



... for a brighter future

Materials Performance in CO₂ and in CO₂-Steam Environments

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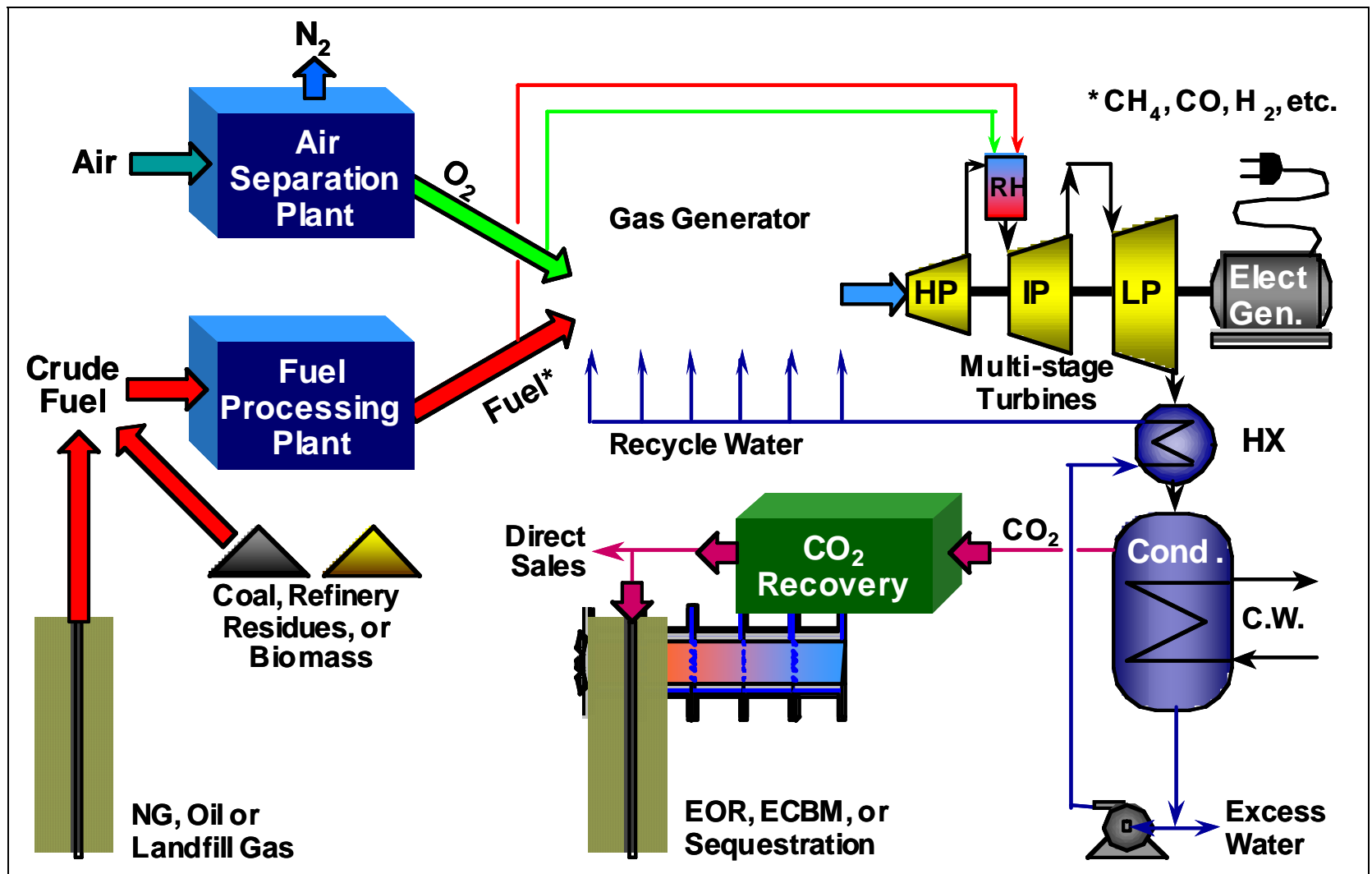
Outline

- ***Background***
- ***Objectives***
- ***Materials and experimental procedure***
- ***Alloys for evaluation***
- ***Corrosion performance of alloys***
- ***Data on creep properties in CO₂ environments***
- ***Project Summary***

What and why Oxy-fuel Combustion

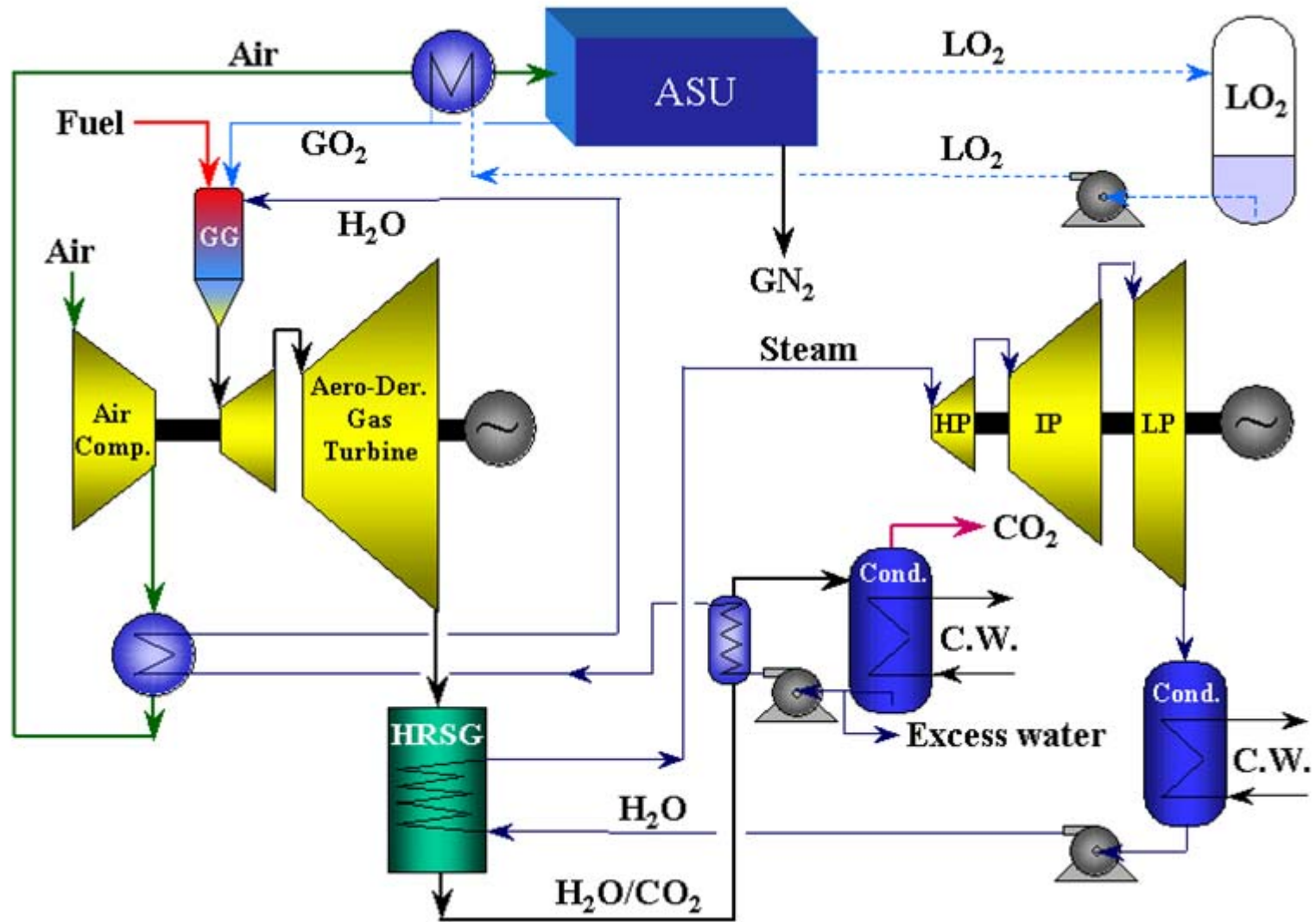
- ***Global climate change - One of the causes identified is CO₂ increase in atmosphere - one of the source for CO₂ is exhaust from fossil fuel combustion plants***
- ***Energy production (in particular, electricity) is expected to increase due to population increase and per capita increase in energy consumption***
- ***To meet the energy needs fossil fuels (coal, gas, oil, etc.) will play a major part in production even with a projected increase from alternate sources***
- ***To minimize CO₂ emission - current systems emphasize capture from power plants and sequestration***
- ***Oxy-fuel combustion systems - recycle CO₂ to the compressor, use novel gas turbines, and emphasize reuse***

