Degradation of TBC Systems in Environments Relevant to Advanced Gas Turbines for IGCC Systems

***Principal Investigators:* Brian Gleeson, Meltem Yanar, Gerald H. Meier and Frederick S. Pettit**

***Graduate Student:* Nate Bohna**

DOE PROGRAM: DE-FOA-0000459

Patcharin “Rin” Burke, Program Manager, DOE/NETL

Project Awarded 10/01/2011 (36 months duration)

Gas Turbine Needs

- 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

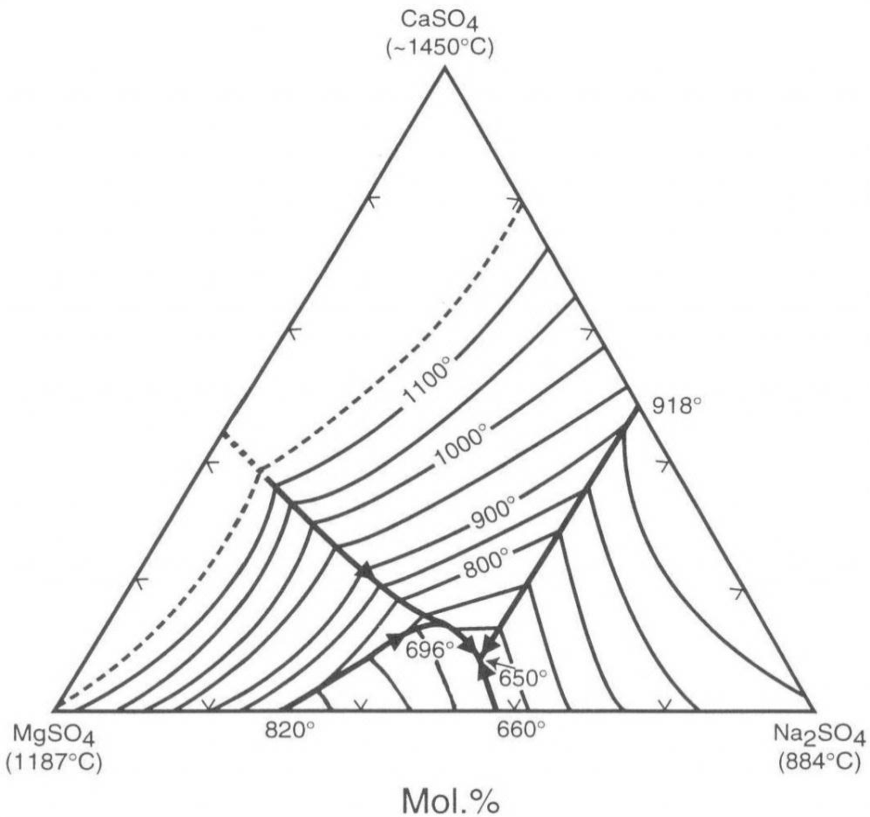
Systematically assess the interplay between prototypical deposit chemistries (*i.e.*, ash and its constituents plus K_2SO_4 and FeS) and environmental oxidants (*i.e.*, O_2, H_2O and CO_2) on the high-temperature degradation behavior of advanced TBC systems.

Combined effects of environment and deposit

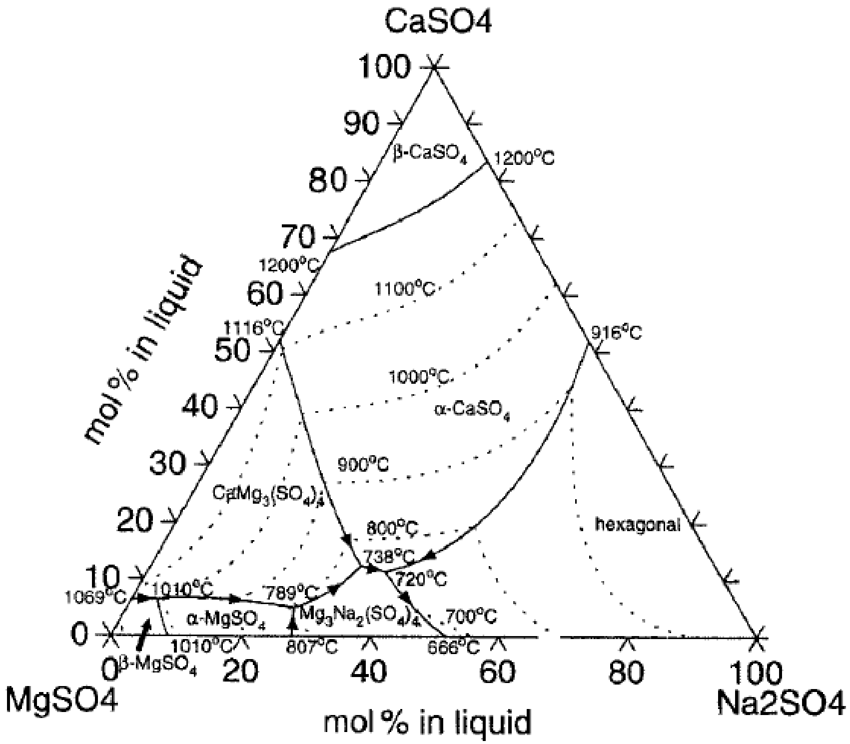
Salt Deposits Found in Practice

Composition of corrosive deposits on industrial and marine turbine components.
(Bornstein, JOM, 1997)

Salt	Mol.%
Na_2SO_4	40-60
K_2SO_4	4-9
$CaSO_4$	15-30
$MgSO_4$	18-30



After S.M. Mikimov and Z.I. Filipopova (1949)



H. Du, "Thermodynamic assessment of K_2SO_4-Na_2SO_4-$MgSO_4$-$CaSO_4$ system", Journal of Phase Equilibria, **21** (2000)

Compositions and Sources of Corrosive Salts

Concentration of SO_2 and Alkali Sulfates in Polluted Air

Air Pollutants		Los Angeles	Beijing	Delhi
Annual Average SO_2, ppm		0.002	0.055	0.007
Sulfate salts in particulate matter in ambient air *(annual average values)*	Total concentration of sulfates, μ mol./m^3	0.006-0.02	0.12-0.41	0.38-0.64
	Na_2SO_4, mol.%	48-52	12-21	32-56
	K_2SO_4, mol.%	7-11	9-28	10-16
	$MgSO_4$, mol.%	17	10-12	10-17
	$CaSO_4$, mol.%	24	41-67	18-42

References:

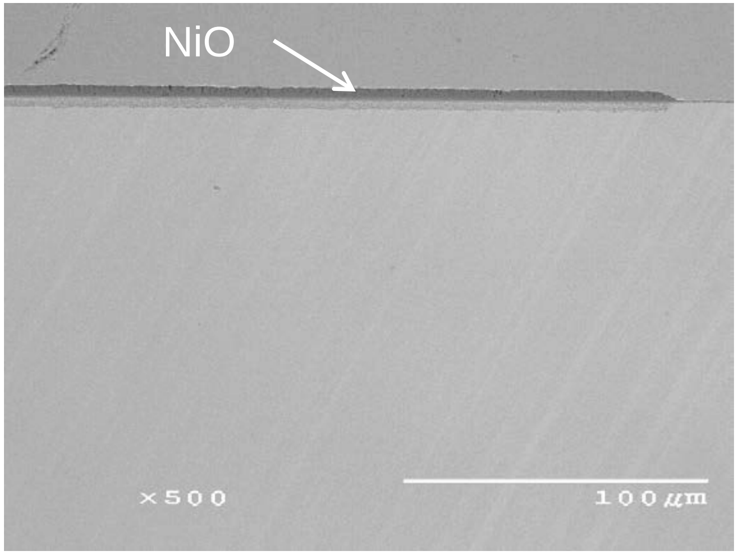
- *Beijing:*
  Sun *et al., Atmospheric Environment,* 2004, pp5991-6004*;* Wang *et al., Atmospheric Environment,* 2005, pp3771-3784.
- *Los Angeles:*
  Krudysz *et al., Atmospheric Environment,* 2008, pp5374-5389*;* Singh *et al., Atmospheric Environment,* 2002, pp1675-1689.
- *Delhi:*
  Tiwari *et al., Journal of Atmospheric Chemistry, 2009, pp193-209;* Datta *et al*, Journal of Atmospheric Chemistry, 2010, pp127-143.

High-Temperature Corrosion at 700°C in Air

PWA 1484 Substrate

No Na_2SO_4 Deposit

after 100h oxidation

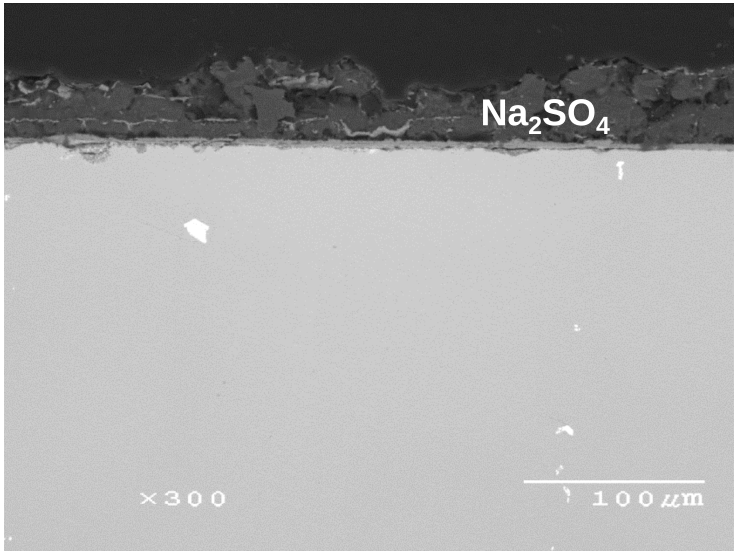


Δm=1.04 mg/cm²

Average Metal Loss: 4 μm

With Na_2SO_4 Deposit

after 5×20h (total=100h)



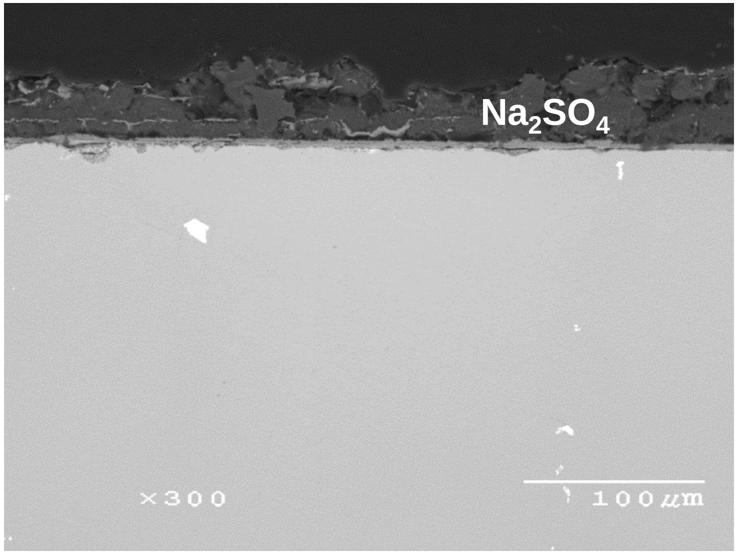
Δm=1.18 mg/cm²

Average Metal Loss: 6 μm

High-Temperature Corrosion at 700°C

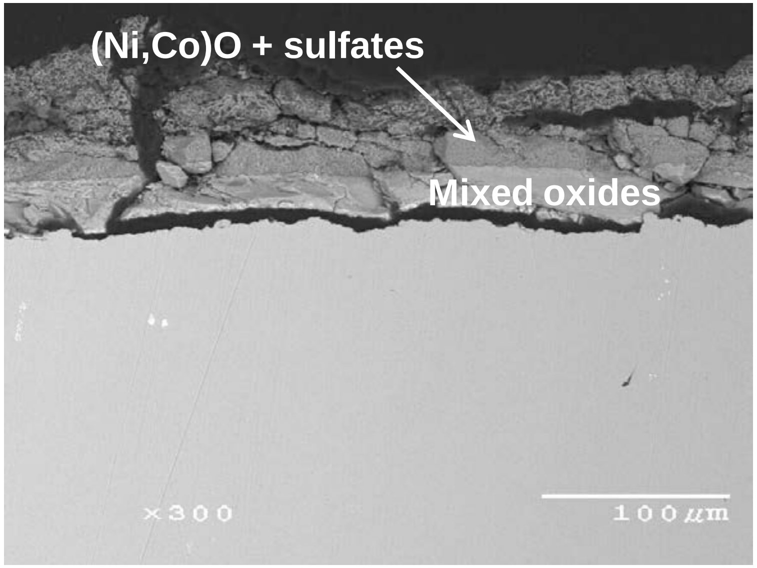
PWA 1484 Substrate

In Air



Average Metal Loss: 6 µm

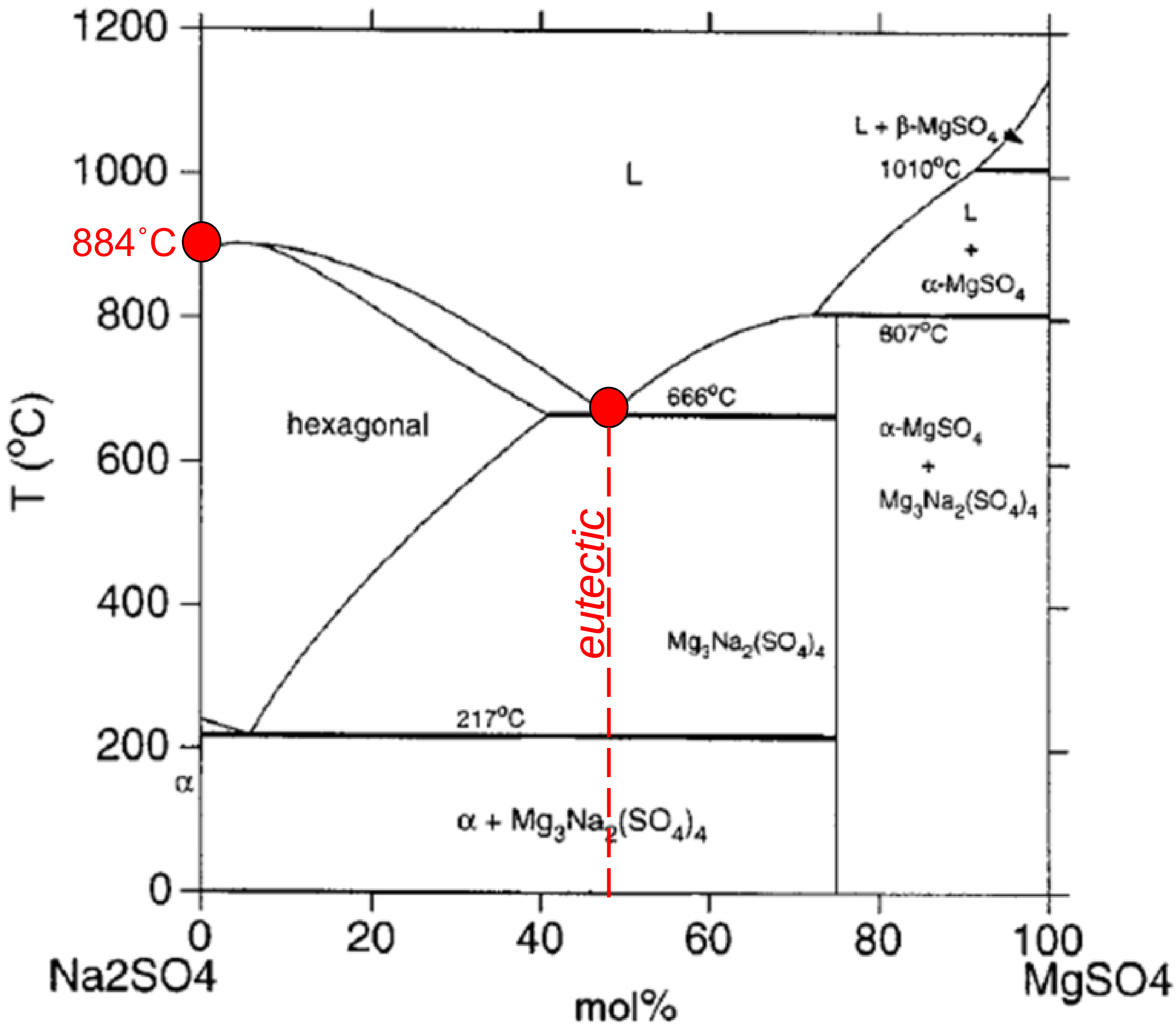
In catalyzed O_2-0.1%SO_2*



Average Metal Loss: 61 µm

**Equilibrium P_{SO_3} in O_2-0.1%SO_2 atmosphere at 1 atm total: 7.2 x 10^{-4} atm*

Na_2SO_4 – $MgSO_4$ System

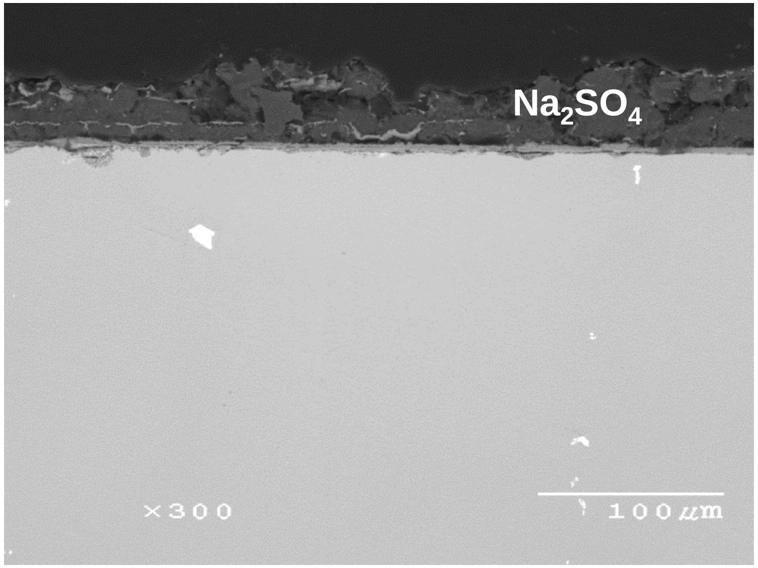


High-Temperature Corrosion at 700°C in Air

PWA 1484 Substrate

With Na_2SO_4

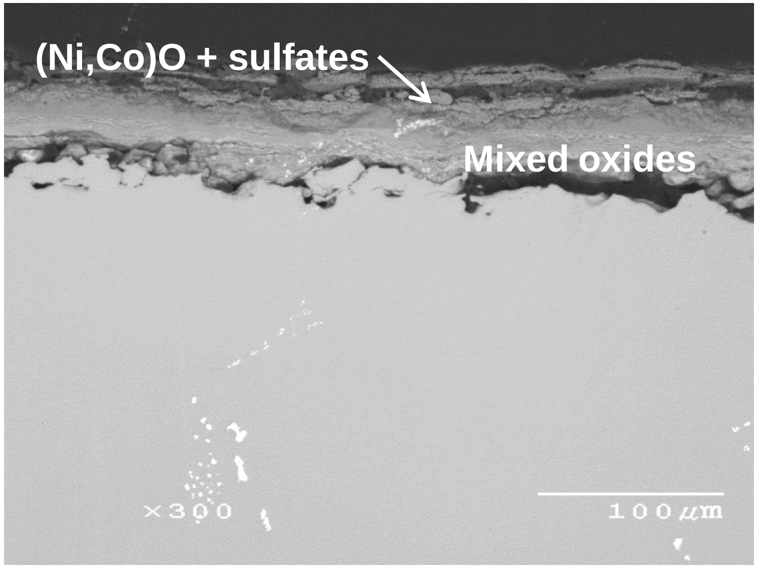
T_m=884°C



Average Metal Loss: 6 µm

With Na_2SO_4-$MgSO_4$ eutectic

$T_{eutectic}$=666°C

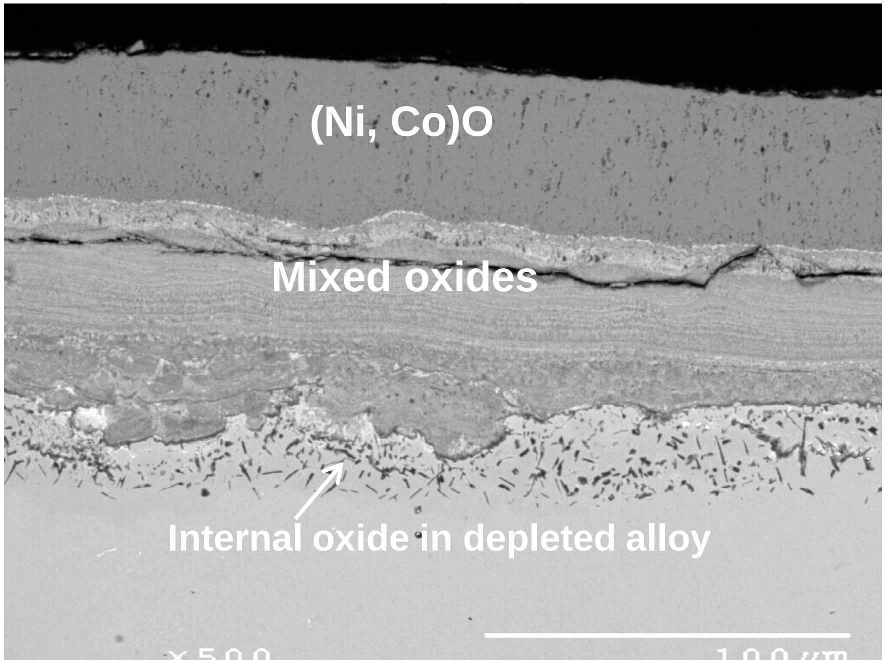


Average Metal Loss: 26 µm

Na_2SO_4-$MgSO_4$ eutectic (T_m=666°C) causes accelerated attack in air at 700°C.

