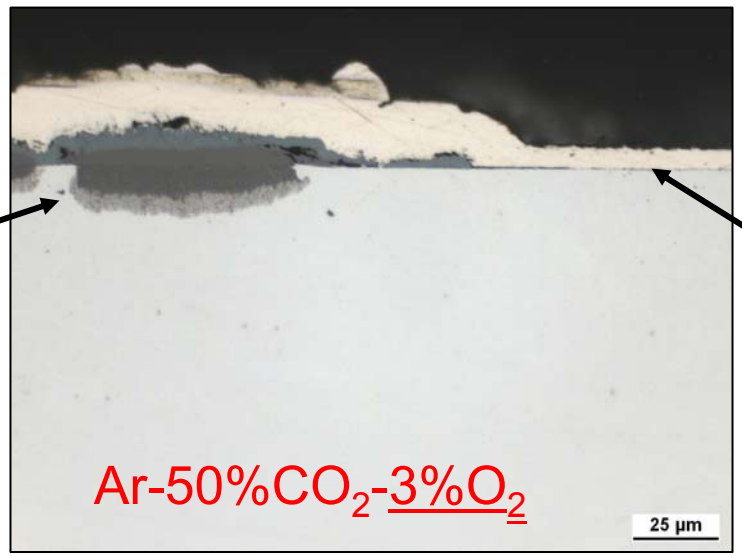
Isothermal Stability Diagram for the Cr-C-O System at 1250K

Task V Excess Oxygen Effects

Fe-9%Cr







Task V Excess Oxygen Effects

Effect of CO_2 On Selective Oxidation of Cr

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

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

$$\uparrow$$

$$O_2(g)$$

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

Work to be Performed in Next Six Weeks

- Complete Task V study of Excess Oxygen Effects (1100°C)
- Complete Evaluation of TBC Degradation

Questions ?