Clean Energy Systems Process

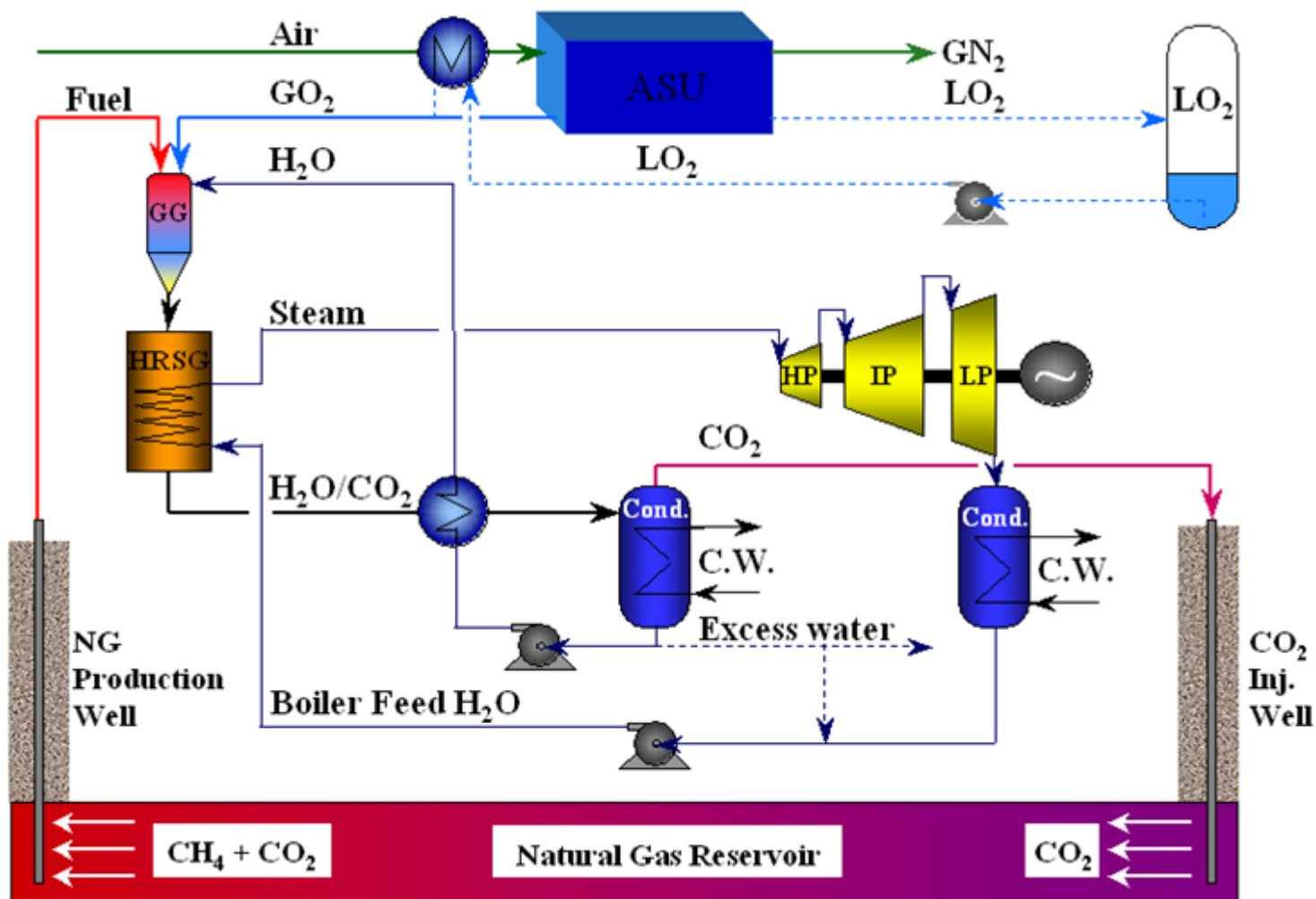


The diagram illustrates a coal gasification process for power generation. The process begins with **Coal** and **Air** entering a **Gasifier**. The **Air** is processed by an **ASU** (Air Separation Unit) to produce **GO₂**, which is fed into the **Gasifier**. The **Gasifier** produces **Syngas** and **GO₂**. The **Syngas** is sent to **Gas Cleanup**, then to a **Gas Generator**. The **Gas Generator** feeds into a **HRSG** (Heat Recovery Steam Generator). The **HRSG** feeds into a steam turbine cycle (HP, IP, LP) and a **CO₂** separation unit. The **CO₂** separation unit produces **CO₂** and **Excess water**. The **CO₂** separation unit feeds into a **Cond.** (Condenser), which is cooled by **C.W.** (Cooling Water). The **Cond.** feeds into a pump, which feeds back into the **HRSG**. The **HRSG** also feeds into a pump, which feeds back into the **Gasifier**.

Gas Turbine Demonstration at Kimberlina Facility in CA



Dutch Project



ANL Program Objectives

- **Evaluate oxidation/corrosion performance of metallic structural alloys in pure CO₂ and in CO₂-steam environments over a wide temperature range**
- **Establish the kinetics of scaling and internal penetration, if any, and develop correlations for long term performance**
- **Identify viable alloys for structural and gas turbine applications**
- **Evaluate the influence of exposure environment on the mechanical properties (especially creep, fatigue, and creep-fatigue) of the candidate alloys**

Current List of Alloys in the Study

Material	C	Cr	Ni	Mn	Si	Mo	Fe	Other
800H	0.08	20.1	31.7	1.0	0.2	0.3	Bal	Al 0.4, Ti 0.3
330	0.05	10.0	35.0	1.5	1.25	-	Bal	-
333	0.05	25.0	45.0	-	1.0	3.0	18.0	Co 3.0, W 3.0
617	0.08	21.6	53.6	0.1	0.1	9.5	0.9	Co 12.5, Al 1.2, Ti 0.3
625	0.05	21.5	Bal	0.3	0.3	9.0	2.5	Nb 3.7, Al 0.2, Ti 0.2
602CA	0.19	25.1	62.6	0.1	0.1	-	9.3	Al 2.3, Ti 0.13, Zr 0.19, Y 0.09
230	0.11	21.7	60.4	0.5	0.4	1.4	1.2	W 14, Al 0.3, La 0.015
693	0.02	28.8	Bal	0.2	0.04	0.13	5.8	Al 3.3, Nb 0.67, Ti 0.4, Zr 0.03
740	0.07	25.0	Bal	0.3	0.5	0.5	1.0	Co 20.0, Ti 2.0, Al 0.8, Nb+Ta 2.0
718	-	19.0	52.0	-	-	3.0	19.0	Nb 5.0, Al 0.5, Ti 0.9, B 0.002
MA956	-	20.0	-	-	-	-	Bal	Al 4.5, Ti 0.5, Y ₂ O ₃ 0.6