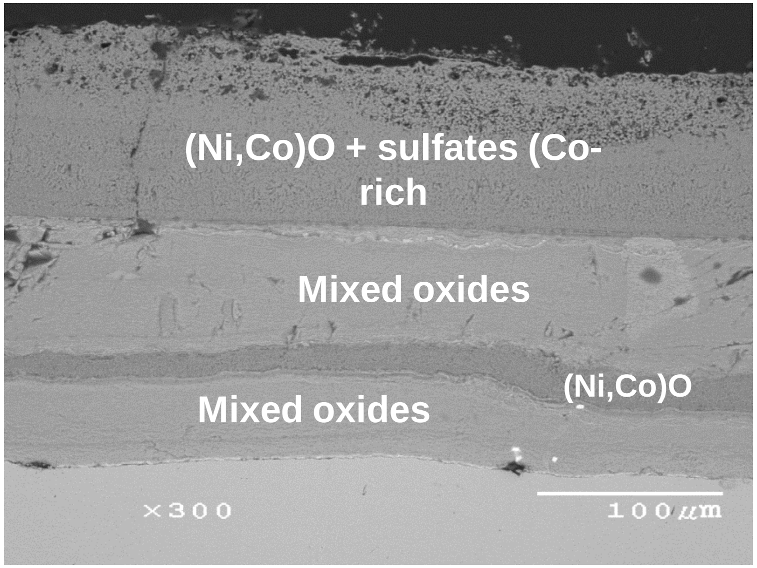
Na_2SO_4-$MgSO_4$ Induced Corrosion at 700°C
PWA 1484 Substrate

Na_2SO_4-48 mol.% $MgSO_4$, $T_{eutectic}$=666°C, 2 mg/cm²/20h, after 5×20h (total=100h)



From the Field (Aero Turbine)

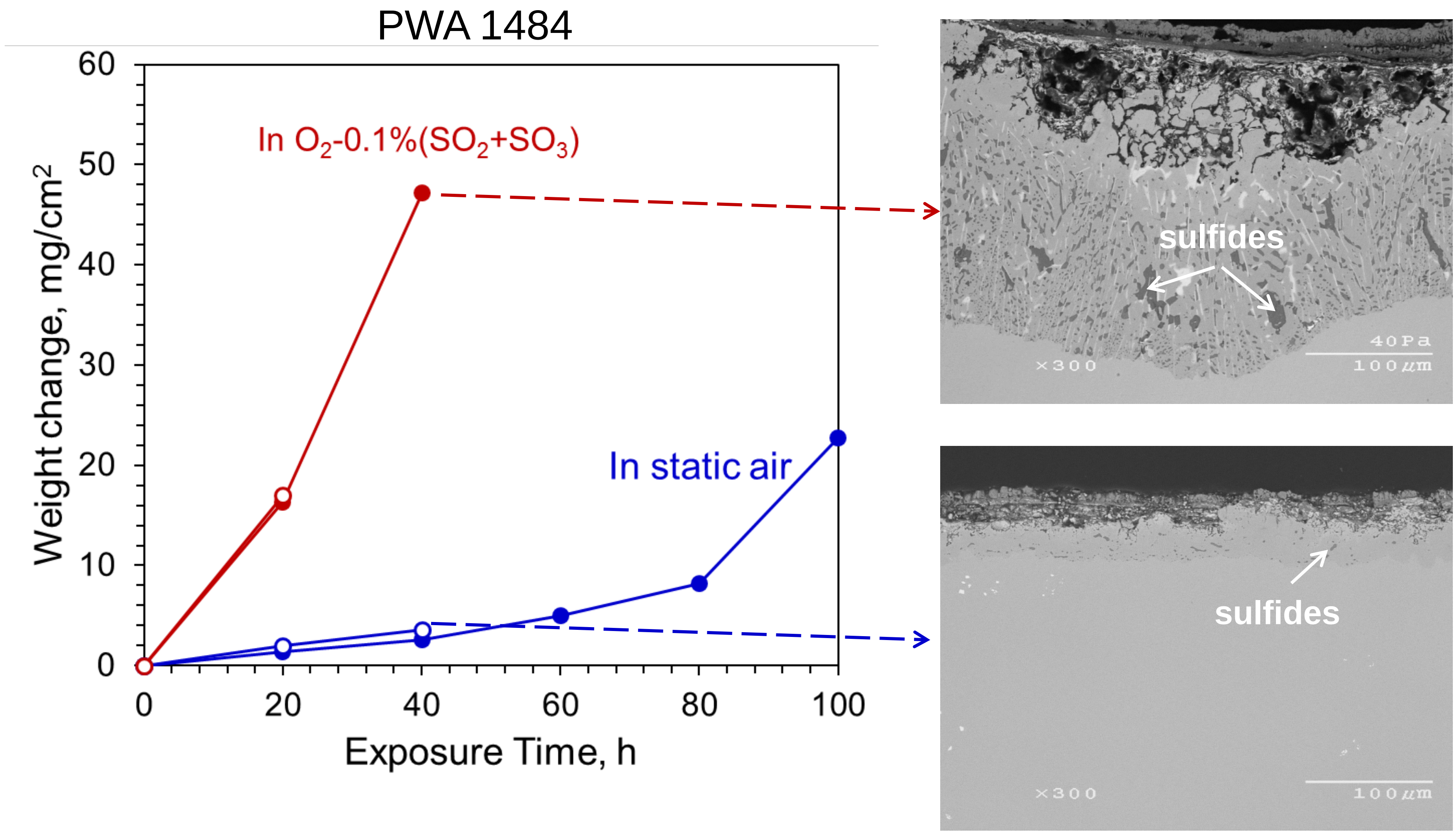
In catalyzed O_2-0.1%SO_2



Average Metal Loss: 124 μm

The presence of SO_2/SO_3 gas significantly increases the corrosion rate of Na_2SO_4-$MgSO_4$ eutectic induced hot corrosion.

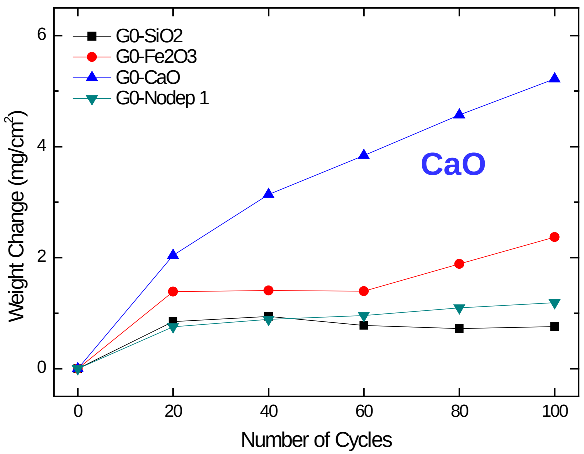
Effect of SO_2/SO_3 on the Na_2SO_4-Induced Hot Corrosion at 900°C



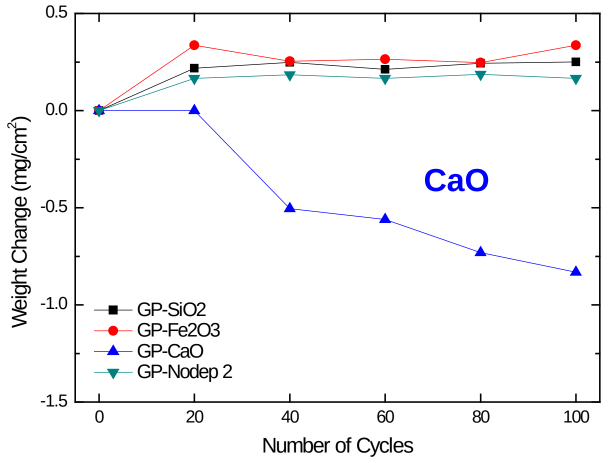
Solid Deposit Effects

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

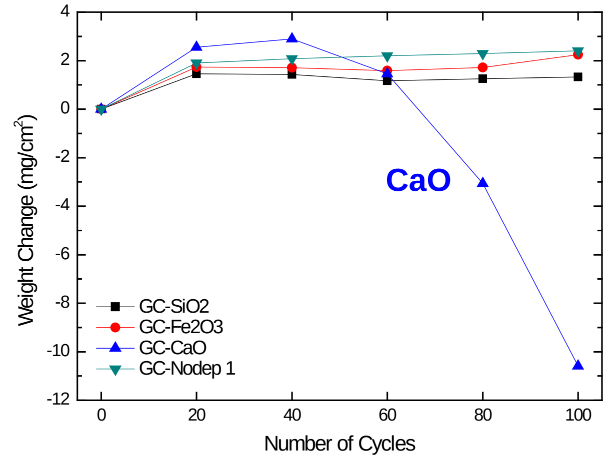
(a) Uncoated alloy



(b) Pt aluminide coating

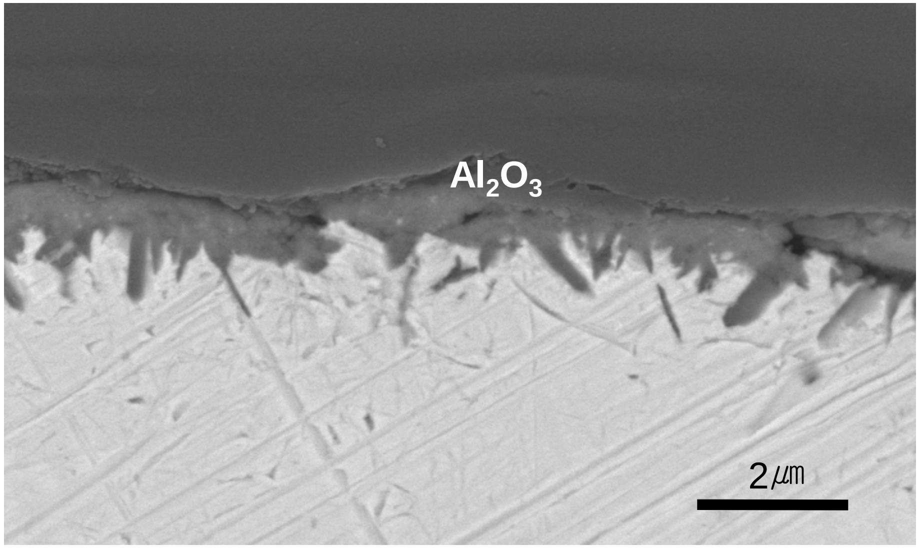


(c) CoNiCrAlY coating

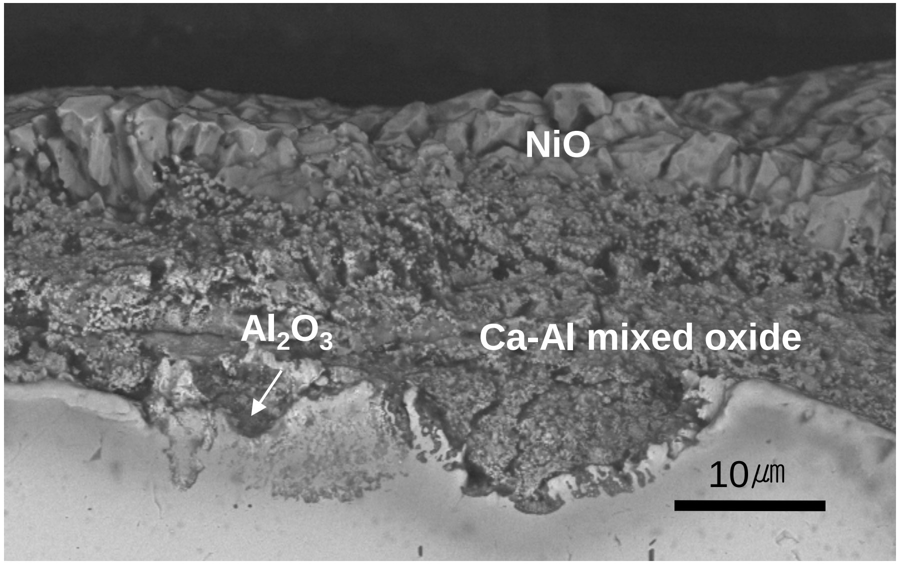


Comparison of Attack of René N5

950˚C / **Dry Air** / 140 hours exposure



No deposit



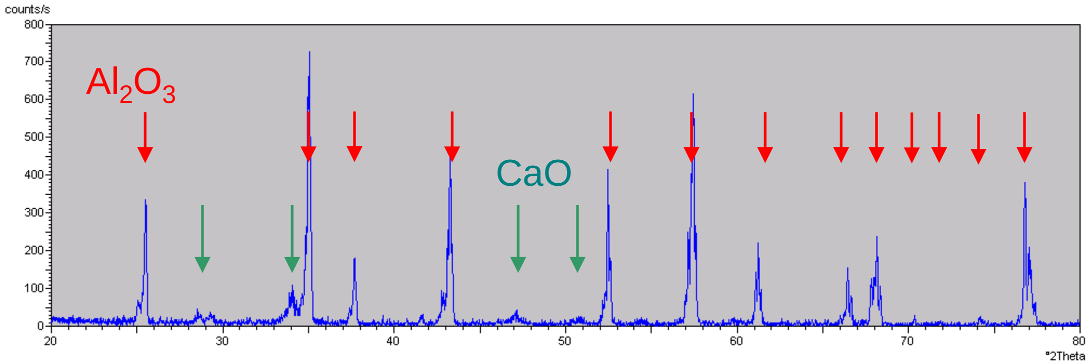
CaO deposit

Solid-state breakdown of protective oxides

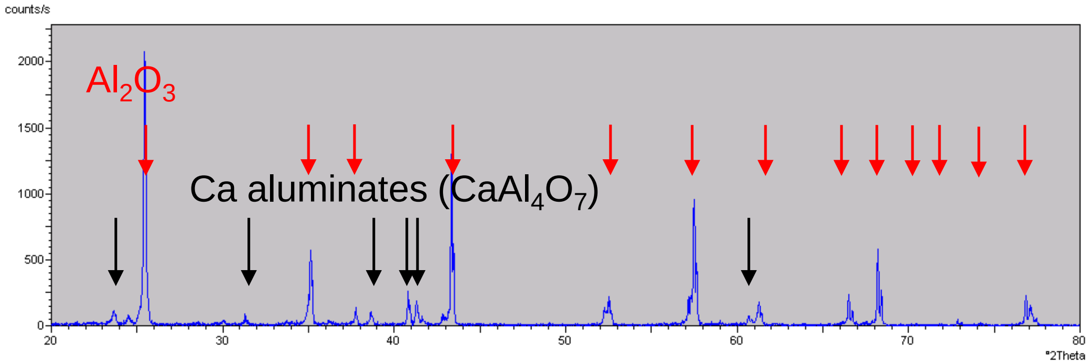
$CaO + Al_2O_3 = CaAl_2O_4$ (m.p. 1360°C)
$CaO + Cr_2O_3 = CaCr_2O_4$ (m.p. 1022°C)

CaO destroys protectiveness of α-Al_2O_3 and Cr_2O_3.

XRD results for exposed alumina coated with CaO



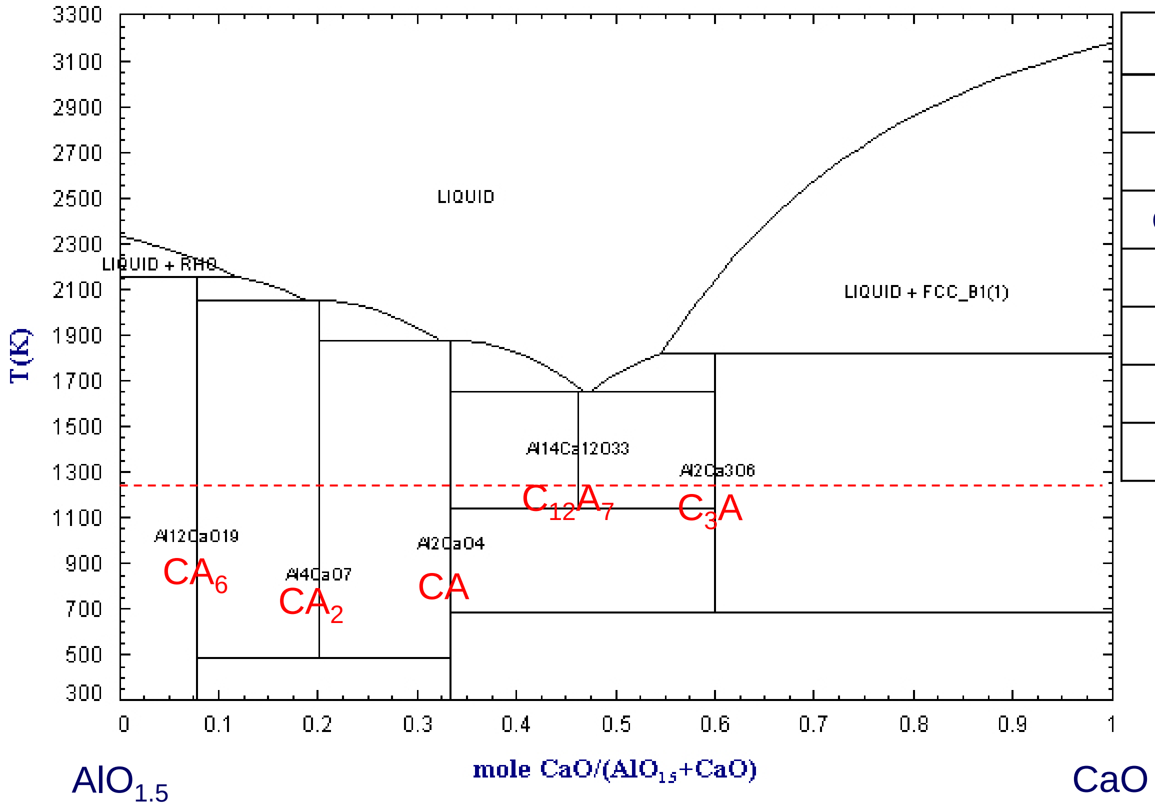
As-deposited (before exposure)



After 20h exposure at 950˚C followed by ultrasonic cleaning.

- Remaining CaO was cleaned.
- $CaAl_4O_7$ was detected.