Laboratory Test Details

Key variables: Temperature, time, alloy composition

Materials: Fe- and Ni-base alloys, coatings

Environment: Pure CO₂ and CO₂-steam mixtures

Test temperature range: 650-1000°C

Test times: up to 10,000 h

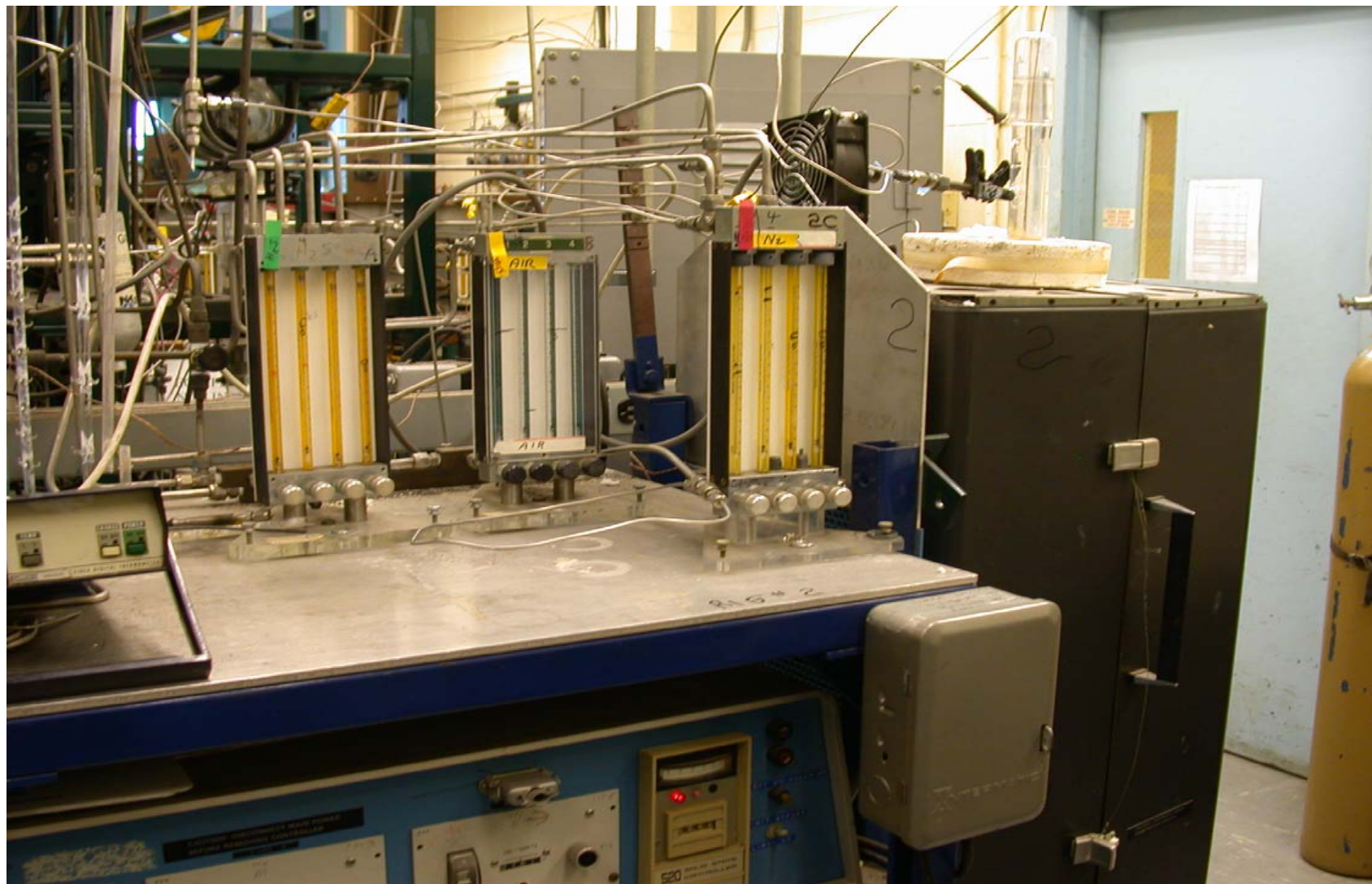
Specimen evaluation:

- weight change**
- scanning electron microscopy**
- energy dispersive X-ray analysis**
- X-ray diffraction**
- synchrotron nanobeam analysis**

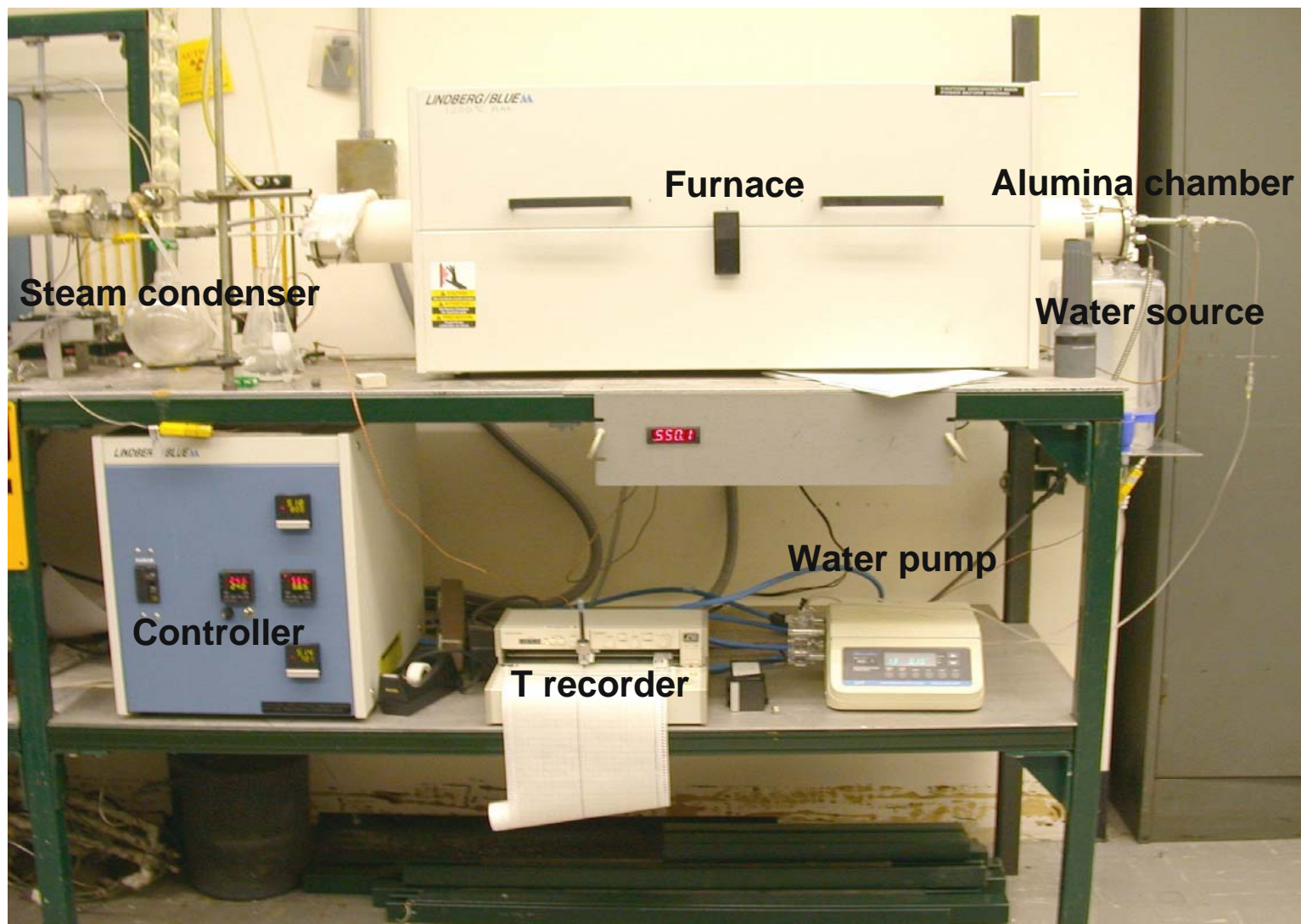
Specimen Exposure Environments

Environment	Exposure temperature (°C)	Exposure time (h)
CO ₂	650	1,865
	750	2,760
	850	5,426
	950	2,547
50% CO ₂ & 50% Steam	650	10,090
	750	10,090
	850	1,400
Steam	750	1,220
	850	510
Air	750	3,000
	850	3,000

CO₂ Exposure Test Facility



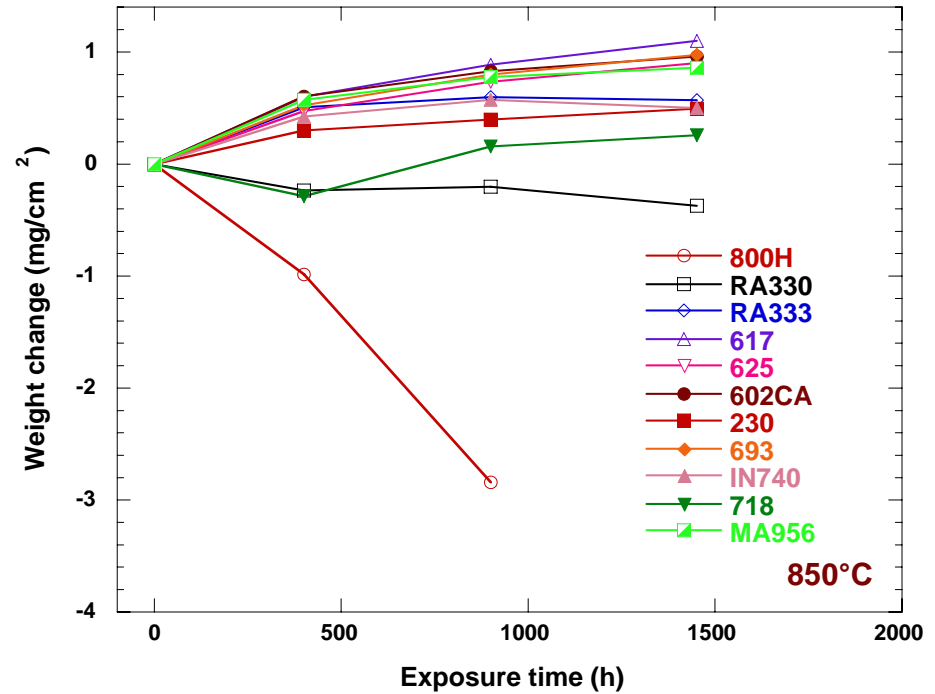
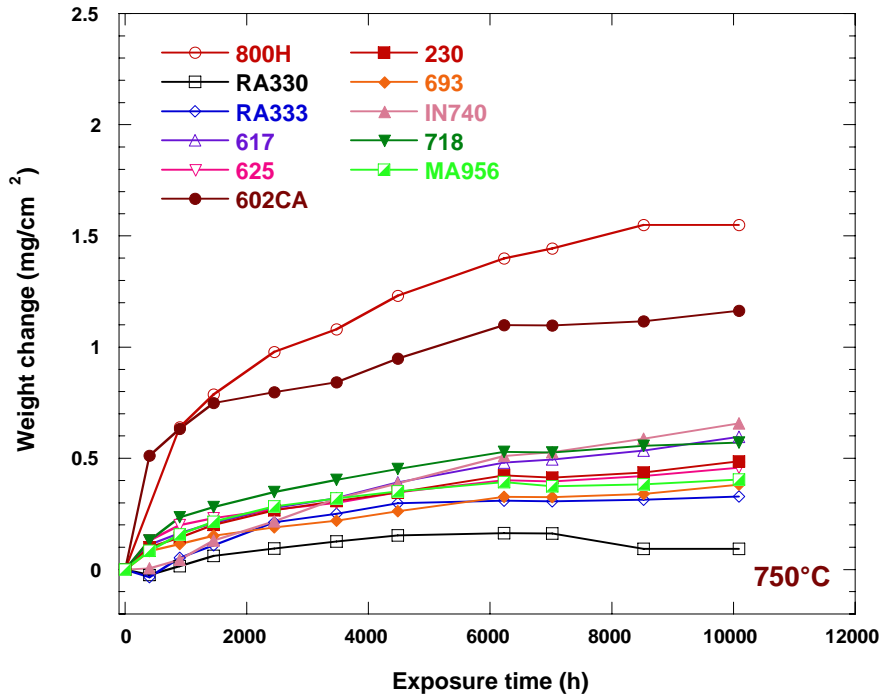
CO₂-Steam Exposure Test Facility



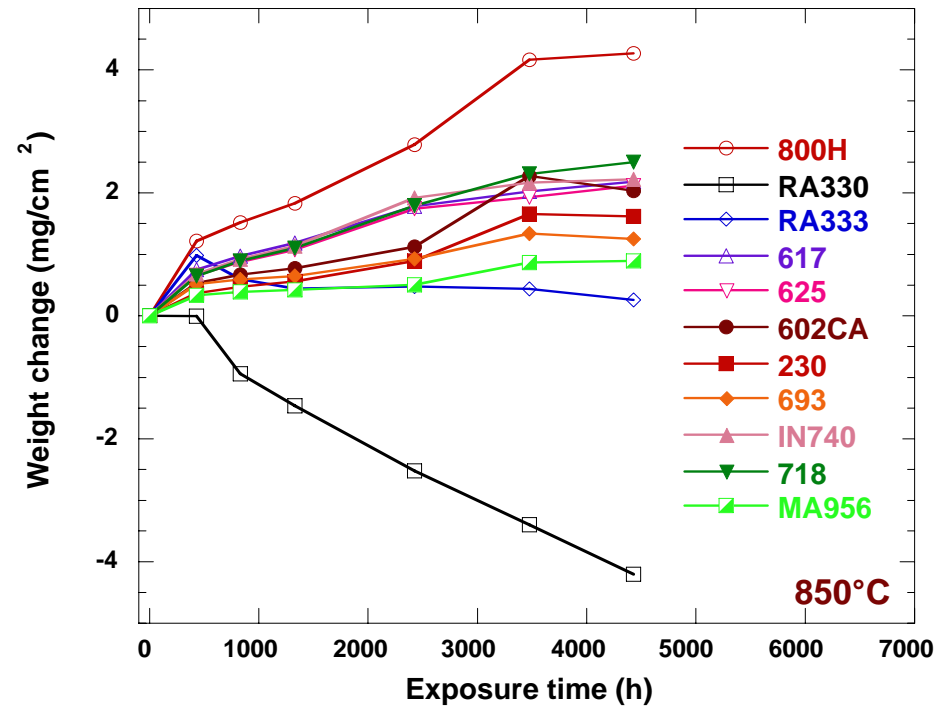
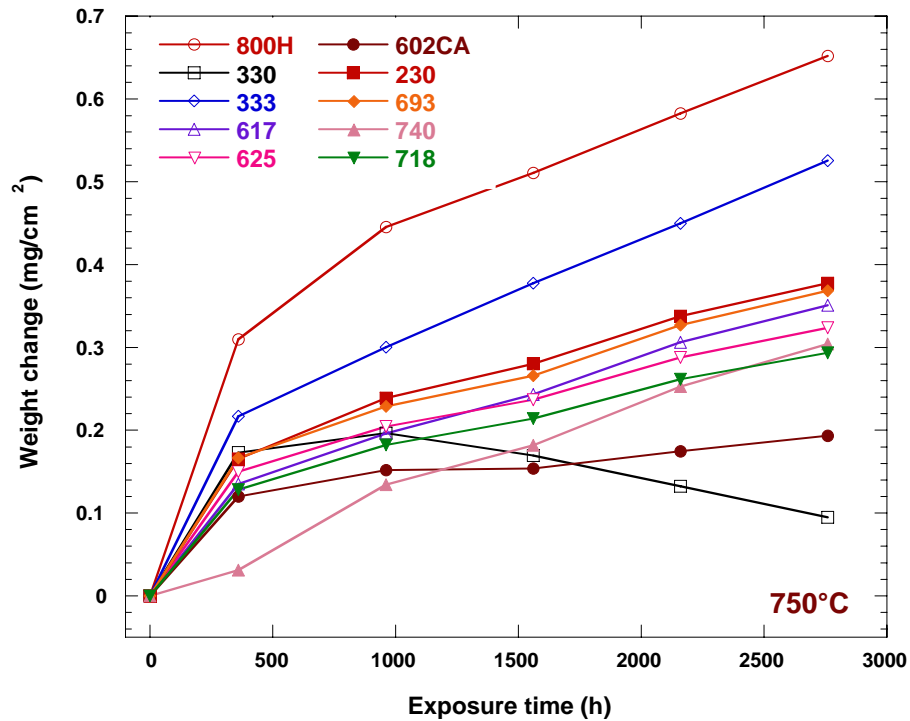
Creep Test Facility



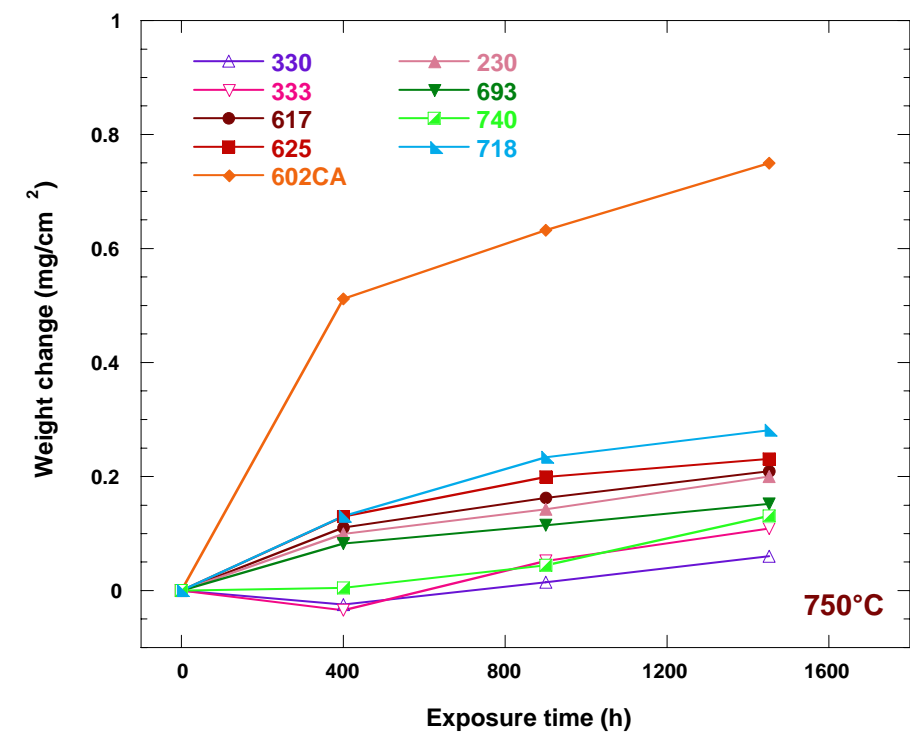
Oxidation Performance in Pure CO₂ at 750 and 850°C