Potential Interactions Between CaO and Al_2O_3



Abbreviated	Molecular Formula	ΔG^{o}_{950C}
C	CaO	-506.11
C_3A	$Ca_3Al_2O_6$	-13.8
$C_{12}A_7$ (= C_5A_3)	$Ca_{12}Al_{14}O_{33}$	-86.8
CA	$CaAl_2O_4$	-2.1
CA_2	$CaAl_4O_7$	-13.6
CA_6	$CaAl_{12}O_{19}$	-18.6
A	Al_2O_3	-1287.0

- - - - - - At 950°C (1273K)

Surface Images of 7YSZ TBC Specimens

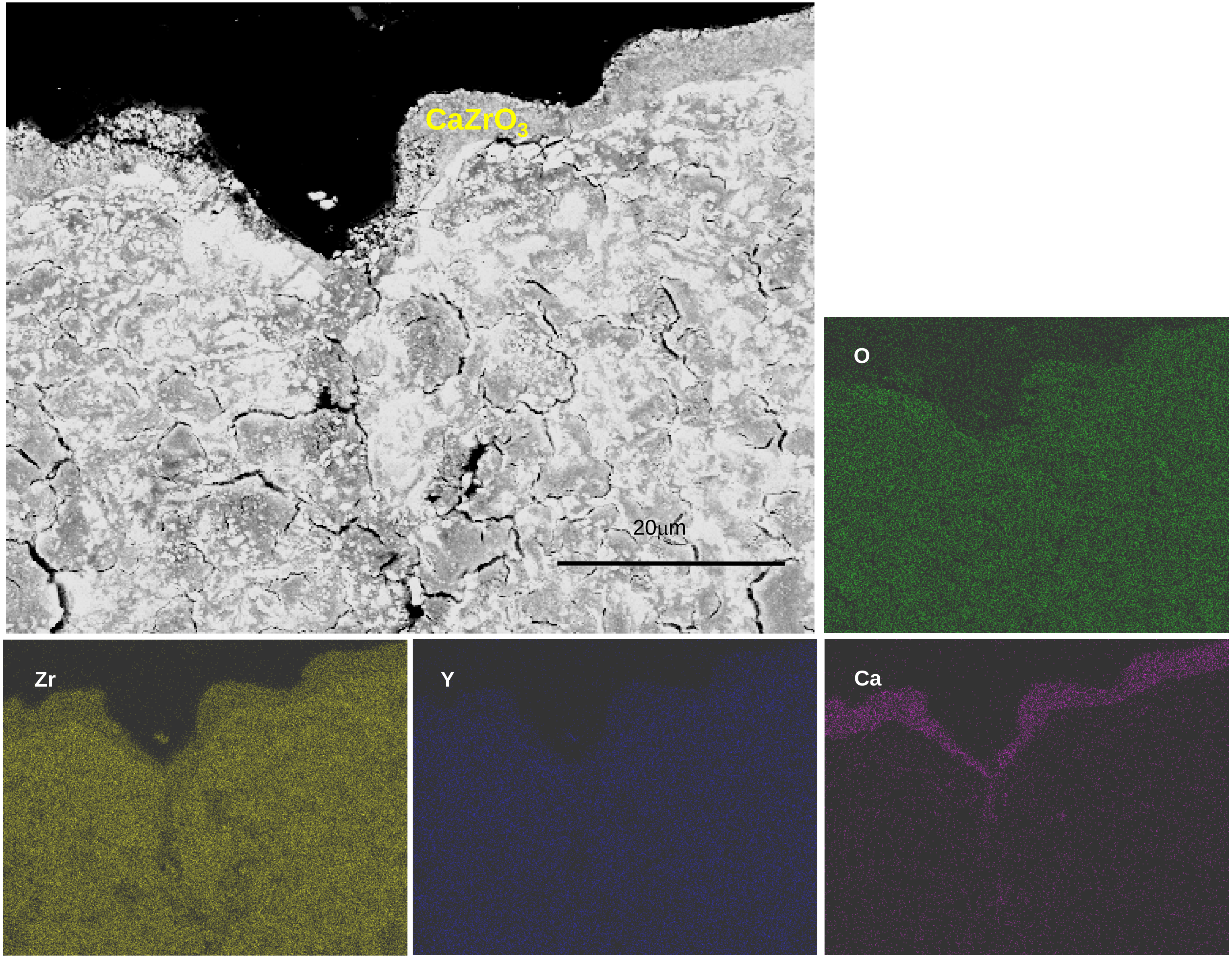
950˚C in dry air up to 200 hours with and without CaO deposits

No Deposit

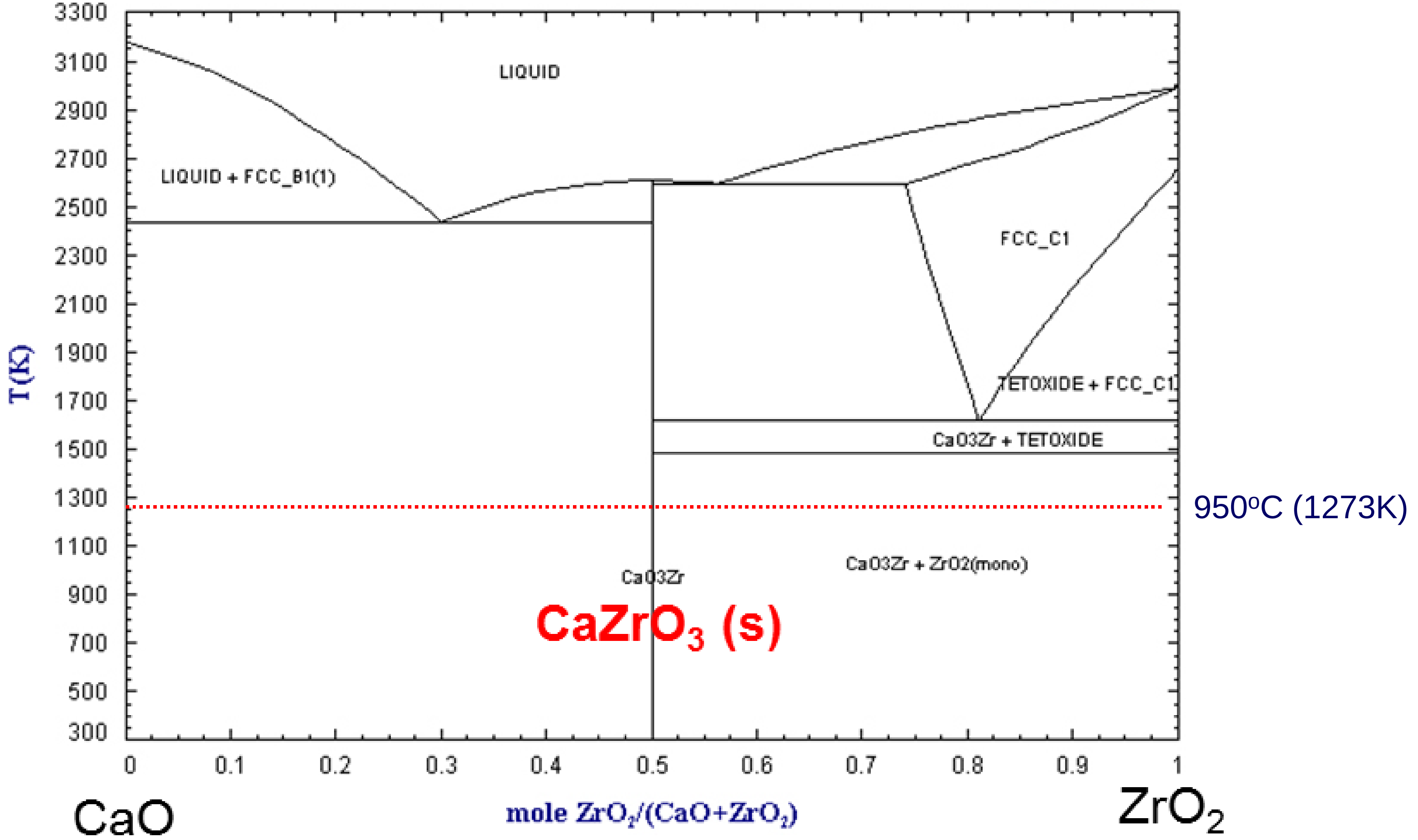
CaO Deposit

Elemental mapping showing the formation of Ca zirconates

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



Calculated CaO-ZrO_2 Phase Diagram



Program Objectives

Systematically assess the interplay between prototypical deposit chemistries (*i.e.*, ash and its constituents plus K_2SO_4 and FeS) and environmental oxidants (*i.e.*, O_2, H_2O and CO_2) on the high-temperature degradation behavior of advanced TBC systems.

Specific Objectives

- To characterize and determine the main factors governing the degradation of a state-of-the-art NiCoCrAlY bond coat and two differently processed YSZ TBCs in gaseous atmospheres that are relevant to IGCC systems.
- To characterize and determine the main factors governing the degradation of the same systems with the added complexity of the presence of a surface deposit based on coal fly ash, with particular emphasis on the fly-ash components CaO and SiO_2, as well as K_2SO_4 and FeS.

Combined effects *of environment and deposit*

- To establish an effective experimental procedure for assessing high-temperature, deposit-induced degradation in IGCC-relevant environments.

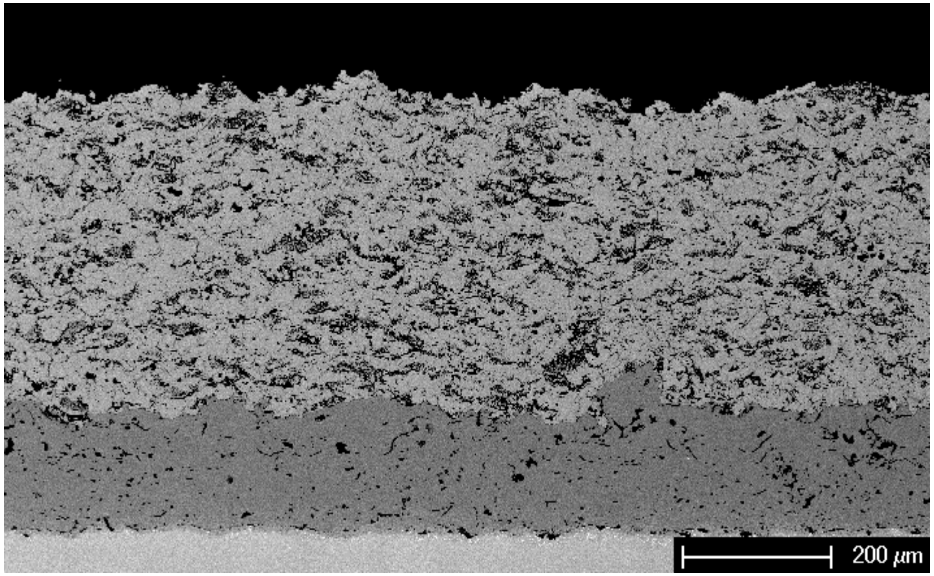
Systems and Environments to be Studied

- Substrate: *2^{nd} generation Ni-base single crystal superalloy (René N5 or PWA 1484)*
- Bond Coat: *NiCoCrAlY (Ni-22Co-16Cr-13Al-0.5Y wt.%) applied by Ar-shrouded plasma spraying at PST*
- TBC: *Standard YSZ composition – 7wt.%Y_2O_3 – deposited by APS at thickness of ~380 μm*
  - *Dense vertically cracked (DVC)*
  - *High purity – low density (HP-LD)*

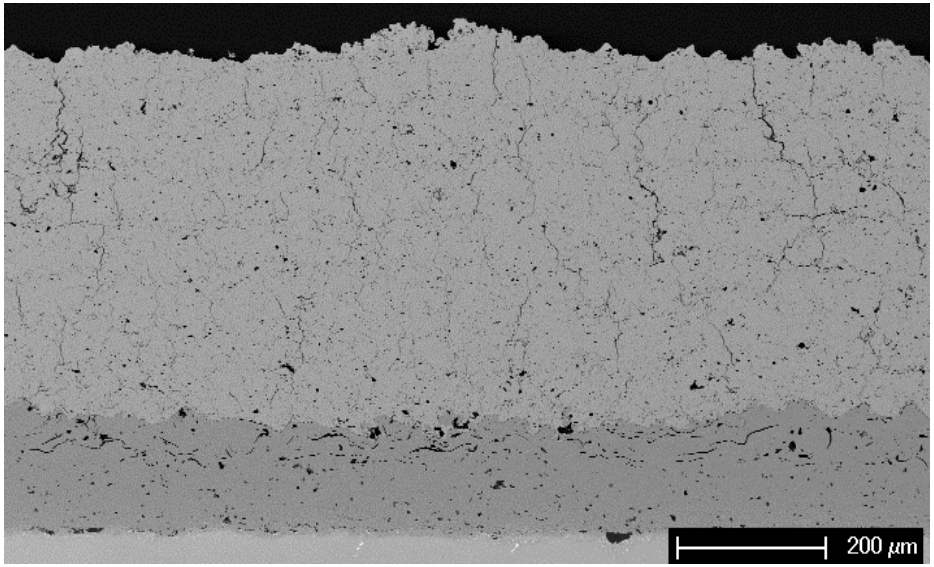
An active and contributing collaborator on this project is ***Praxair Surface Technologies (PST)***

TBC Systems Being Tested

High Purity/Low Density TBC

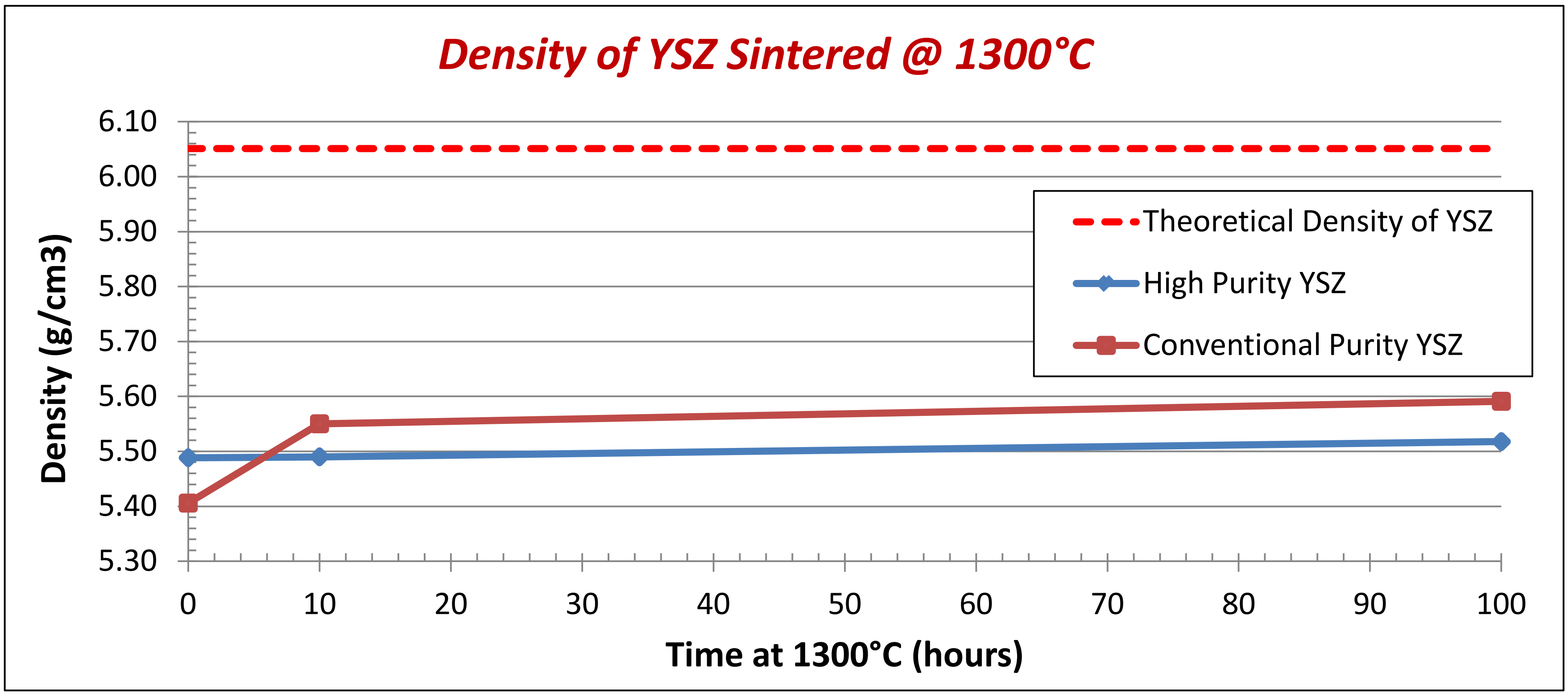


DVC TBC



YSZ Sintering Behavior

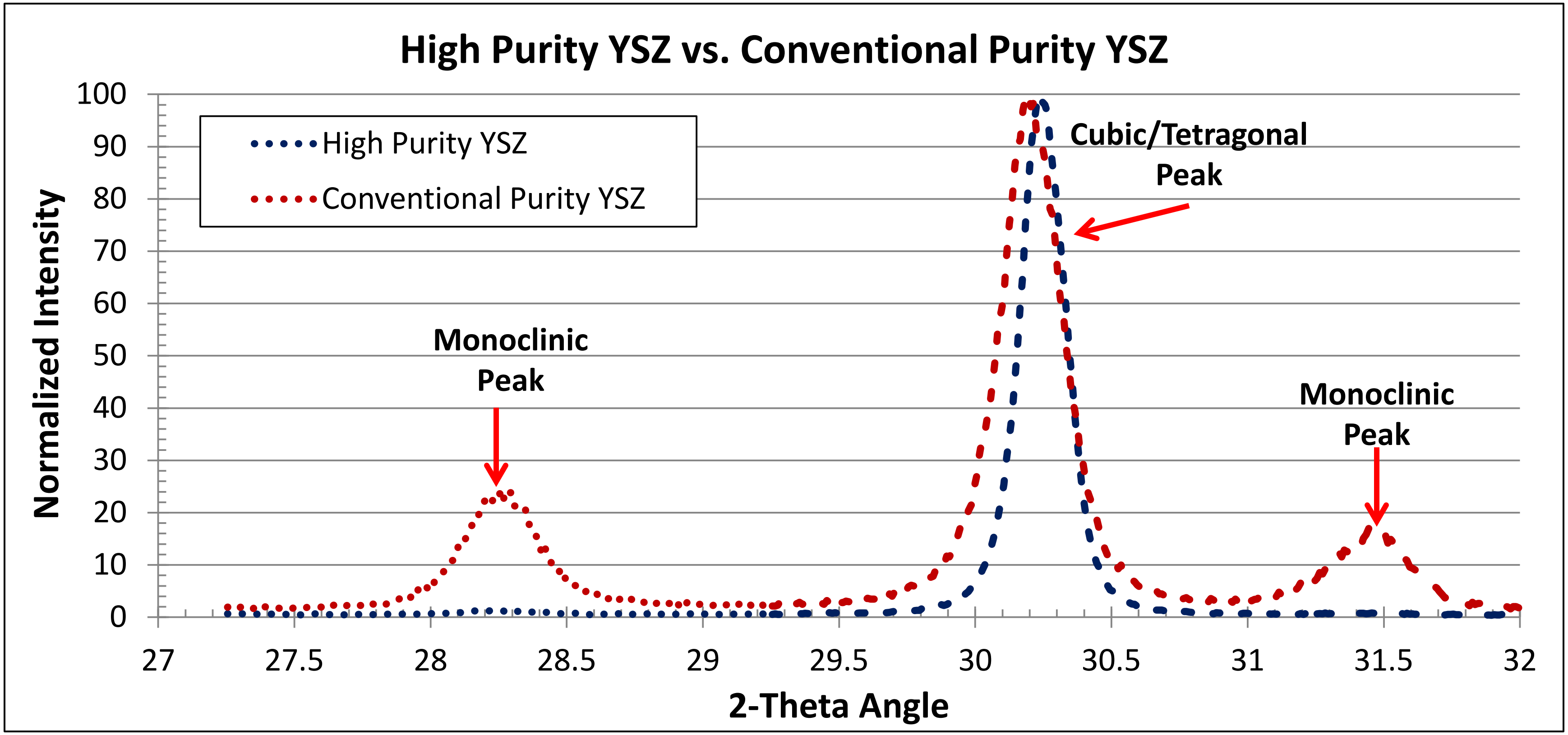
Type of YSZ	YSZ Powder Compositions (wt%)									
	ZrO_2	Y_2O_3	HfO_2	Al_2O_3	SiO_2	TiO_2	CaO	Fe_2O_3	MgO	Other
High Purity	Bal	7.90	1.7	**0.010**	**0.007**	0.004	0.004	0.010	0.004	0.078
Conventional Purity	Bal	7.40	1.6	**0.100**	**0.500**	0.027	0.004	0.033	0.002	0.350



YSZ Phase Stability

Thermal history of specimens:

- Free-standing YSZ coatings sintered at 1300°C for 100 hours in laboratory air
- Rapid quench from 1300°C to 20°C
- Reheat to 150°C for 165hr in laboratory air
- Ambient cooling from 150°C to 20°C



Systems and Environments to be Studied

- Substrate: *2^{nd} generation Ni-base single crystal superalloy (Rene N5 or PWA 1484)*