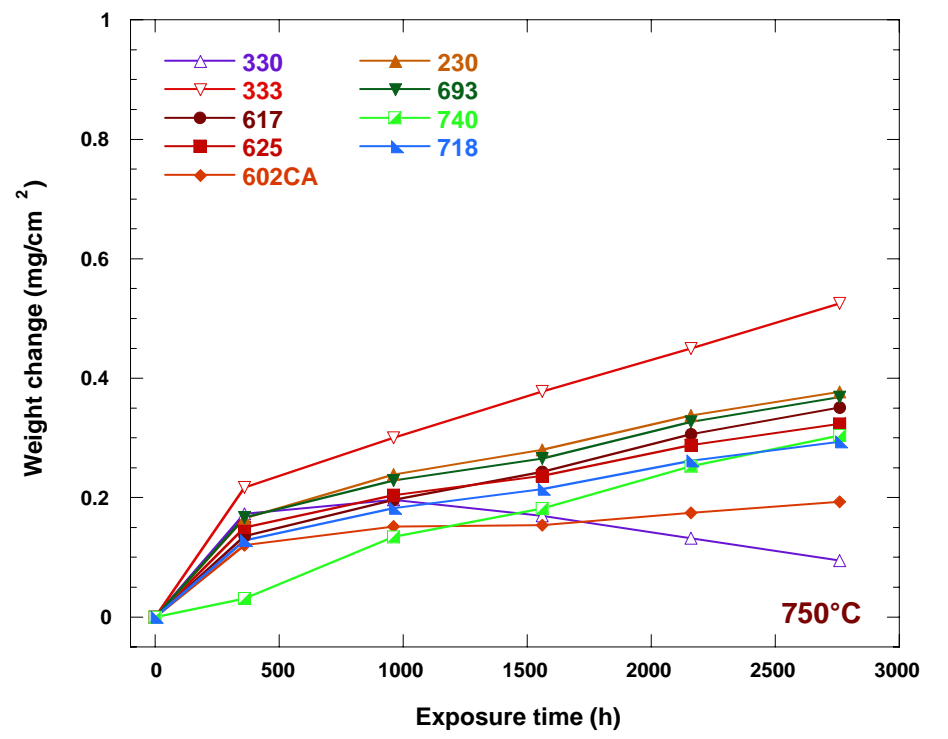
Oxidation Performance in 50% CO₂- 50% H₂O at 750 and 850°C



Oxidation Performance in CO₂ and in 50% CO₂-50% H₂O at 750°C

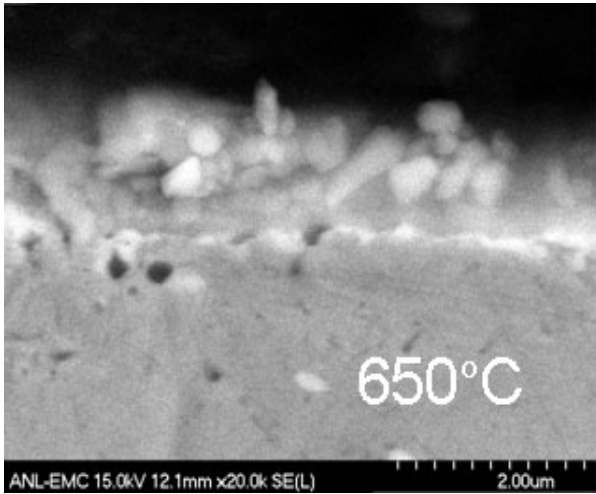


Pure CO₂

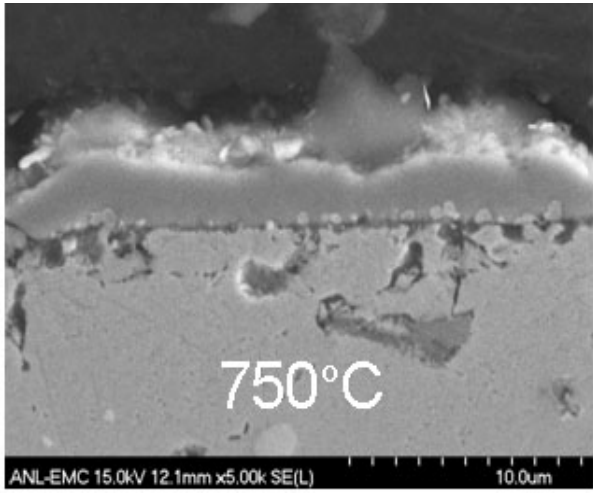


50% CO₂ -50% H₂O

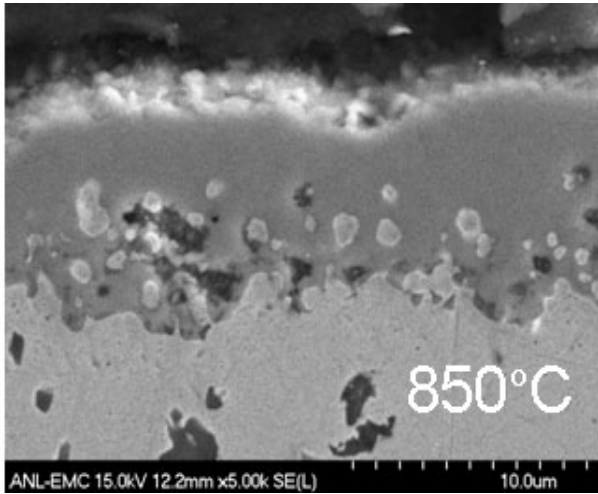
Alloy 617 exposed to pure CO₂



1452 h

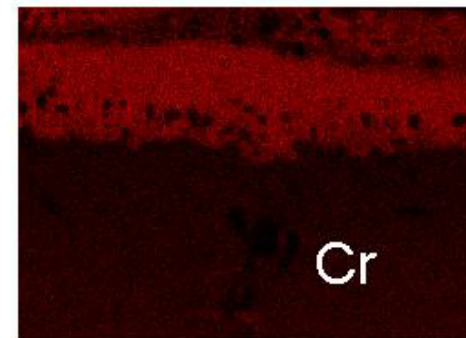
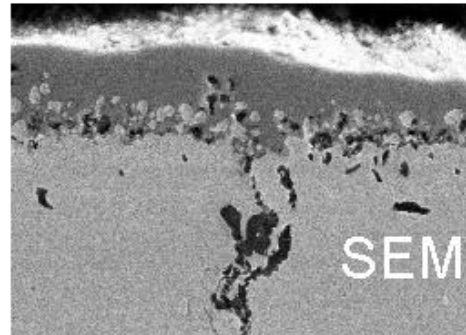
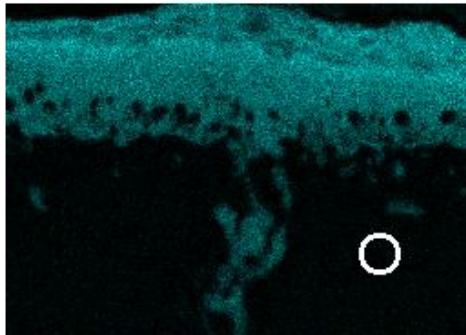
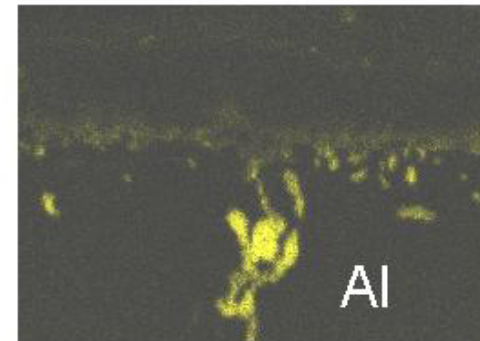
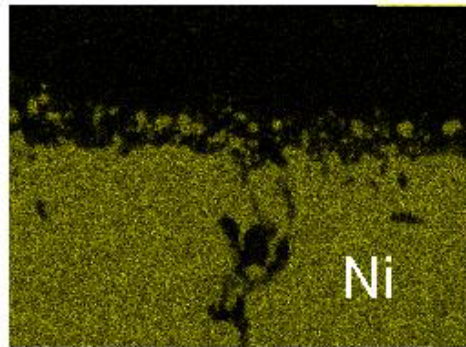


1452 h

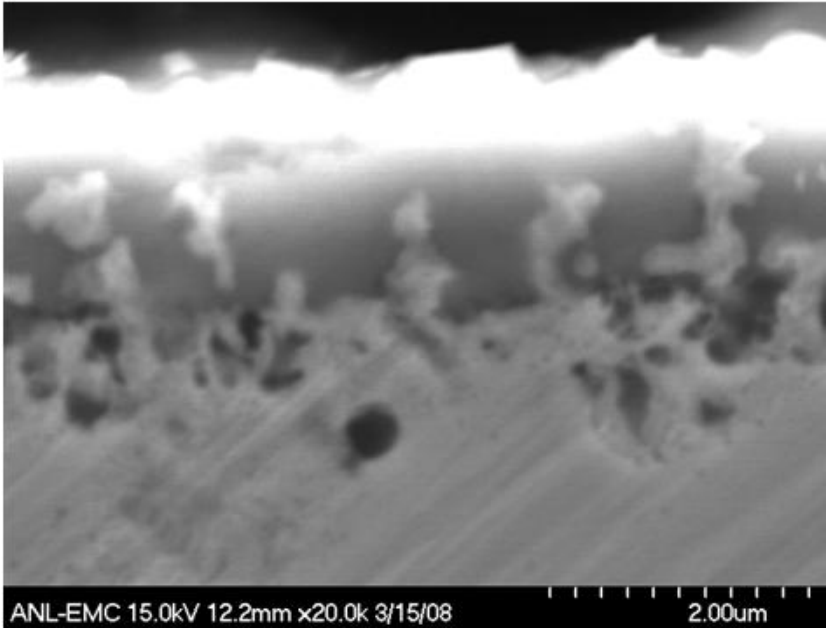
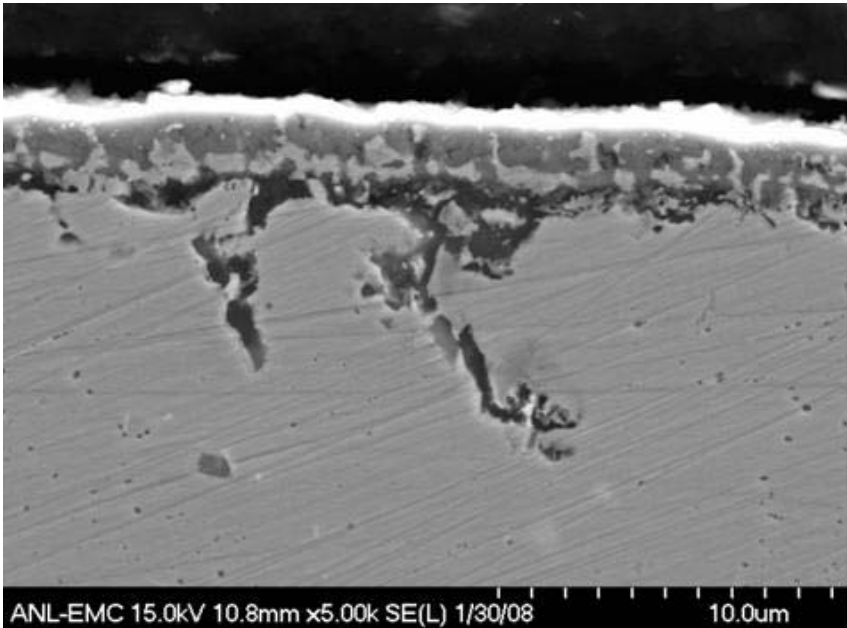


1400 h

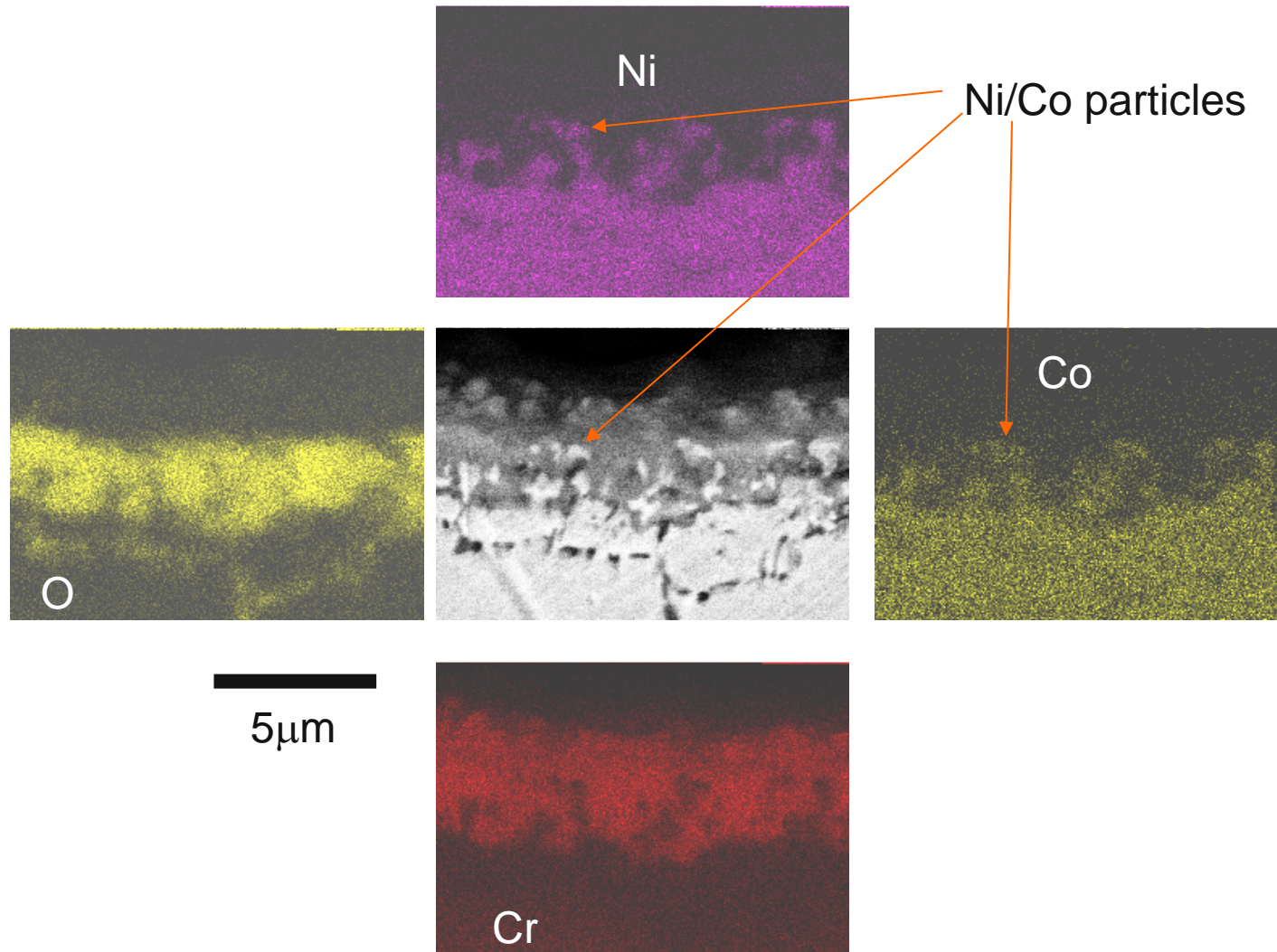
EDX mapping: Alloy 617 exposed to pure CO₂ for 1,400 h at 850°C



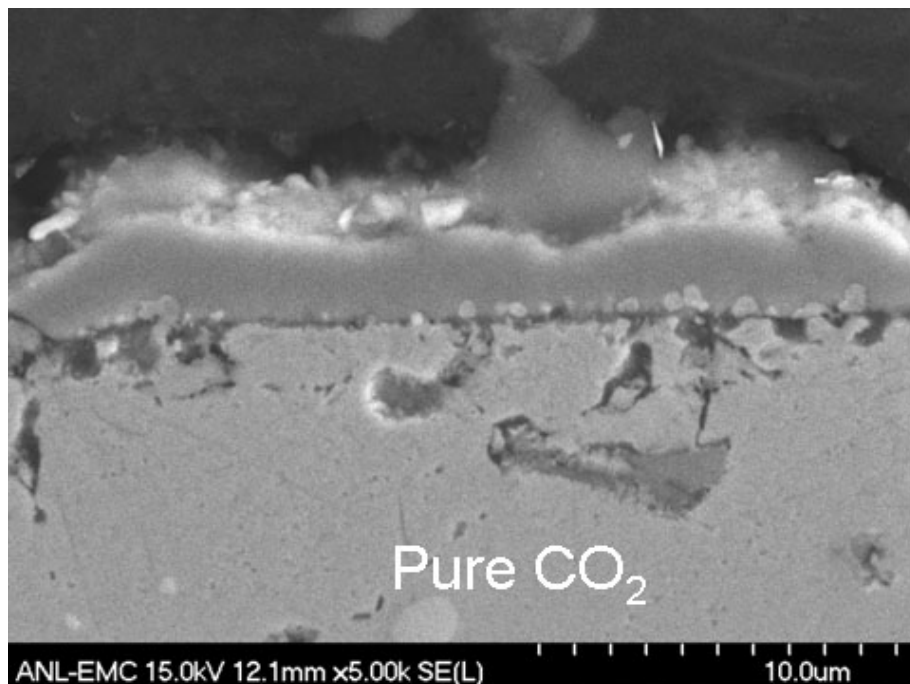
Alloy 617 after 2,760-h exposure to 50% CO₂-50% steam at 750°C