- Bond Coat: *NiCoCrAlY (Ni-22Co-16Cr-13Al-0.5Y wt.%) applied by Ar-shrouded plasma spraying at PST*

- TBC: *Standard YSZ composition – 7wt.%Y_2O_3 – deposited by APS at thickness of ~380 μm*
  - *Conventional purity, dense vertically cracked (DVC)*
  - *High purity – low density (HP-LD)*

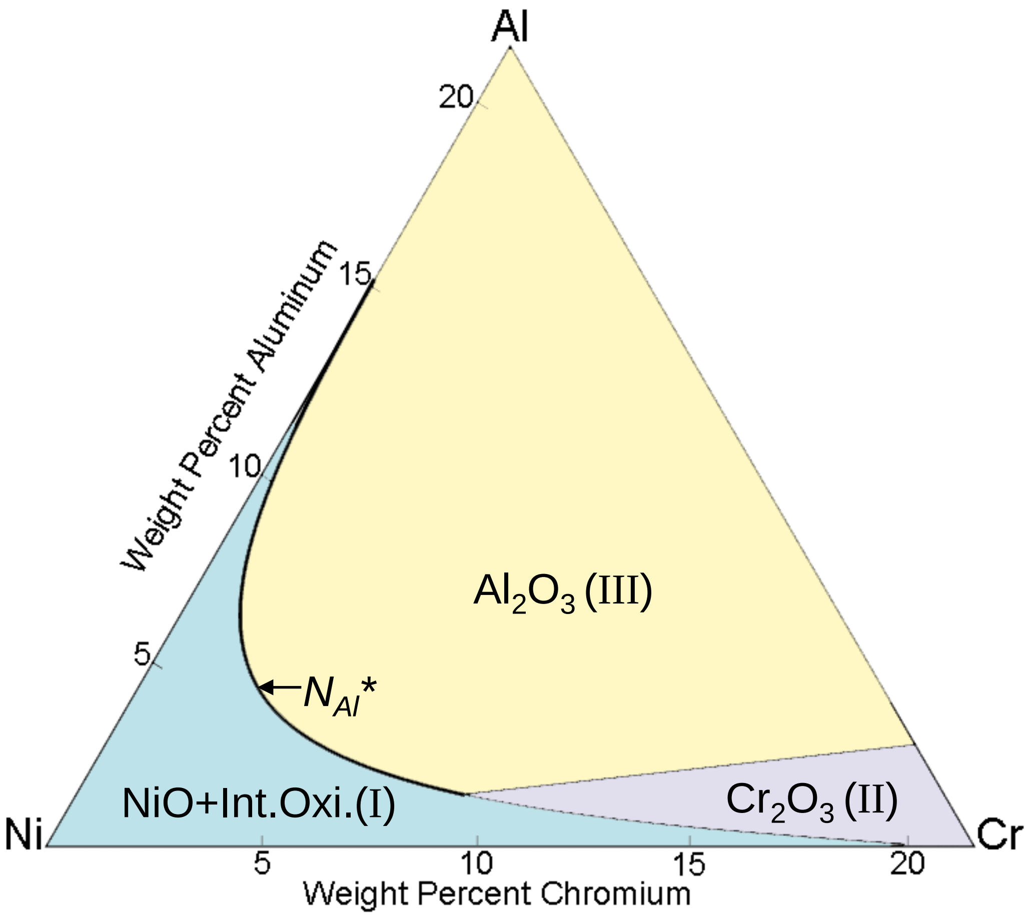
- Gaseous Atmospheres:
  - *air*
  - *air + 20%H_2O*
  - *20%H_2O + 70%CO_2*

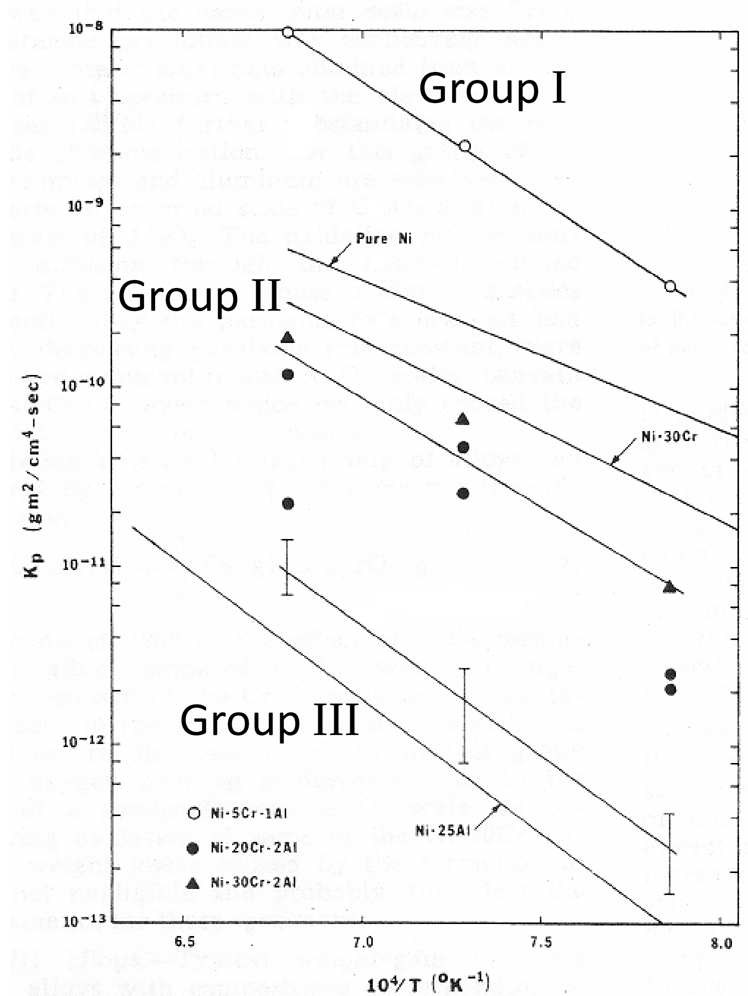
  900 - 1100°C

“Dry” Oxidation of Ni-Cr-Al Alloys

Chromium promotes Al_2O_3 formation

Giggins and Pettit* established the following oxidation map for rolled Ni-Cr-Al alloys in 0.1atm O_2 at 1000°C.

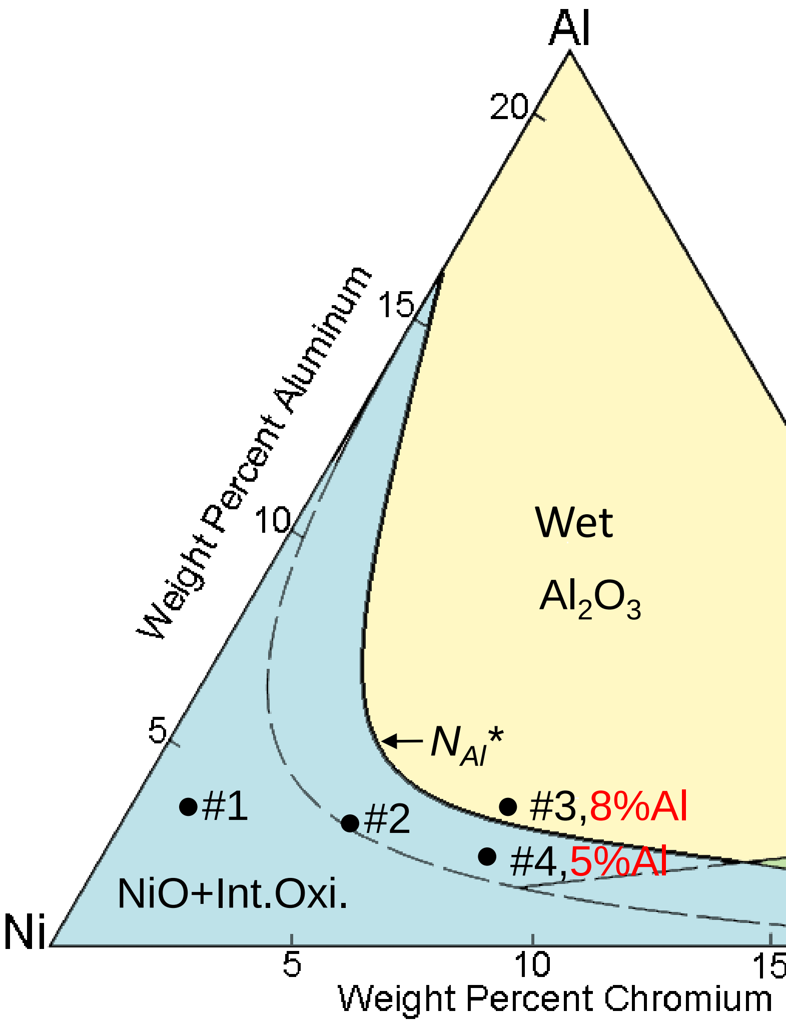


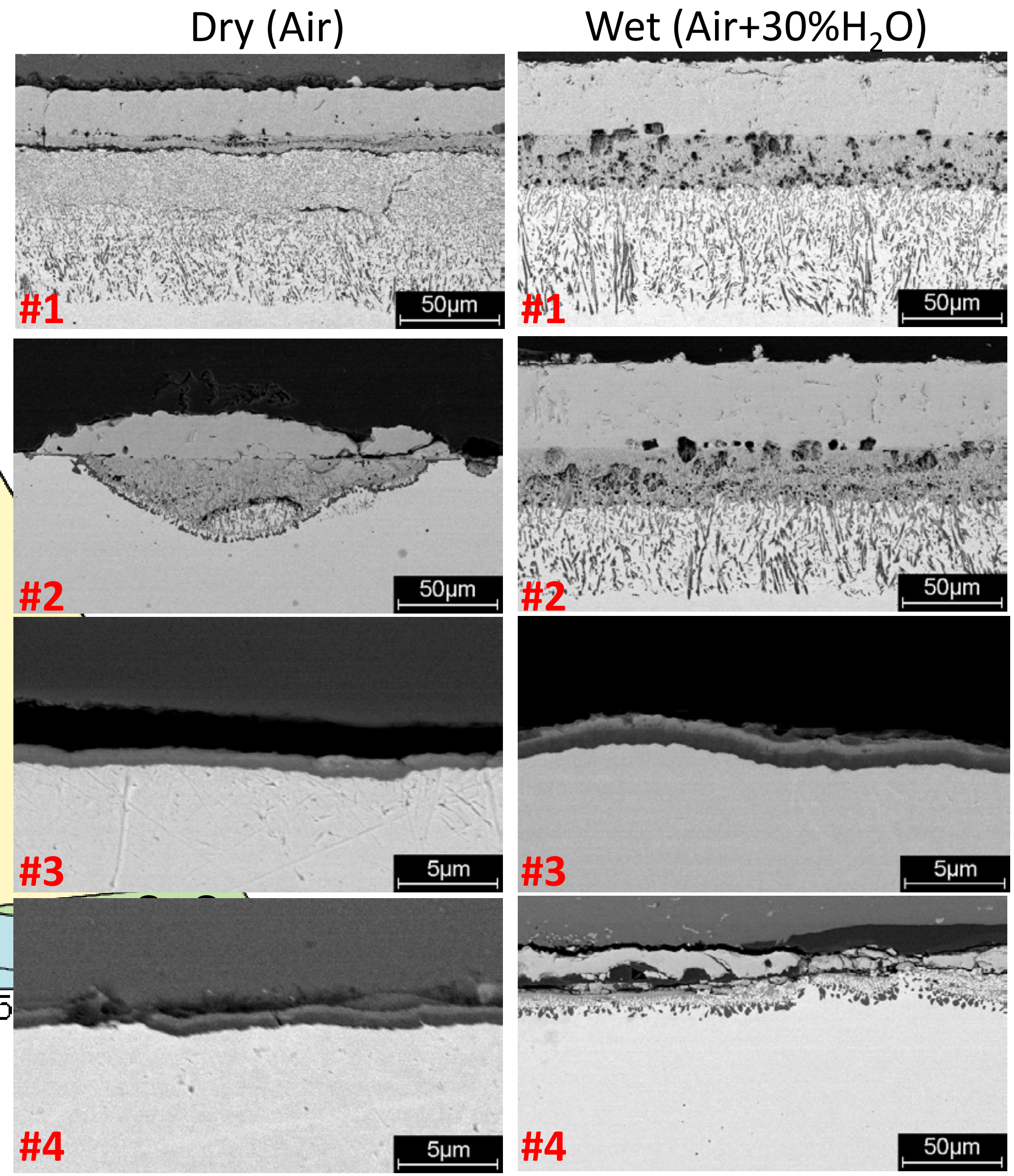


C.S. Giggins and F.S. Pettit, J. Electrochem. Soc.,118, 1782,1971

Oxide Maps for “Dry” and “Wet” Oxidizing Conditions

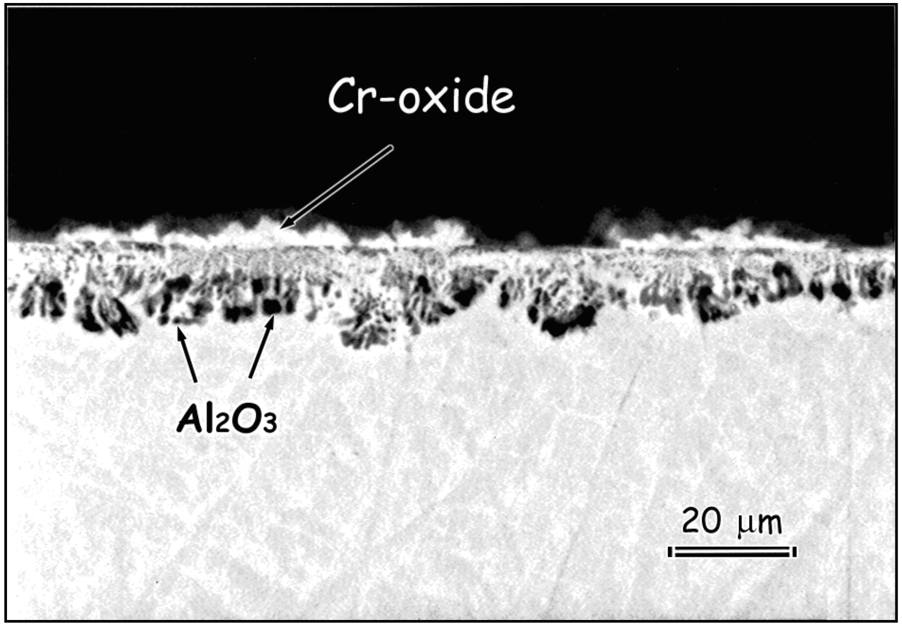
1000°C exposures for 50 h



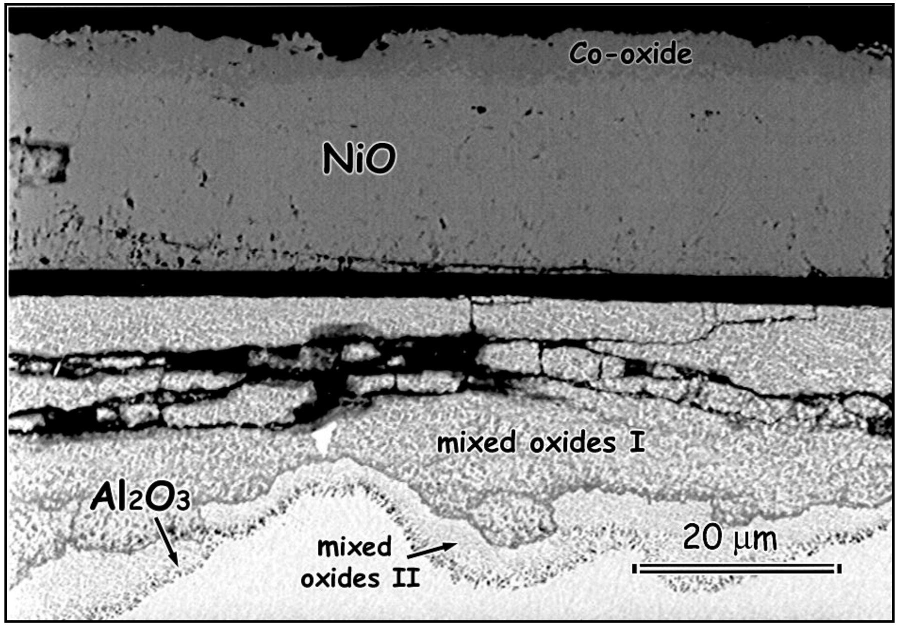


Cyclic Oxidation at 700°C

PWA 1484



Dry Air



Air + 10% H_2O

Environments and Deposits to be Studied Initially

- Gaseous Atmospheres:
  - *air*
  - *air + 20%H_2O*
  - *20%H_2O + 80%CO_2*
  - *air + 20%H_2O + 0.1%SO_2 (some tests)*

  900 - 1100°C (air; air + 20%H_2O; 20%H_2O + 80%CO_2)

- Deposits:
  - *coal fly ash**
  - *individual ash components: CaO and SiO_2*
  - *fly ash with additions of 5%FeS or 5%K_2SO_4*

**May also be synthetic fly ash: 50SiO_2 – 25Al_2O_3 – 12.5CaO – 12.5Fe_2O_3 (wt.%)*

- Free-standing TBCs will be tested at 1100 and 1300°C

Flow Diagram for the Project

Year 1

- Task 1. Project Management and Planning
- **Task 2. Selection of Deposits** and Acquisition of Materials
- **Task 3. Testing of TBCs at 900, 1000 and 1100°C without Deposits in Selected Gas Mixtures**

Current Status

Year2

- **Task 4.1**. Testing of TBCs with Surface Deposits at 900, 1000 and 1100°C in Selected Gas Mixtures
- **Task 4.2**. Testing of Free Standing TBCs at 1100 and 1300°C with and without Deposits

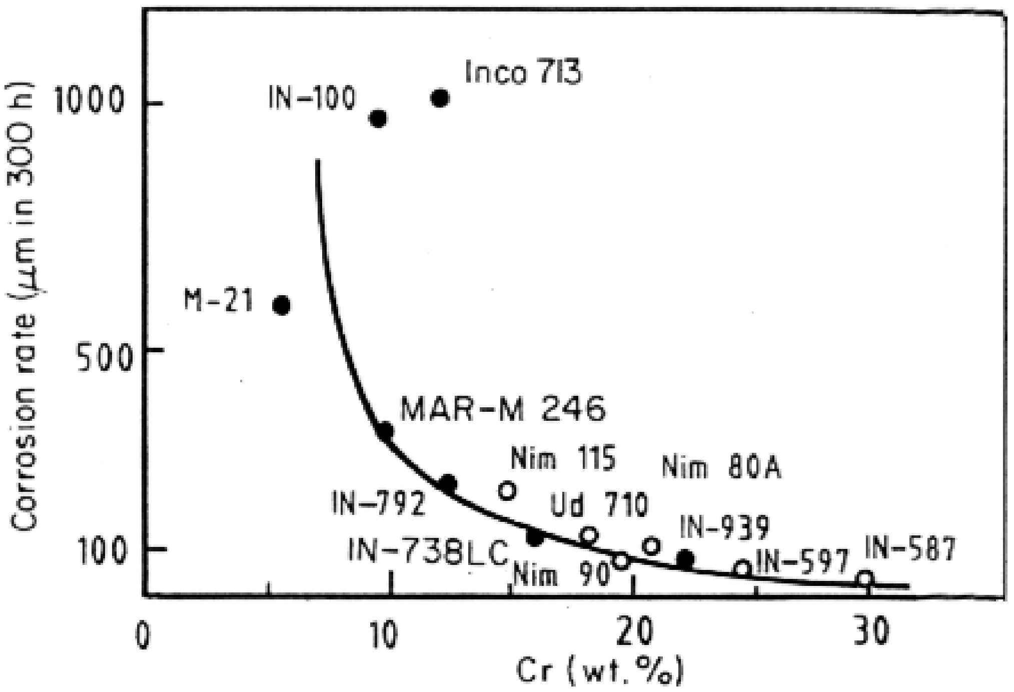
Year3

- **Task 4.3.** Thermal Gradient Testing
- **Task 5.2**. Evaluation of Residual Top Coat Properties (Densification, Phase Transformation, Thermal Conductivity)
- **Task 6.** Analysis of Results