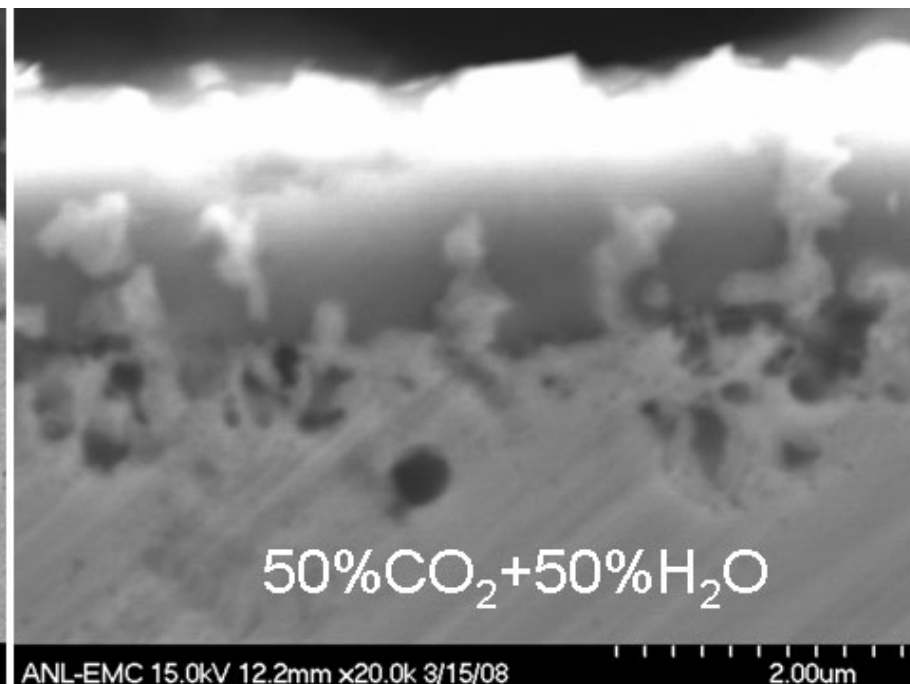
EDX mapping: Alloy 617 after 2,760-h exposure to 50% CO₂-50% steam at 750°C