Task 5.1. Characterization of Exposed Specimens

Chromium and 900˚C Corrosion Resistance to Sulfate Deposits

Cr is known to improve the hot-corrosion resistance of an alloy

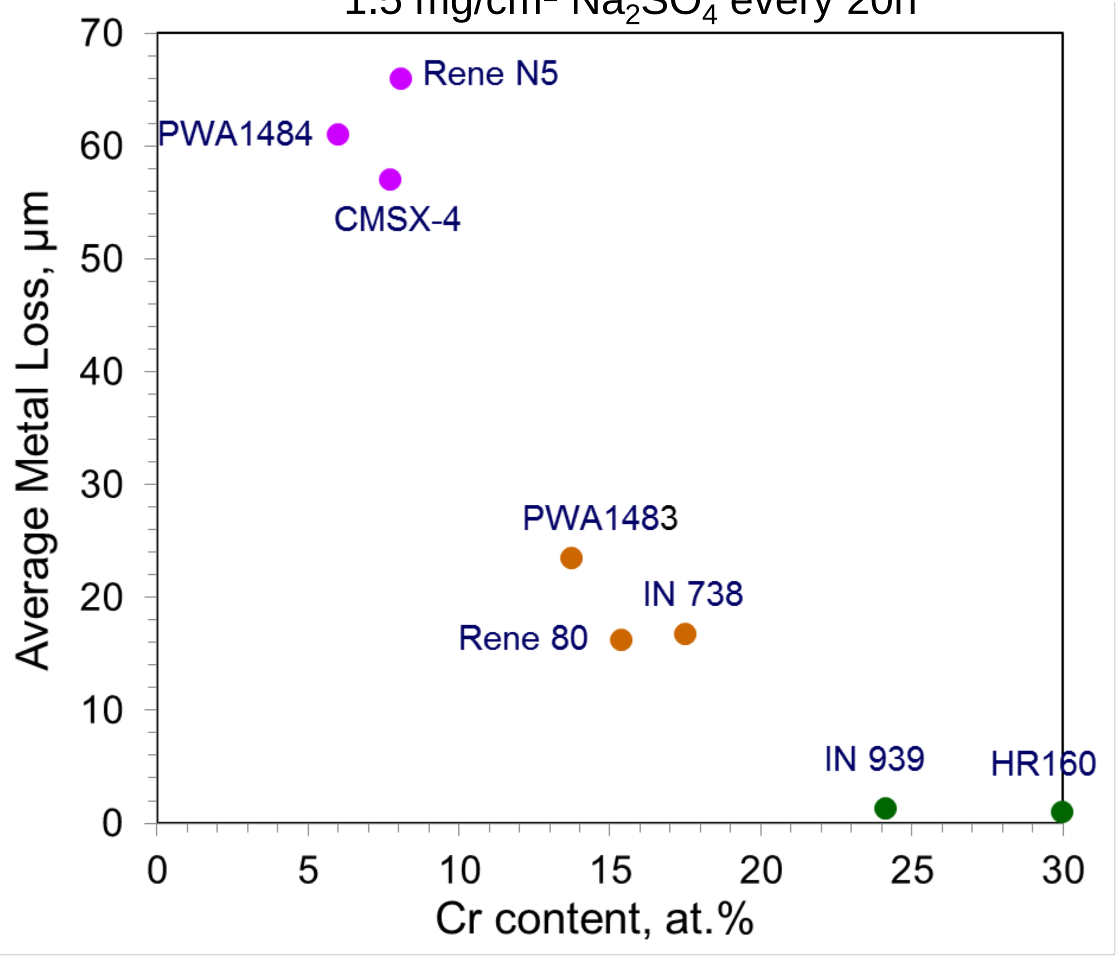


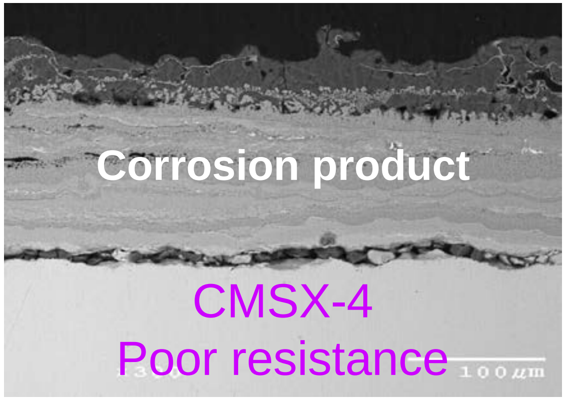
From P. Hancock, Materials Science and Engineering. 88 (1987) 303.

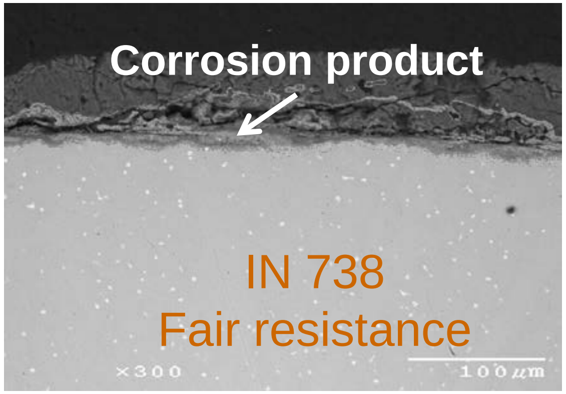
700ºC Hot Corrosion of Commercial Alloys-Cr content

O_2-0.1%(SO_2+SO_3)

1.5 mg/cm^2 Na_2SO_4 every 20h

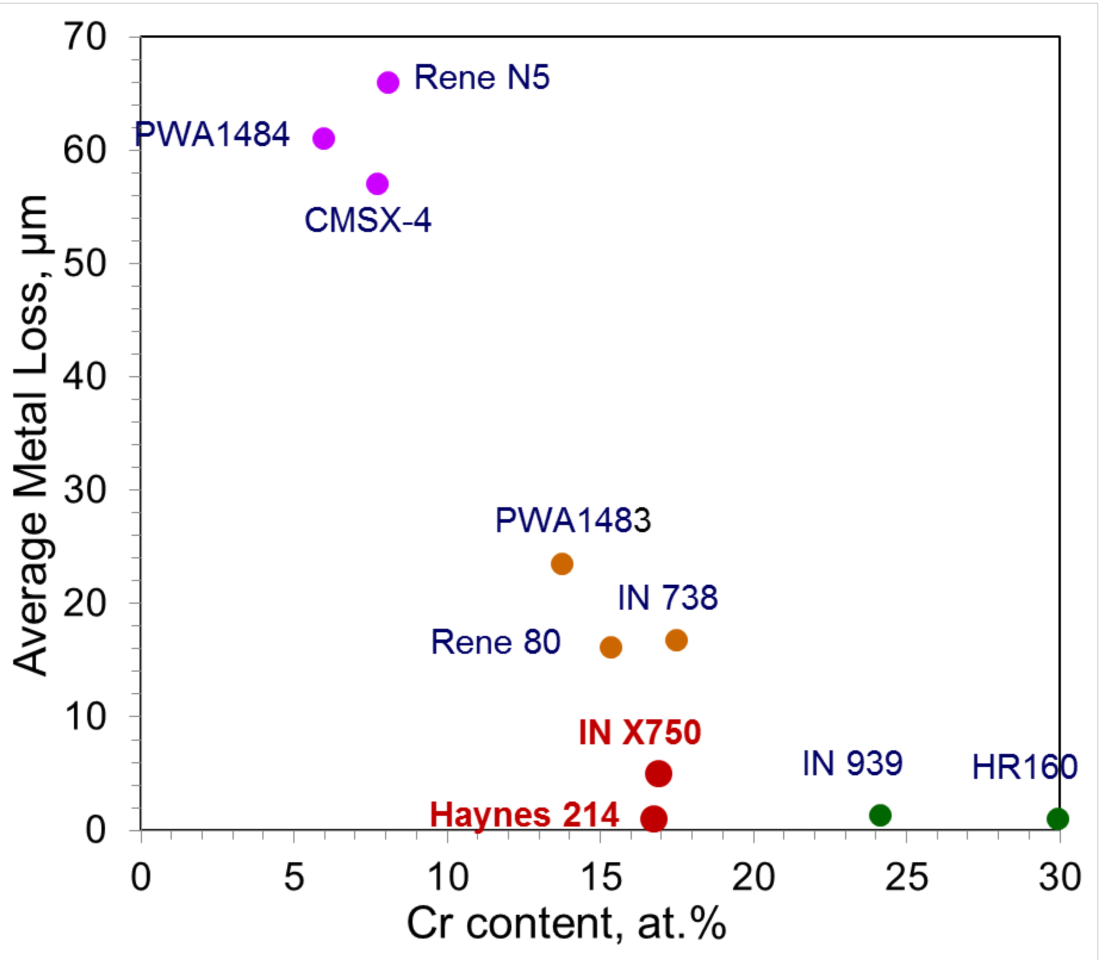


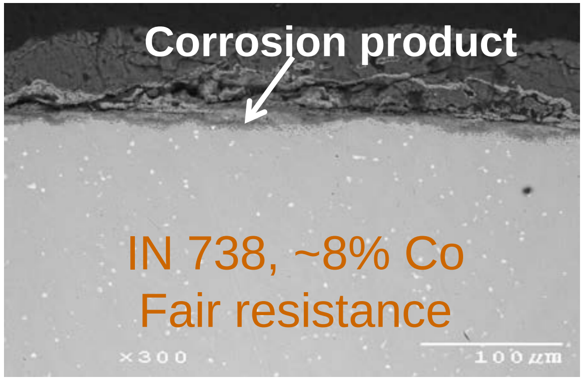




All are Ni-based superalloys that contain 8-29 wt.% Co.

700ºC Hot Corrosion of Commercial Alloys-Co and Cr

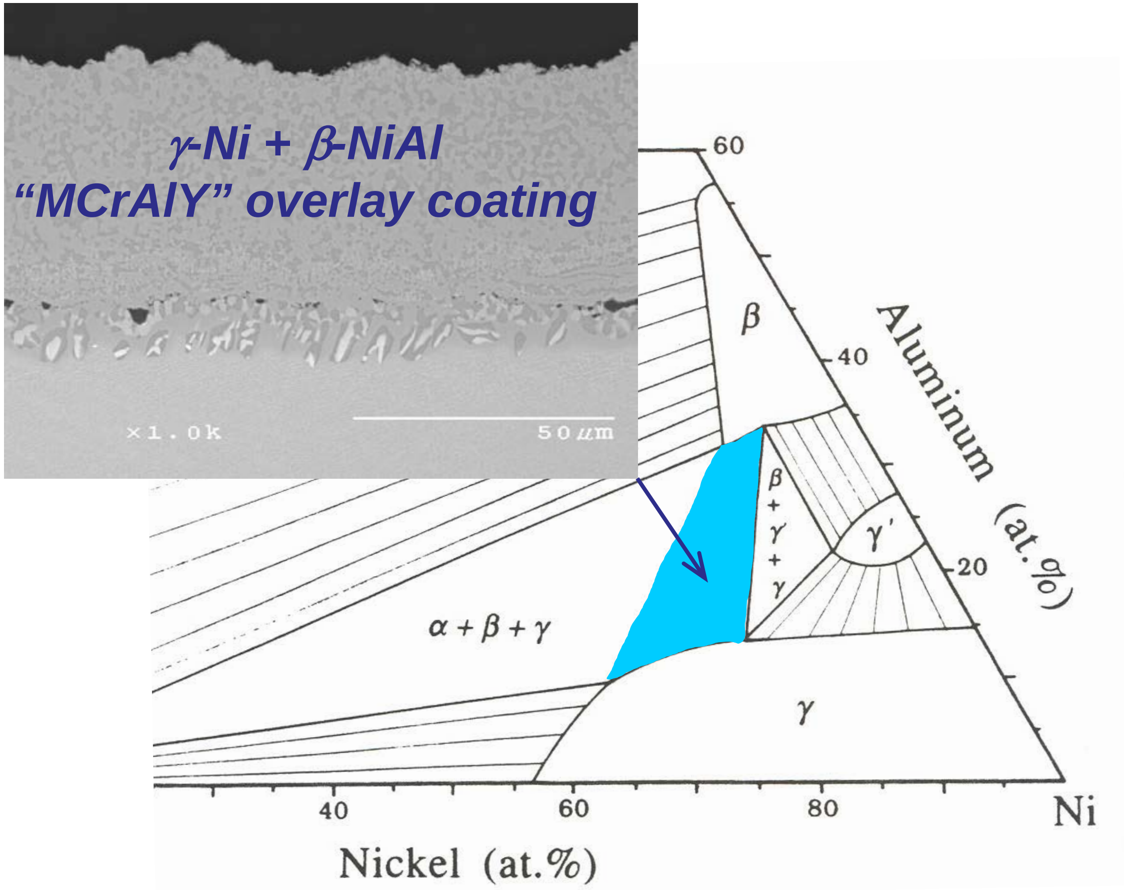


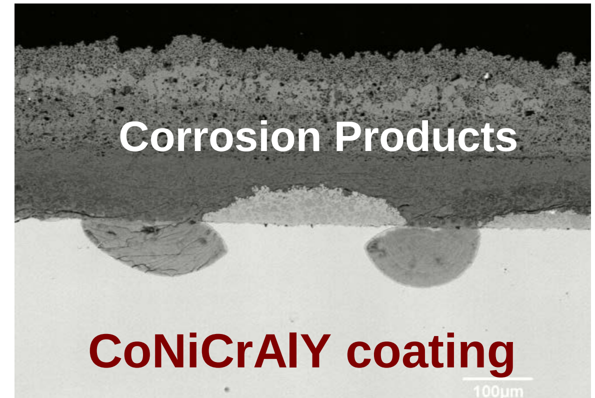


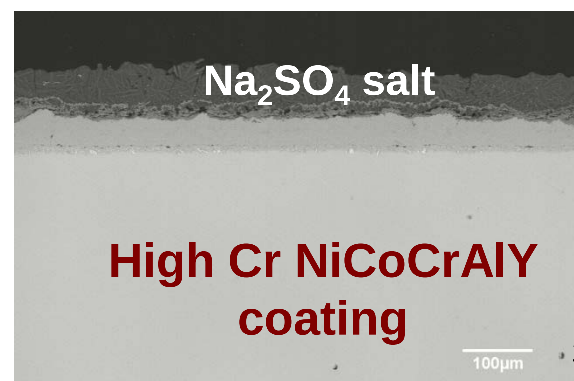
At.%	Ni	Cr	Co	Al	Fe	Ti	Ta	W	Mo
Haynes 214	Bal.	16.8	-	9	2.9	-	-	-	-
IN X750	Bal.	17.2	<1	1.7	8	3.0	-	-	-
IN 738	Bal.	17.5	8.2	7.1	-	4.0	0.6	0.8	1.0

700°C Hot Corrosion of MCrAlY Overlay Coatings

O_2-0.1%(SO_2+SO_3), 5×20h cycles, 2 mg/cm^2 Na_2SO_4





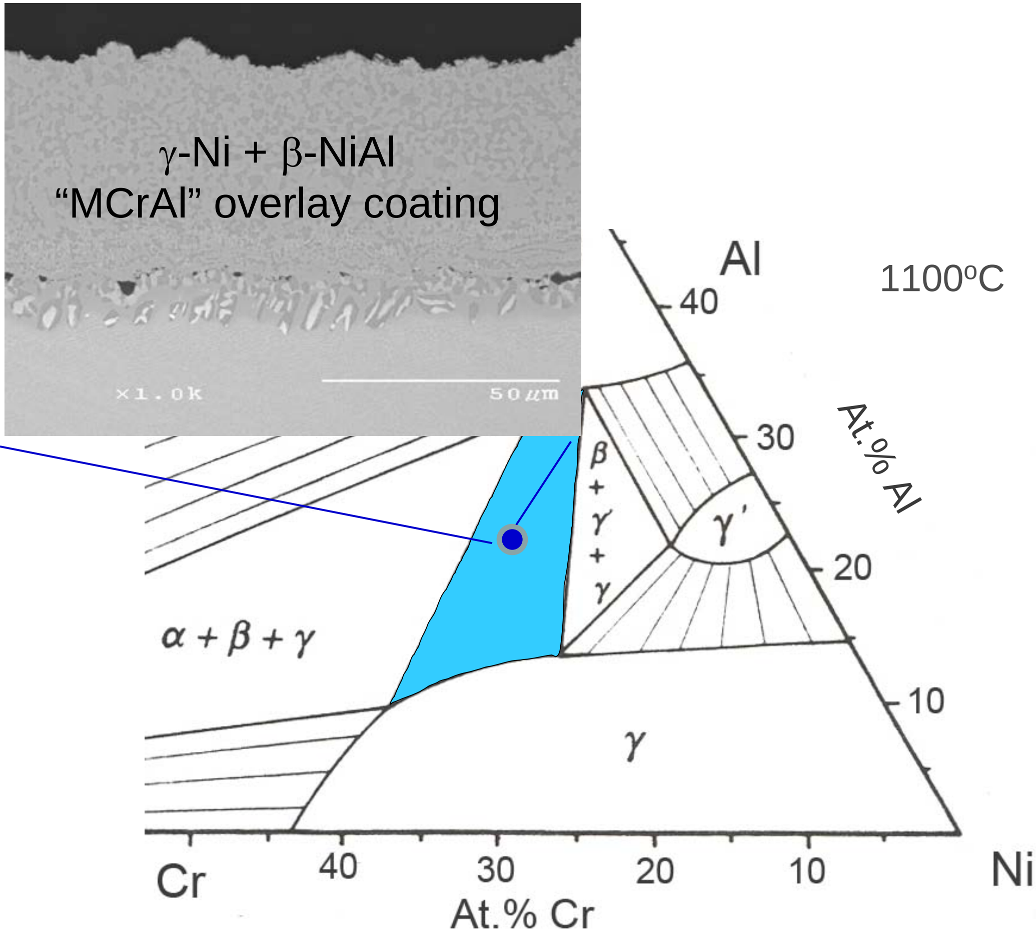


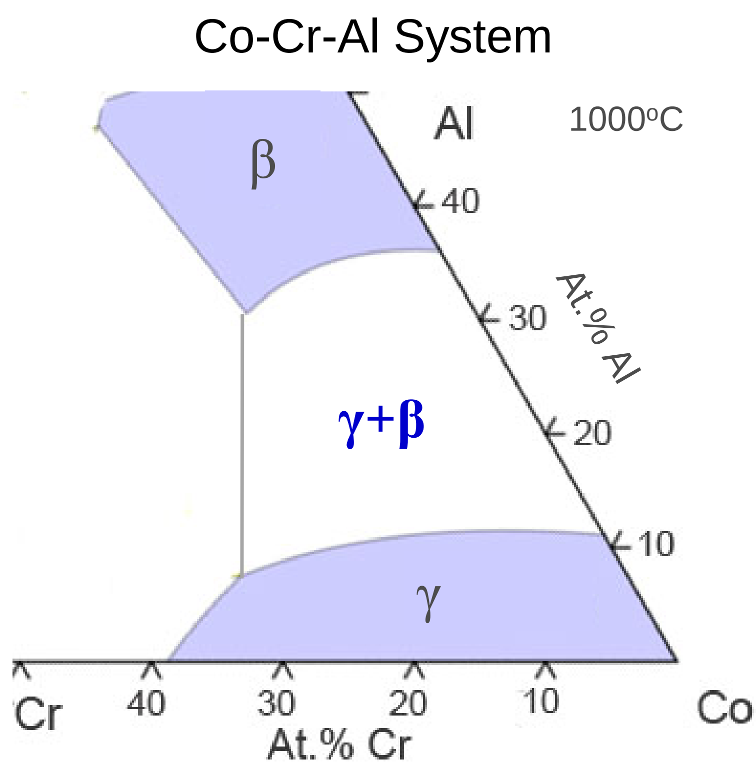
Compositions of MCrAlY coating vary dramatically, *e.g.*, 2002 US patent 6,435,830: "Exemplary" composition

20-40% Cr, 5-35% Al, 0-2% Y, 0-7% Si, 0-2% Hf with a balance of Ni and/or Co.

15-40% Cr, 5-15% Al, 0.8% Y, 0.5% Si, 0.4% Hf with a balance of Ni and Co.

NiCrAlY Coatings and Effect of Co Additions

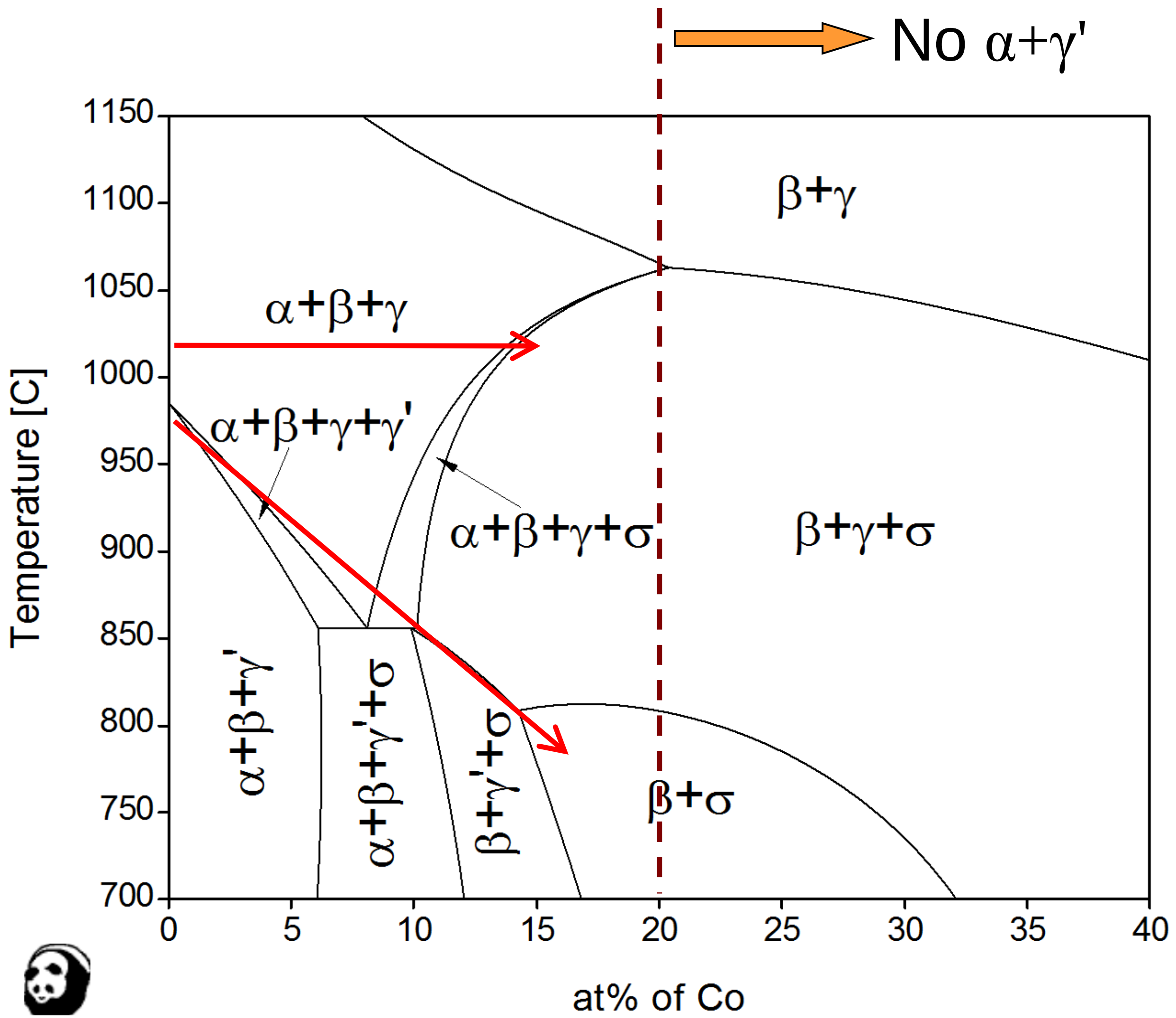




Cobalt additions to NiCrAlY destabilize γ' phase

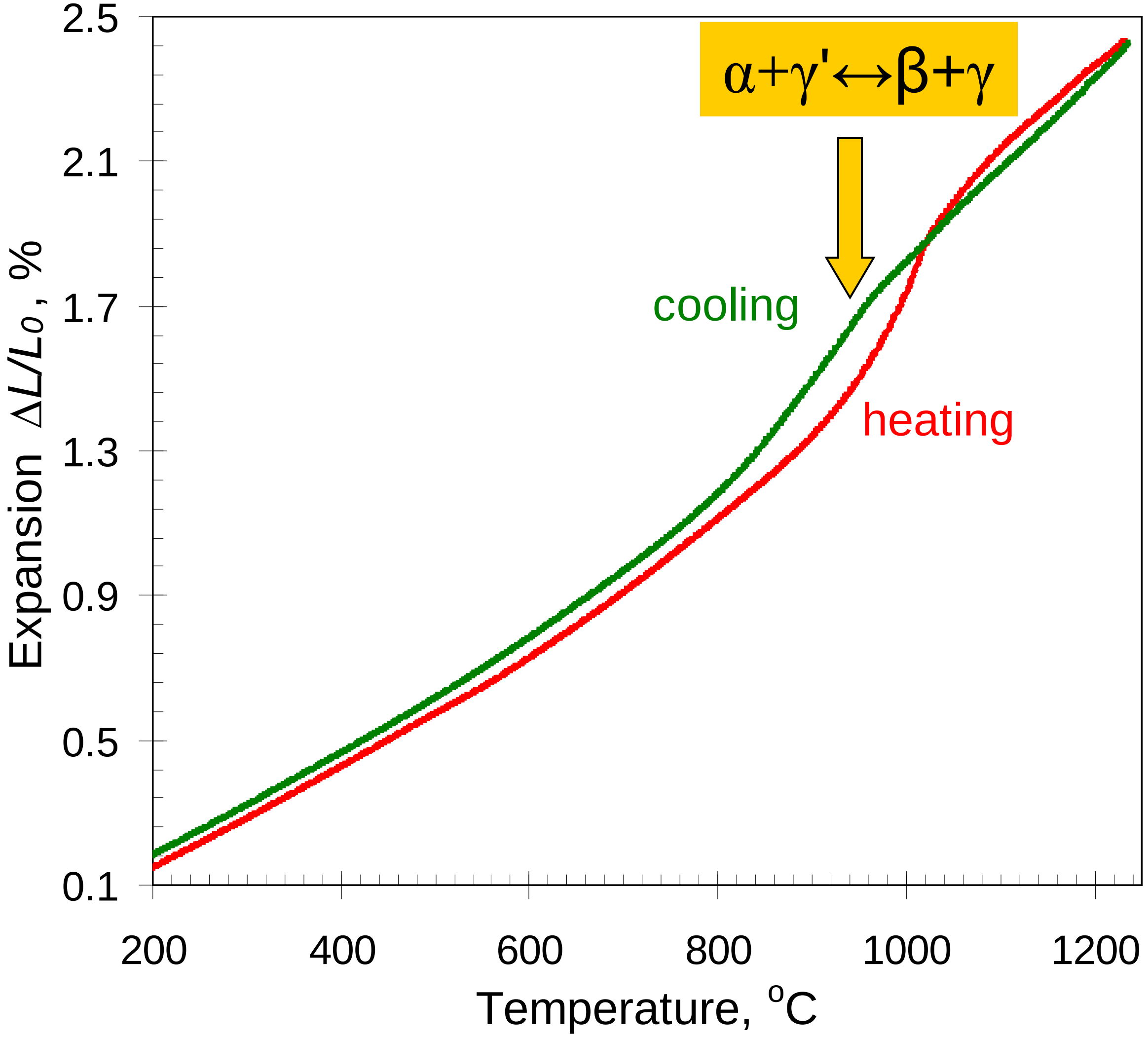
Effects of Co Additions on Phase Equilibria

Calculated Ni-Co isopleth at 26Al and 20Cr, at.%



Thermal Expansion of NiCrAlY Base Alloy

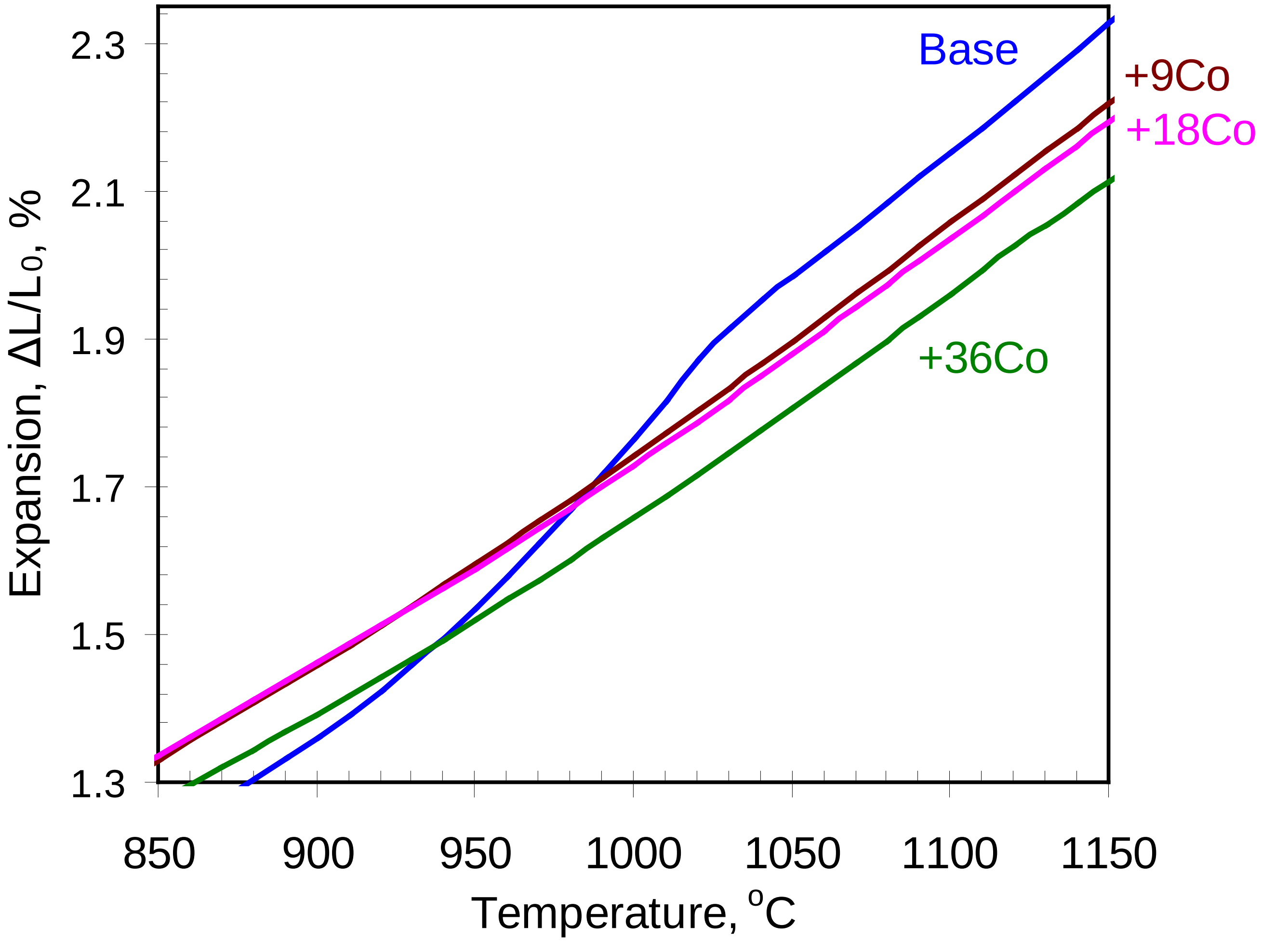
Composition: Ni-26Al-20Cr-0.1Y, at.%



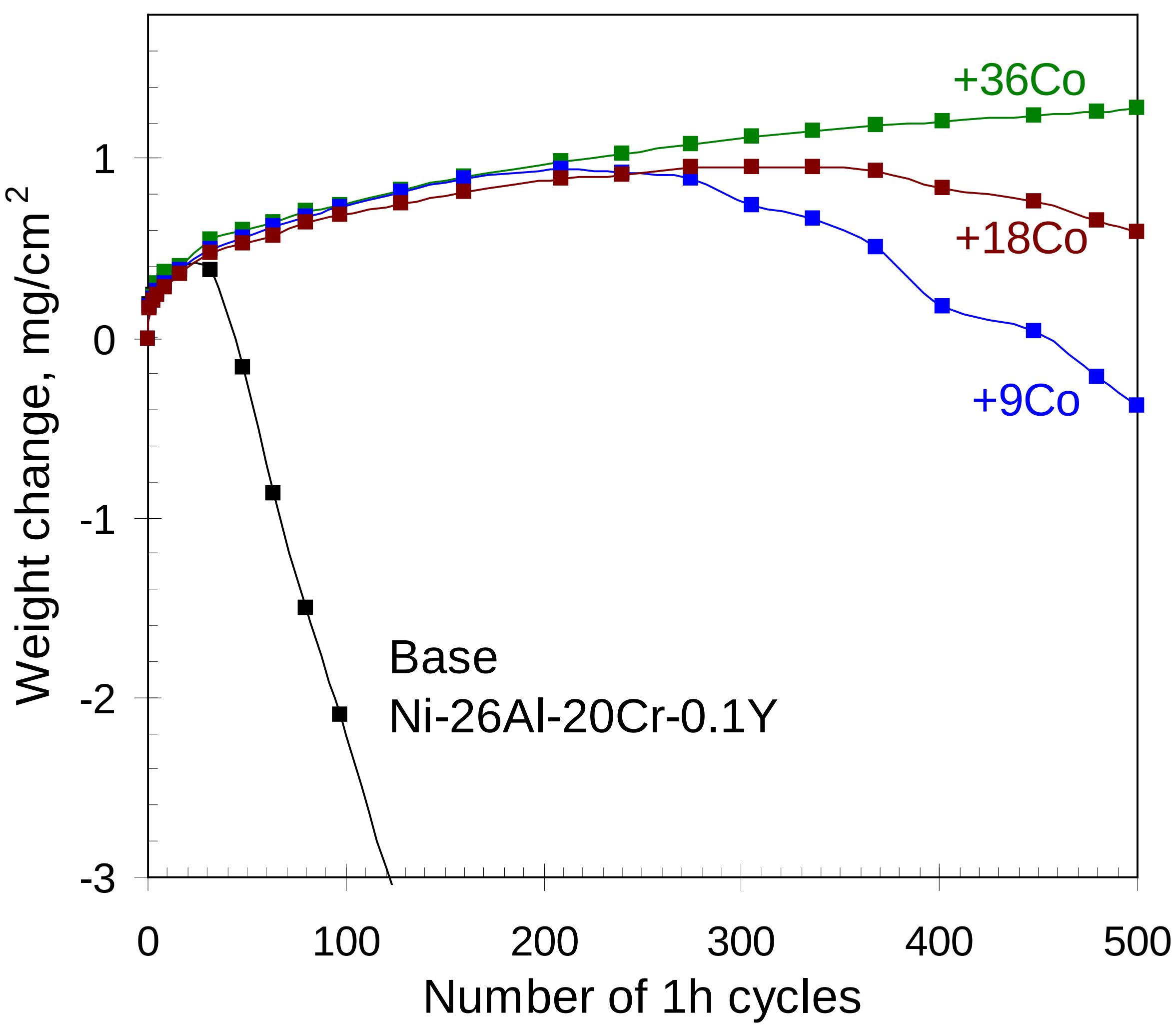
ΔL is difference in length at temperature *T* compared with the starting length L_0 at 25°C

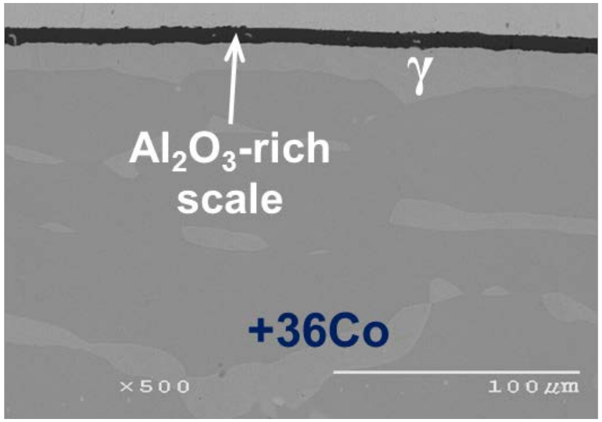
Thermal Expansion Behavior of NiCoCrAlY Alloys

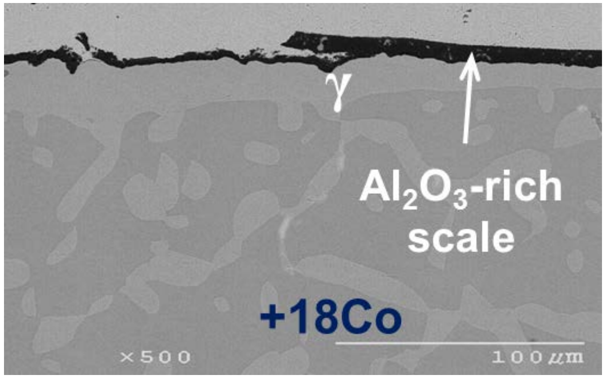
Base composition: Ni-26Al-20Cr-0.1Y, at.%

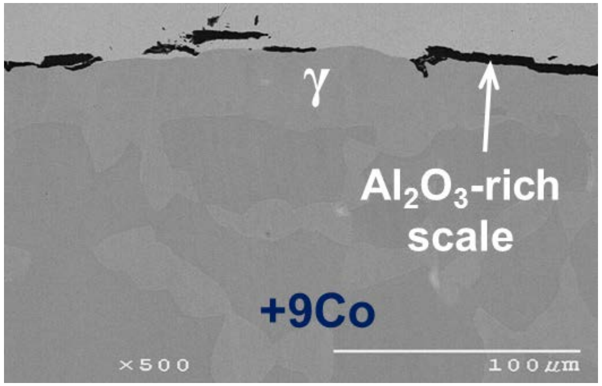


Cyclic Oxidation Kinetics at 1150°C in Air



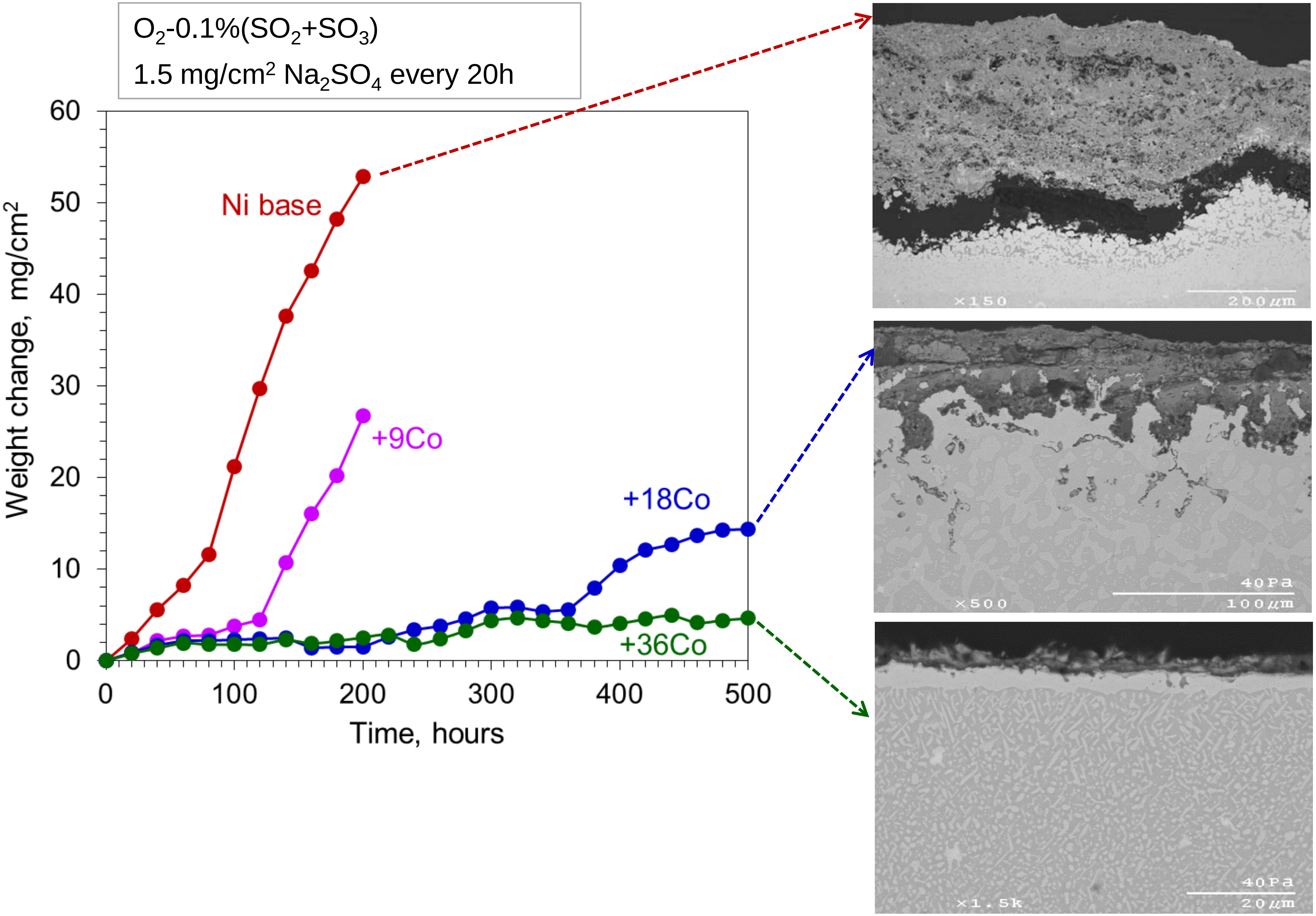






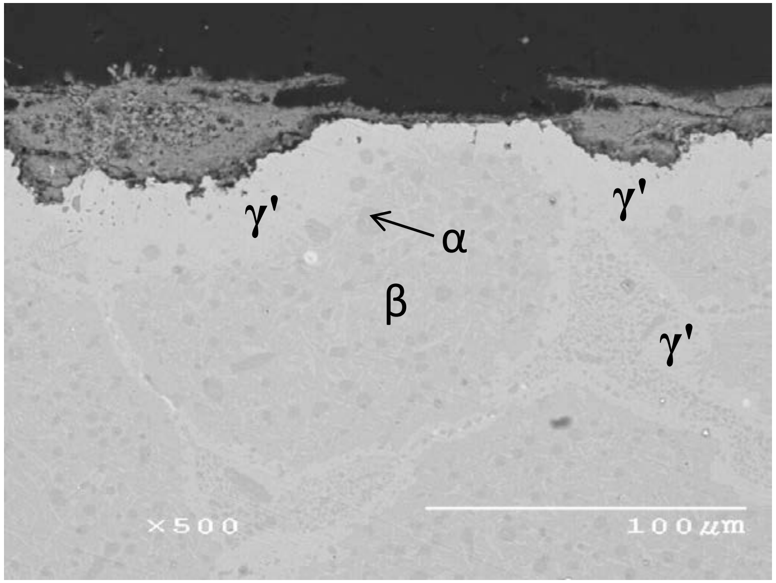
900^{o}C Hot Corrosion-Co Effect

Base: Ni-26Al-20Cr-0.1Y, at.%



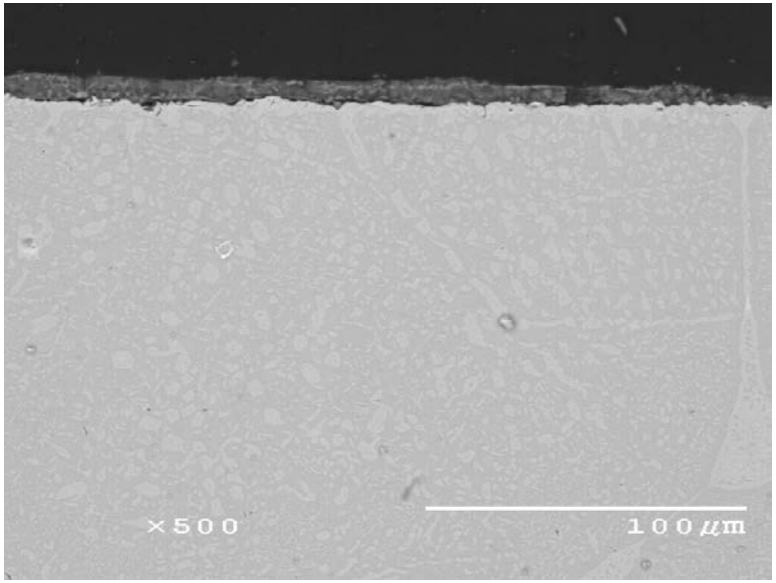
900°C Hot Corrosion-Co Effect

after 20h exposure



Ni-26Al-20Cr-0.4Y, (γ'+β+α)

Δm=2.5 mg/cm²



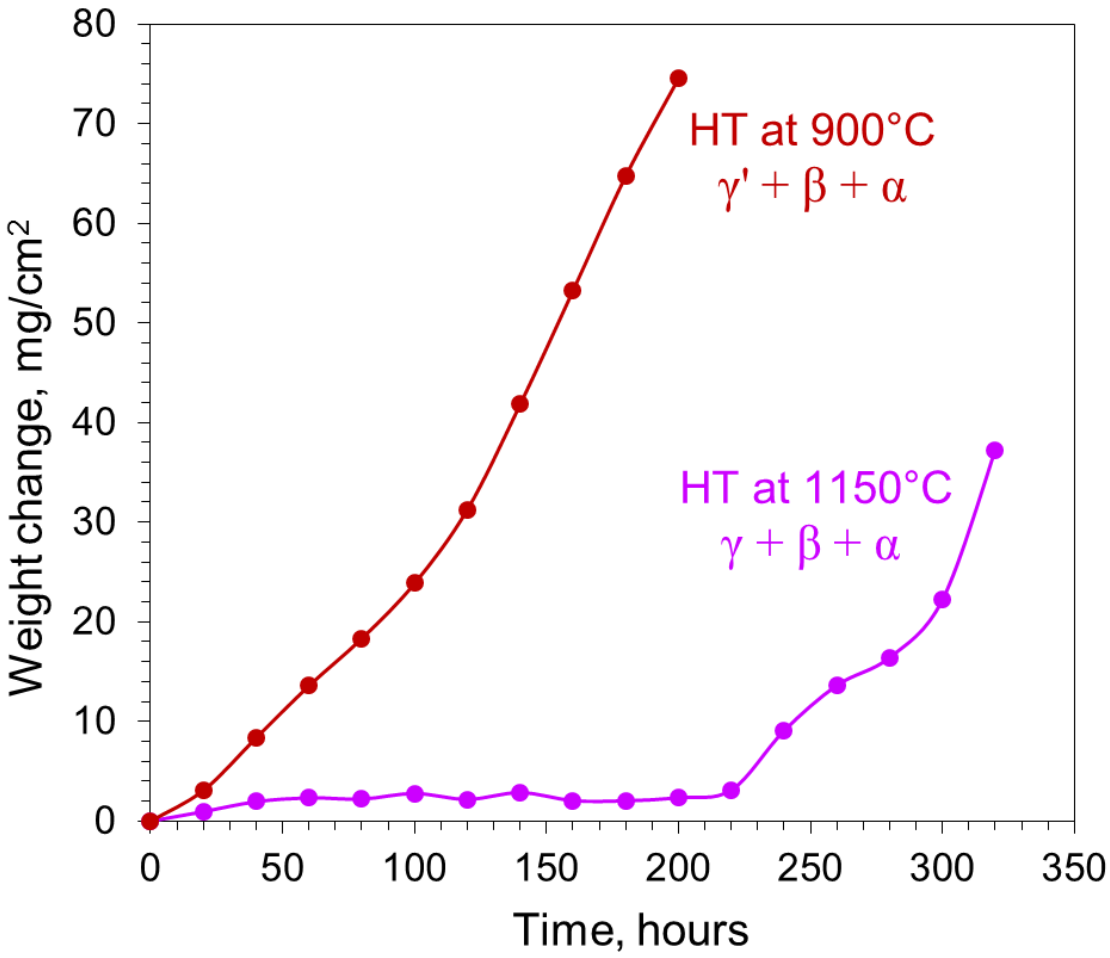
Ni-**18Co**-26Al-20Cr-0.4Y, **γ**+β+σ

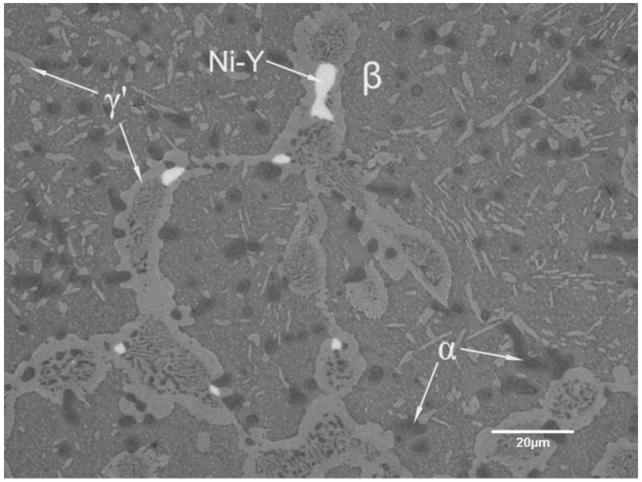
Δm=0.8 mg/cm²

- Preferential attack of γ' phase in NiCrAlY alloy.
- Co addition to NiCrAlY destabilizes γ' phase which, in turn, improves 900°C hot-corrosion resistance.

900°C Hot Corrosion-Starting Microstructure

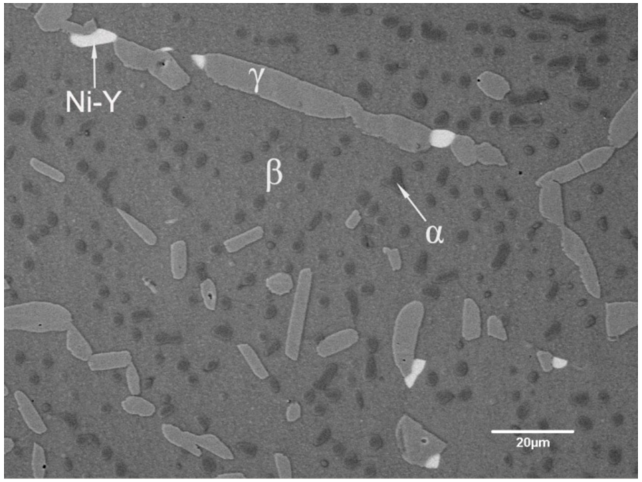
Fixed Composition: Ni-26Al-20Cr-0.1Y, at.%





HT at 900°C

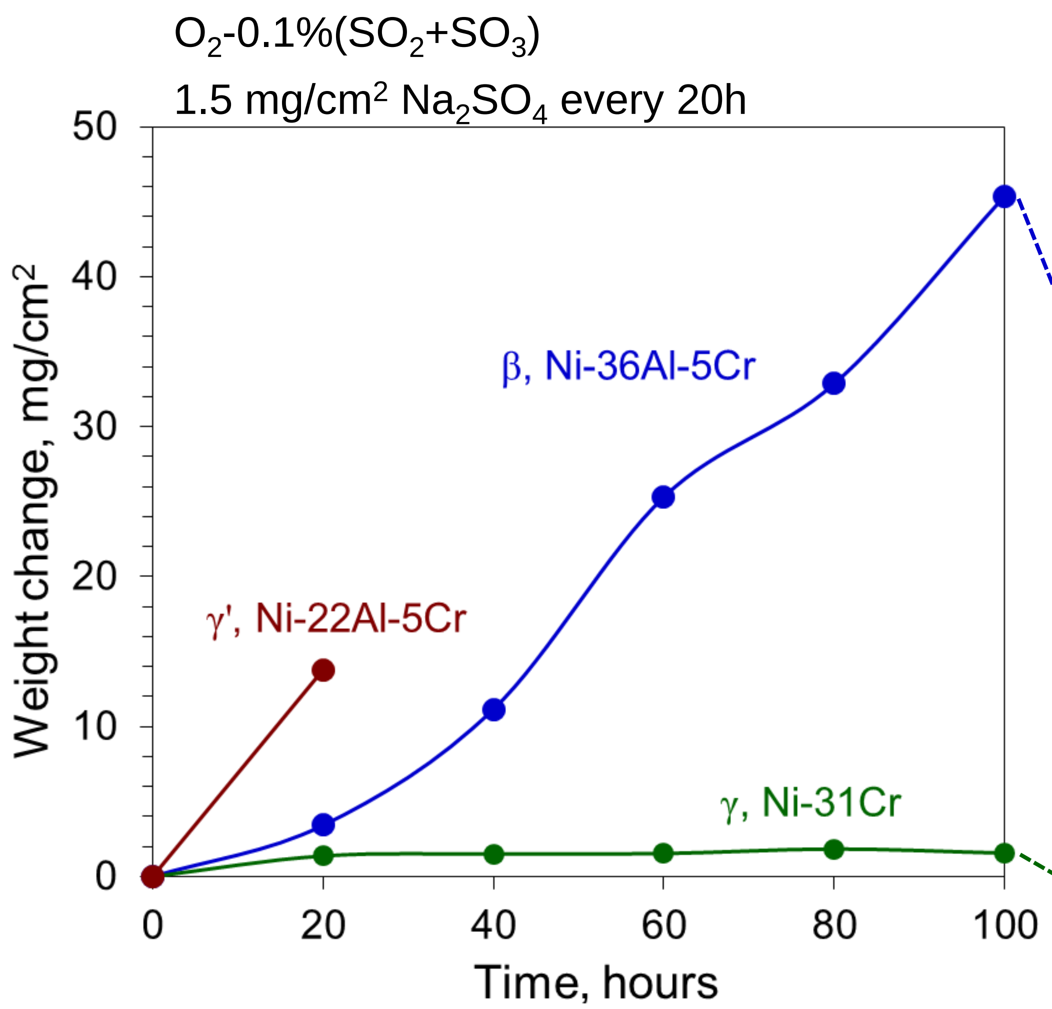
(γ': 28%, β: 56%; α: 15%)

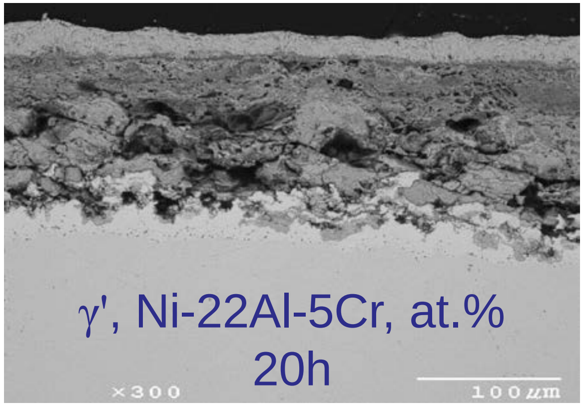


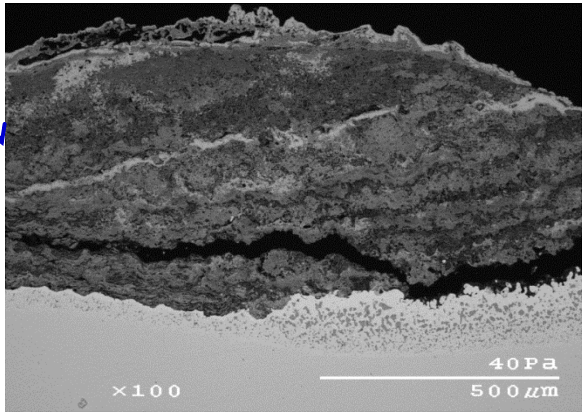
HT at 1150°C

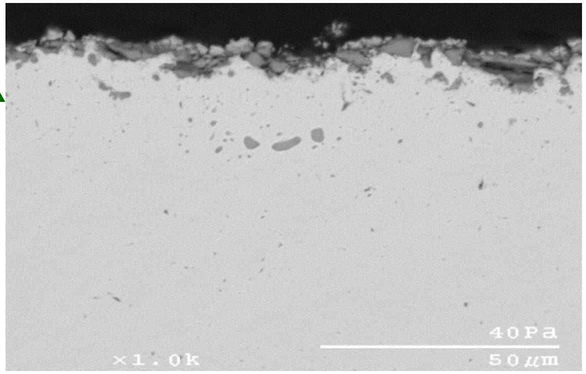
(γ: 13%, β: 80%; α: 7%)

Different Hot Corrosion Behavior of γ, β or γ′ at 900°C







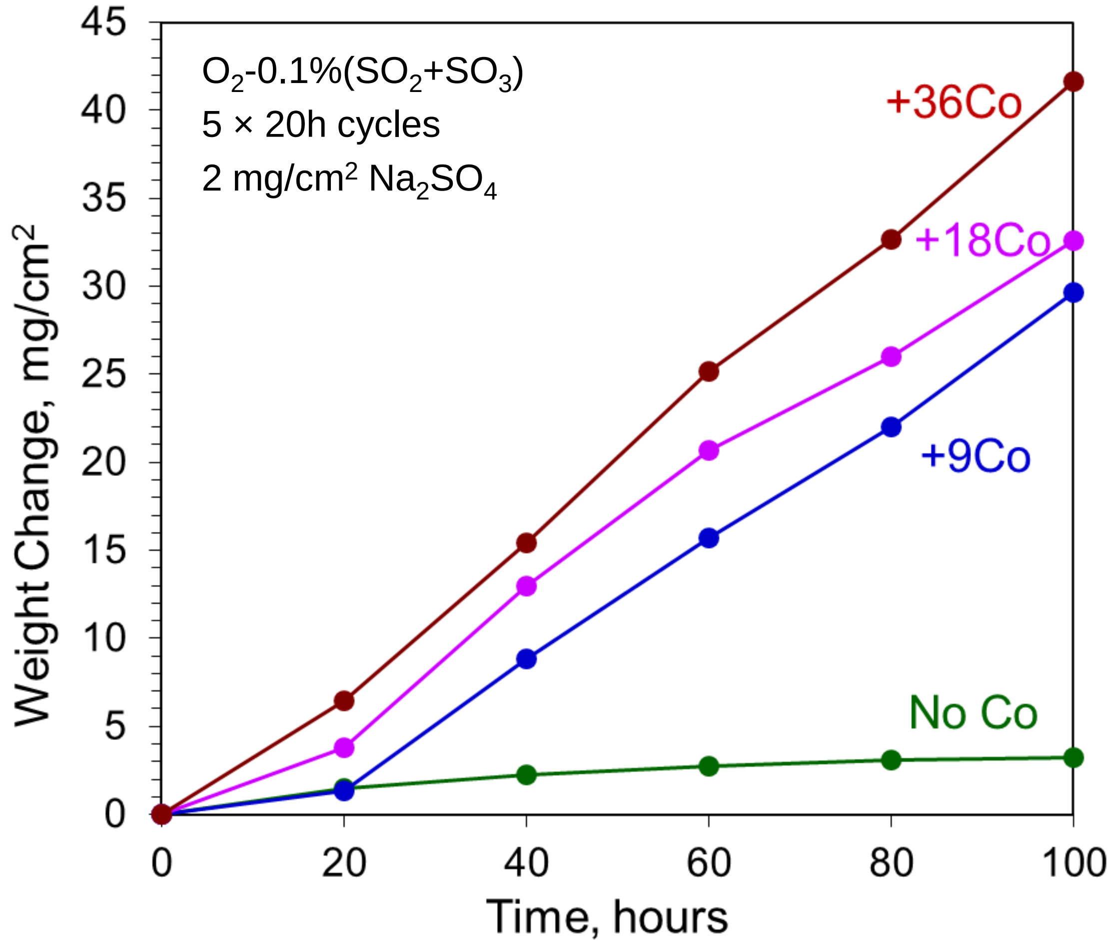


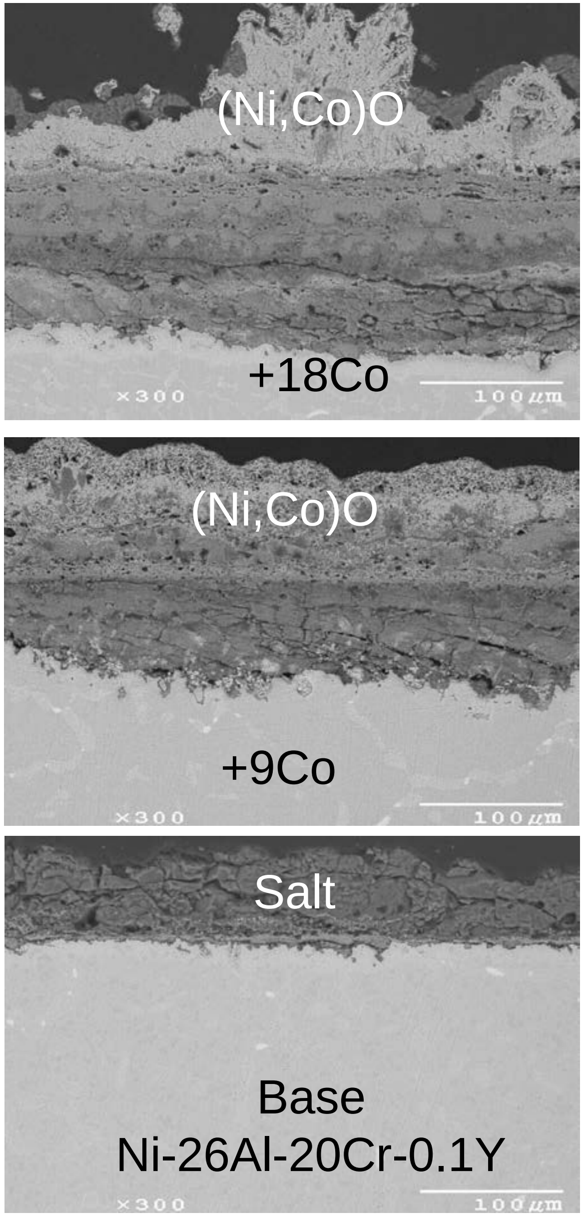
Resistance to hot corrosion at 900°C:

γ >> β > γ'

700°C Hot Corrosion-Co Effect

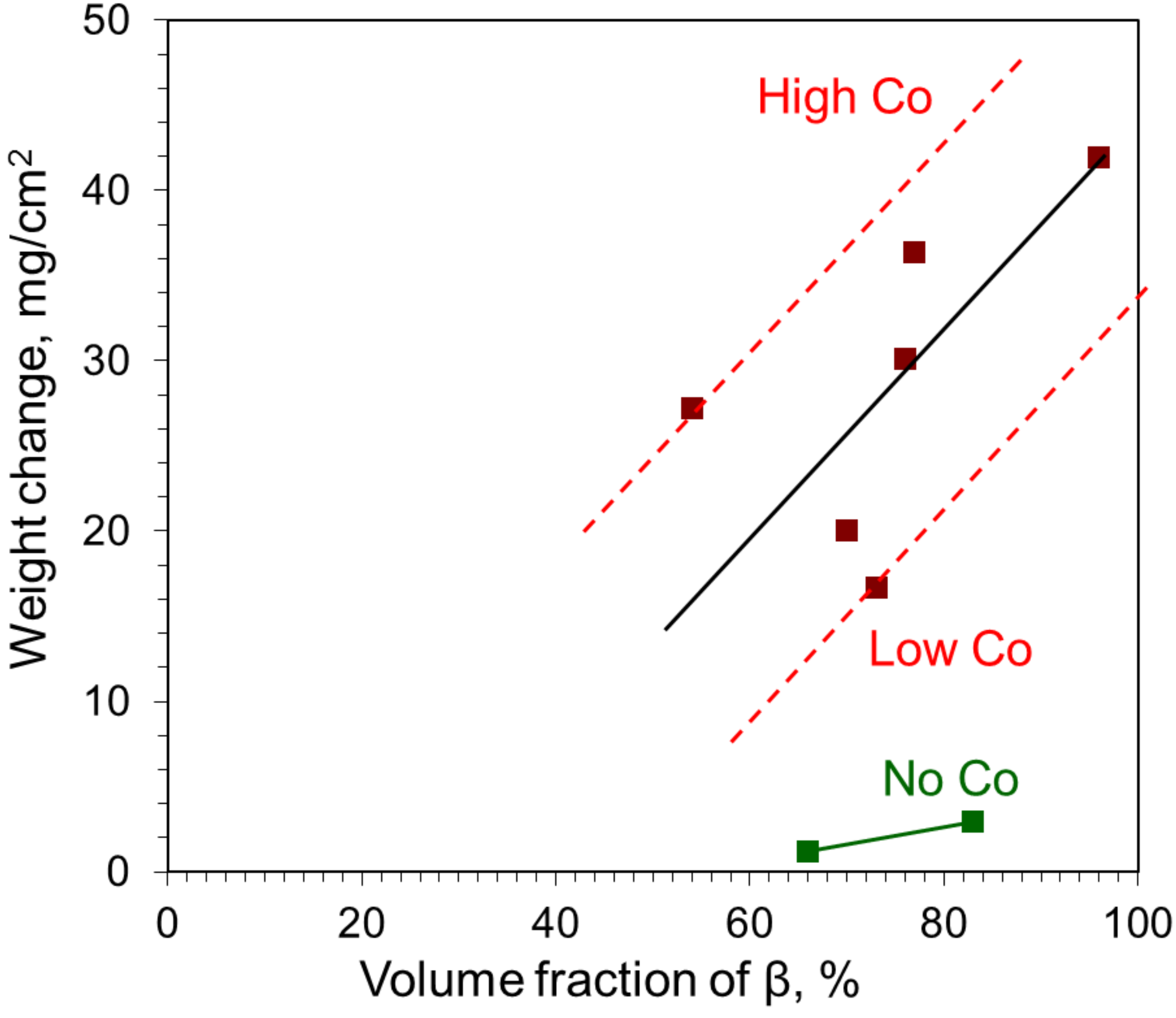
Base: Ni-26Al-20Cr-0.1Y, at.%



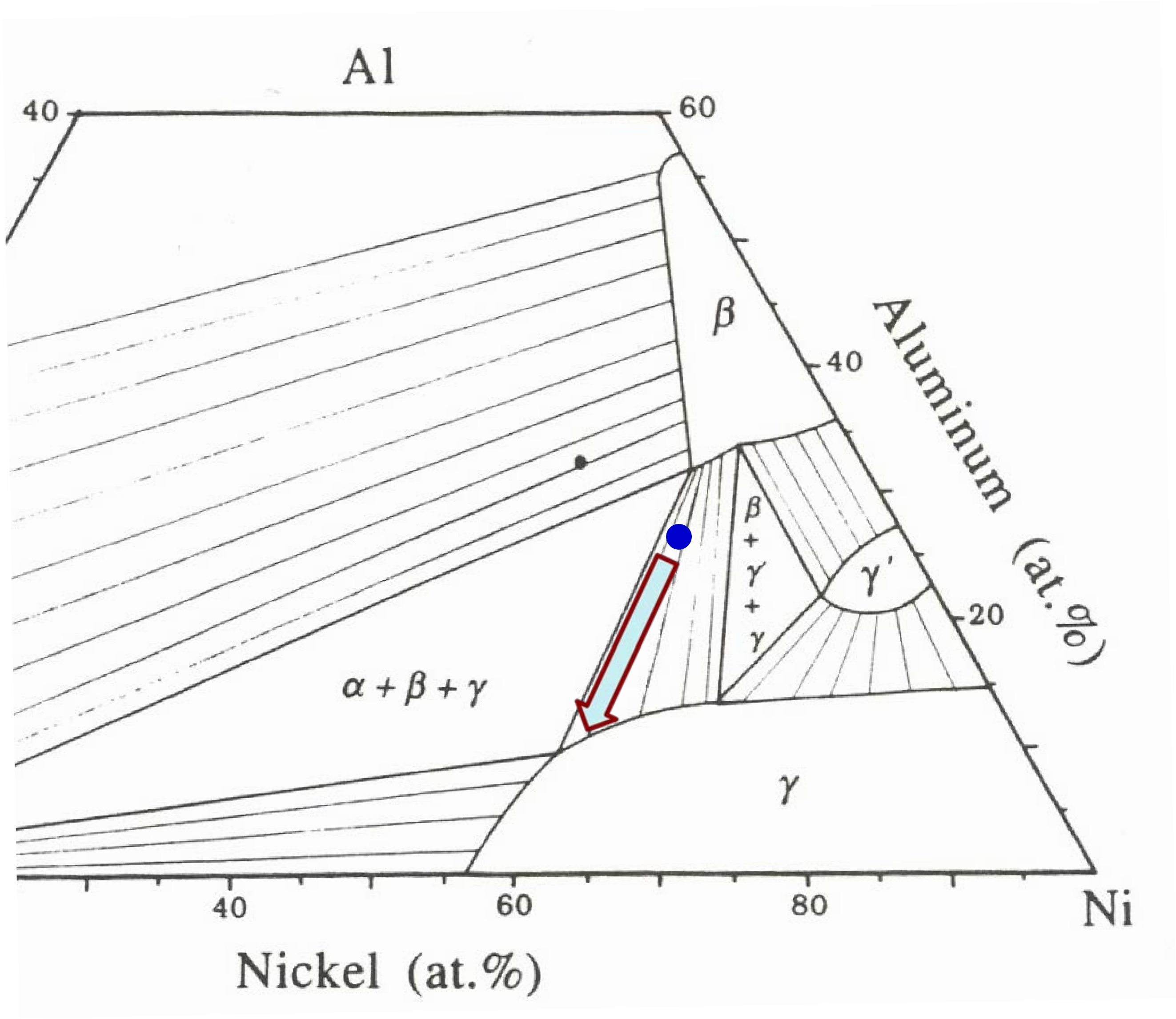


700^{o}C Hot Corrosion-Co and $V_f(\beta)$

Base: Ni-(0, 9, 18, 36)Co-26Al-20Cr-0.1Y, at.%



Approach to Improve 700^{o}C Hot Corrosion

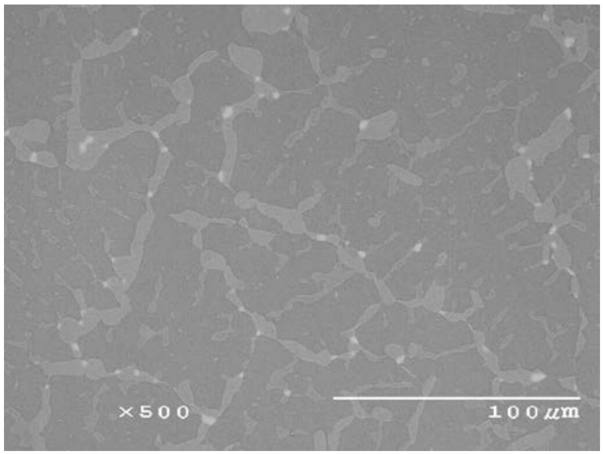


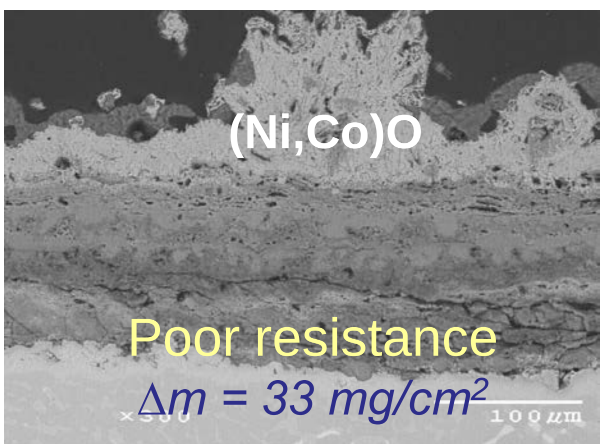
700ºC Hot Corrosion-Volume Fraction of β, $V_f(\beta)$

Al ↓ Cr ↑ →

Ni-18Co-26Al-20Cr-0.1Y

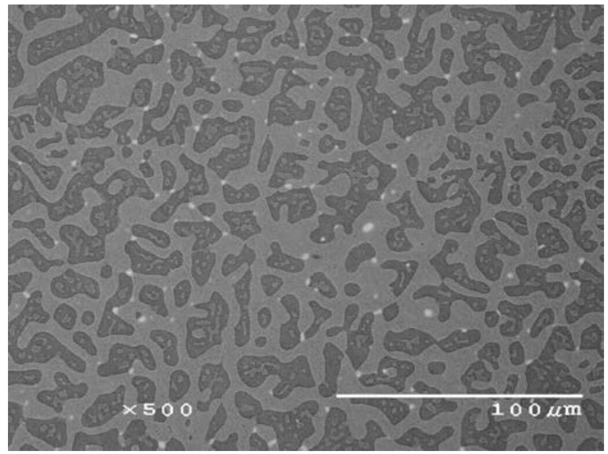
V_f (β)=77%

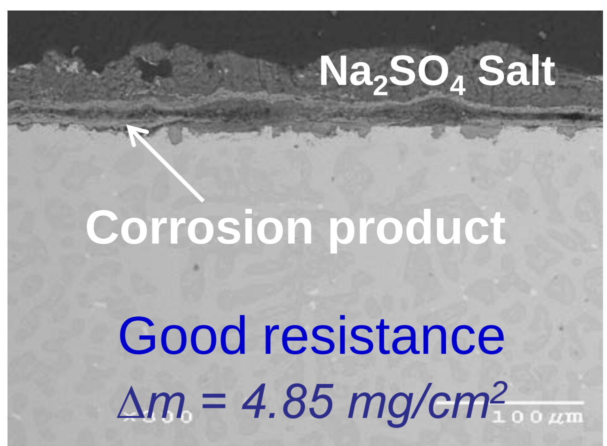




Ni-18Co-18Al-28Cr-0.1Y

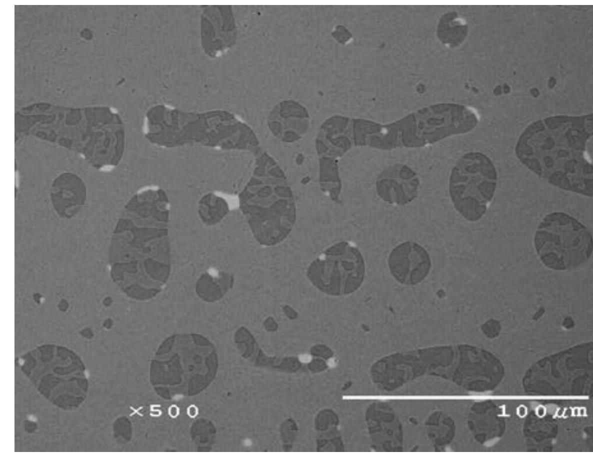
V_f (β)=46%

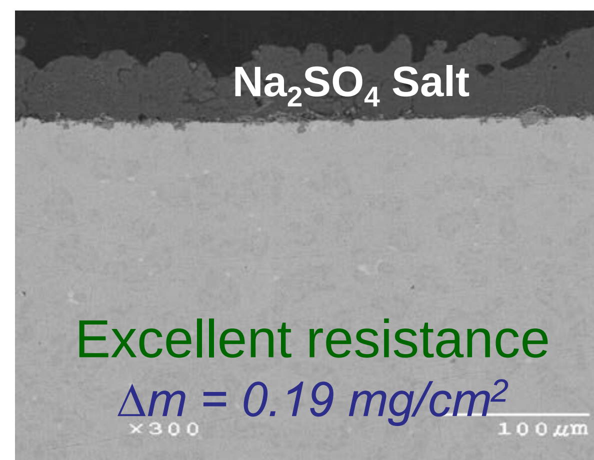




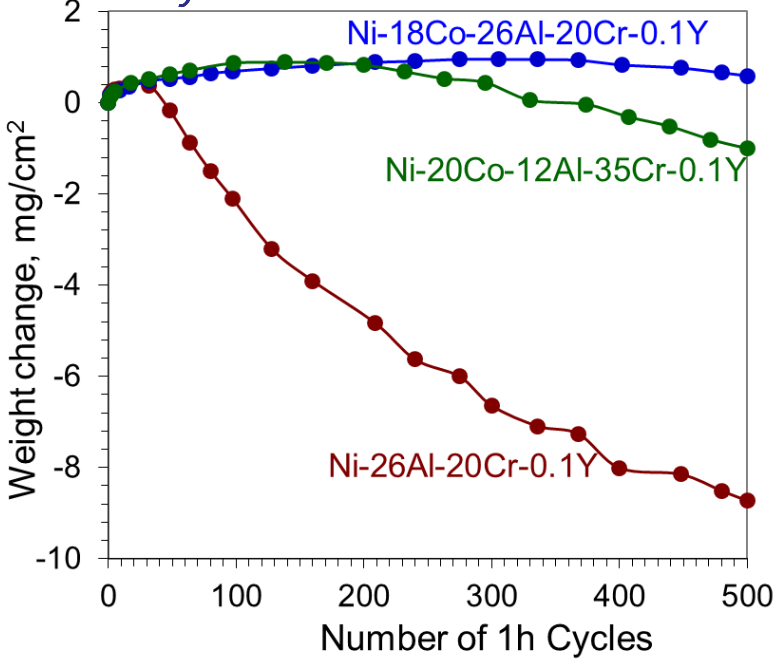
Ni-20Co-12Al-35Cr-0.1Y

V_f (β)=18%

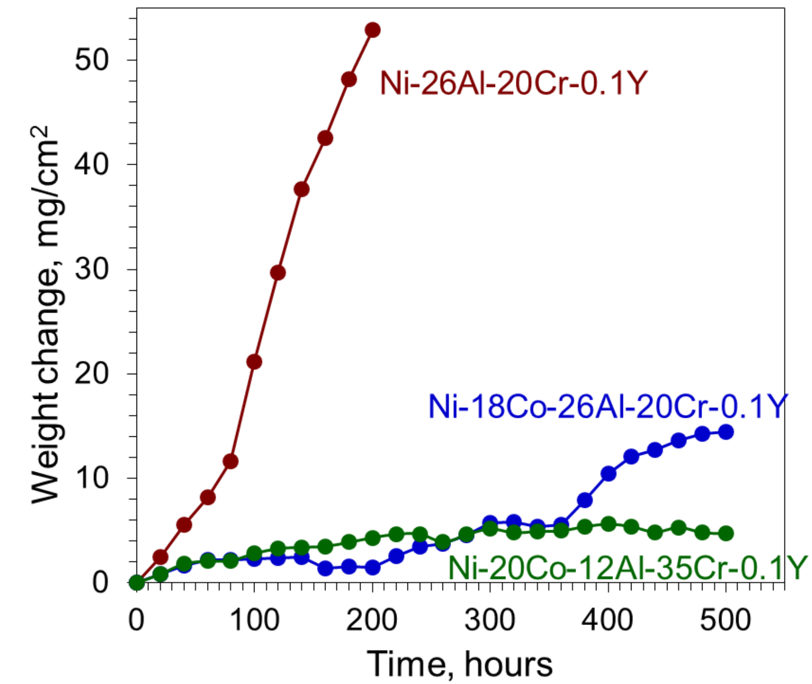


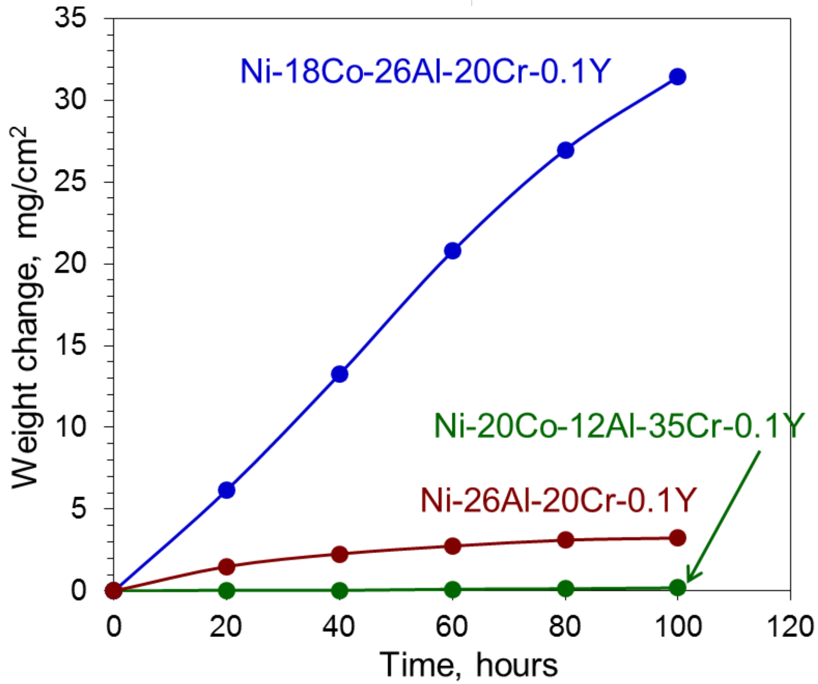


Cyclic oxidation at 1150°C



900°C hot corrosion





700°C hot corrosion

Program Objectives

Systematically assess the interplay between prototypical deposit chemistries (*i.e.*, ash and its constituents plus K_2SO_4 and FeS) and environmental oxidants (*i.e.*, O_2, H_2O and CO_2) on the high-temperature degradation behavior of advanced TBC systems.

Combined effects of environment and deposit ……. with an understanding of the chemical and microstructural aspects of the coating systems.

Questions ?