Alloy 617 exposed to 50%CO₂-50%Steam at 750°C

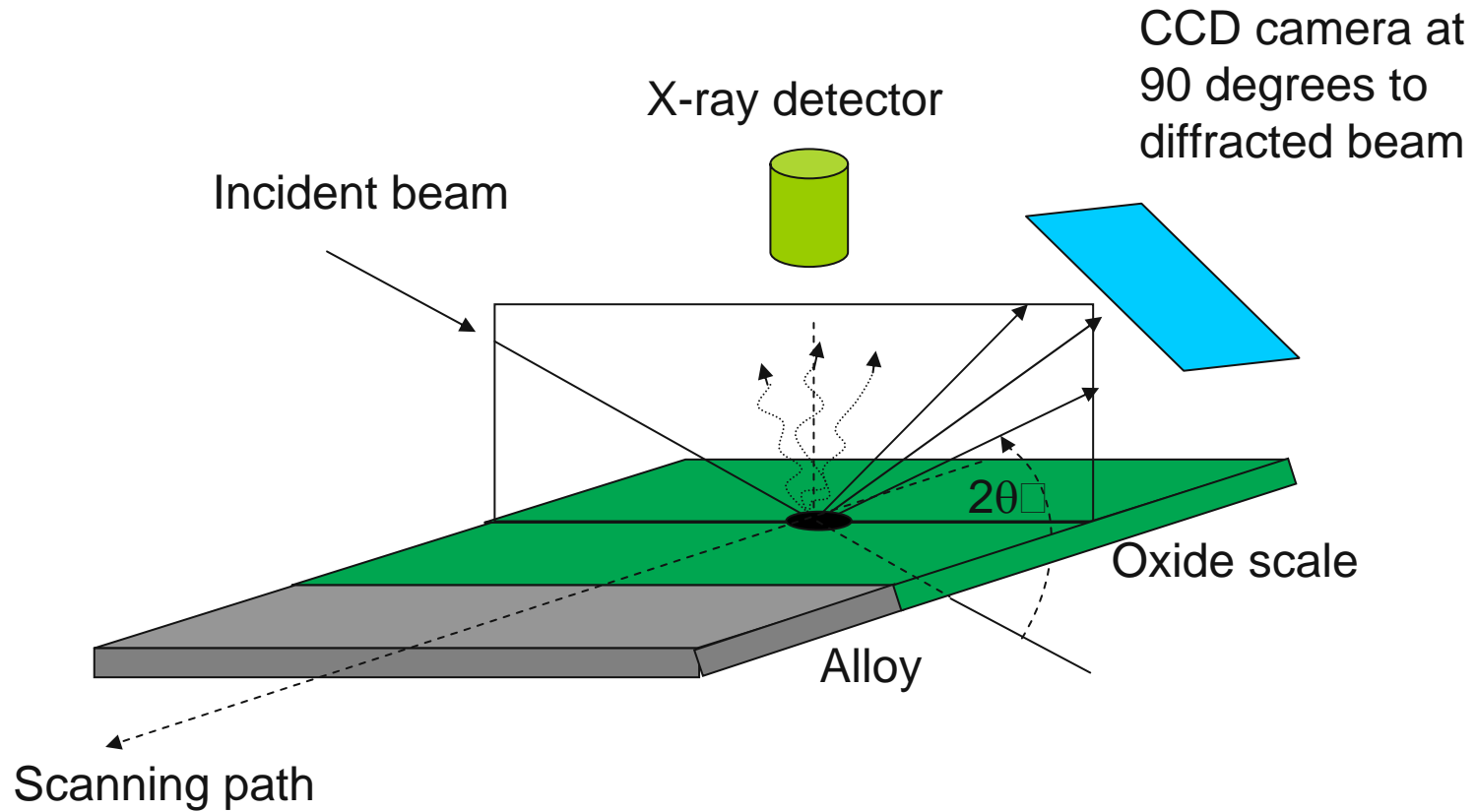


1452 h

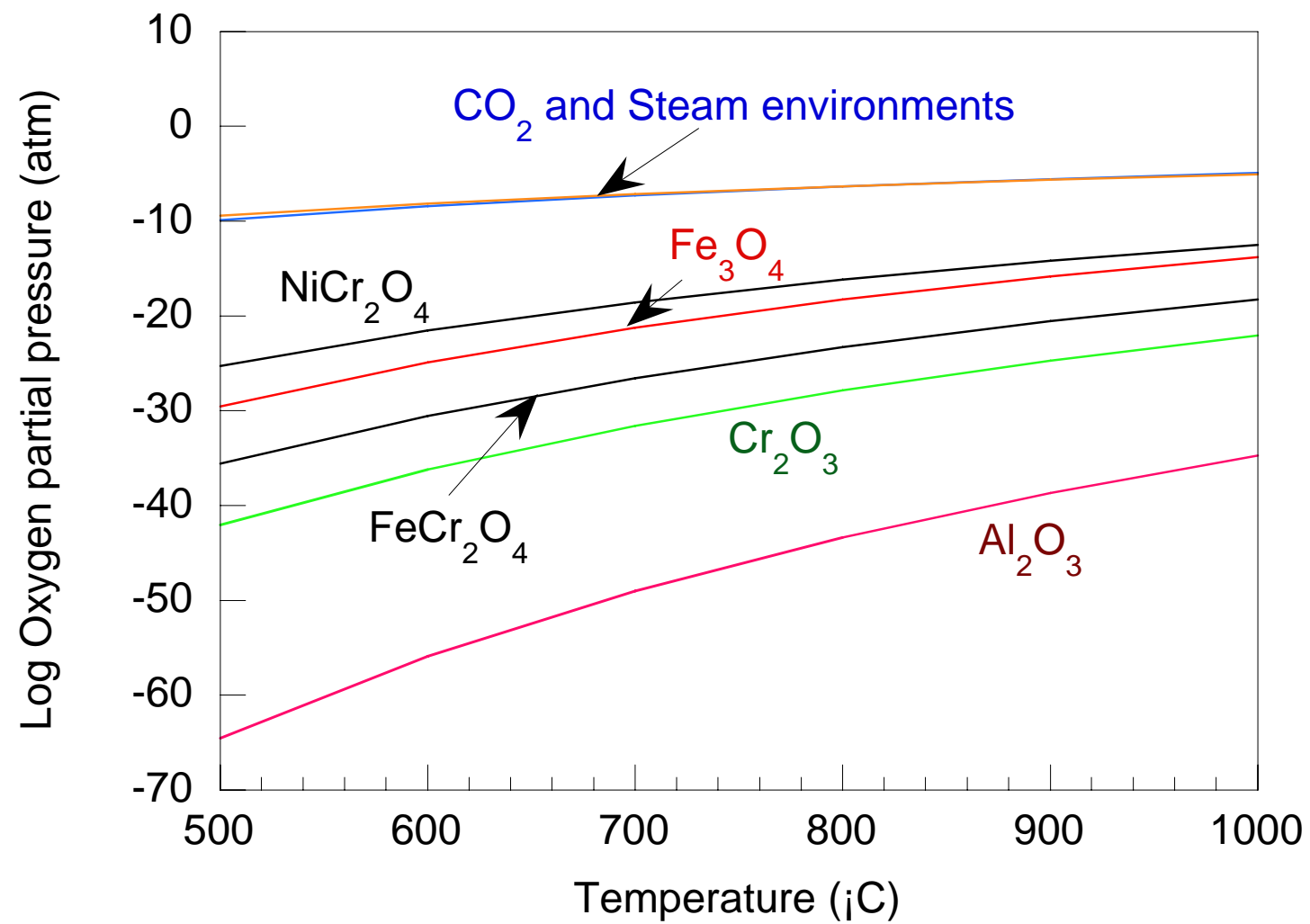


2760 h

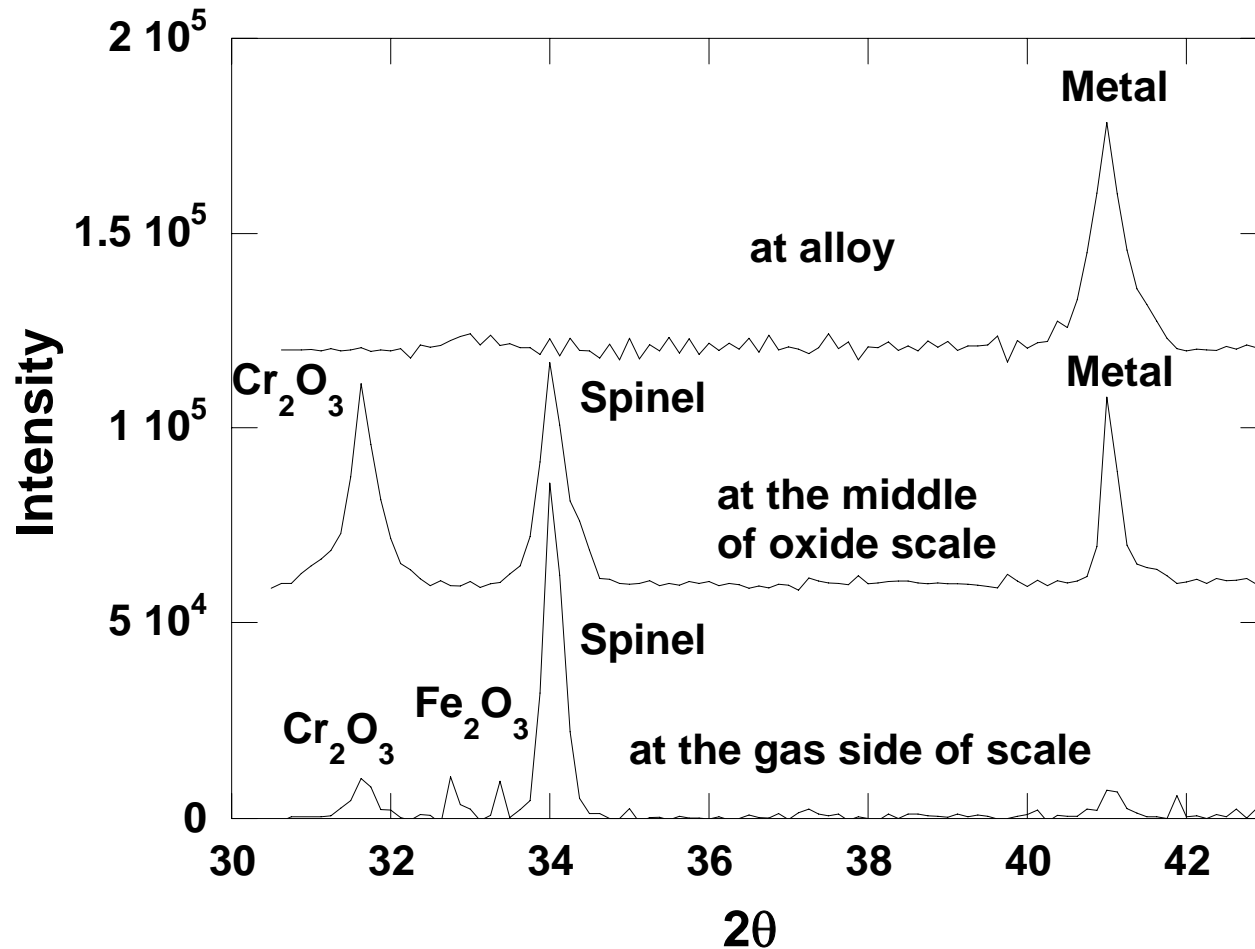
Alloy 617 exposed to 50%CO₂-50%Steam at 750°C



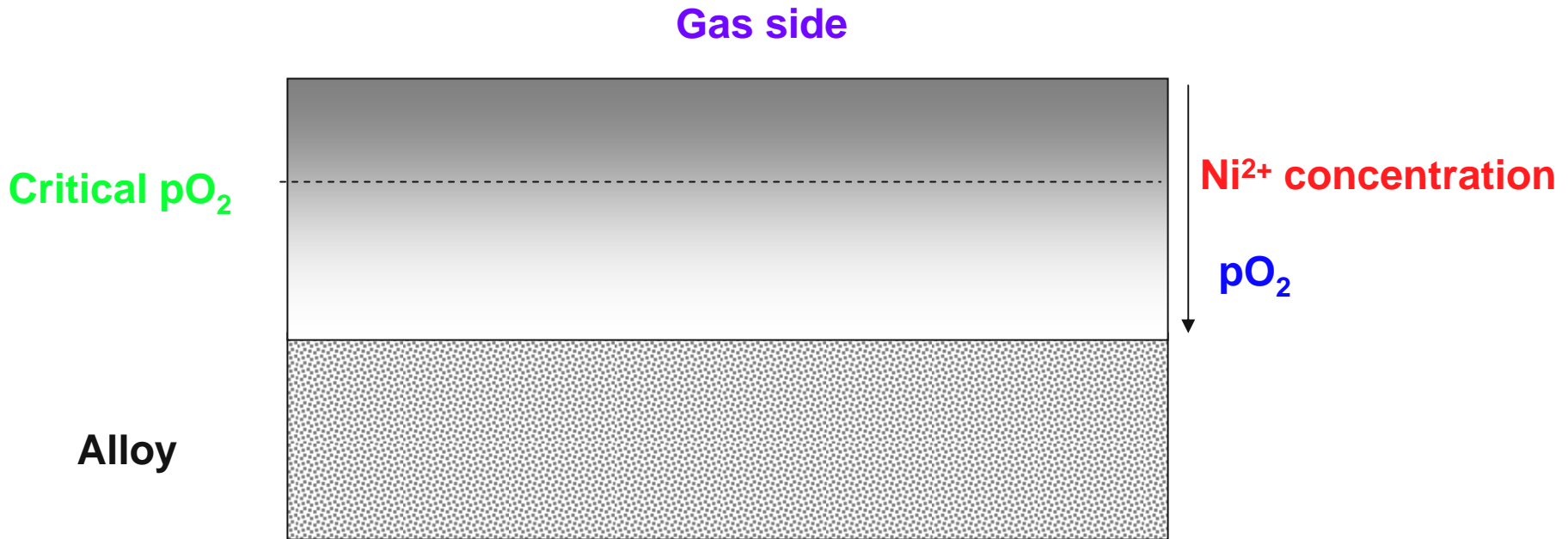
Thermodynamic stability of various oxide phases



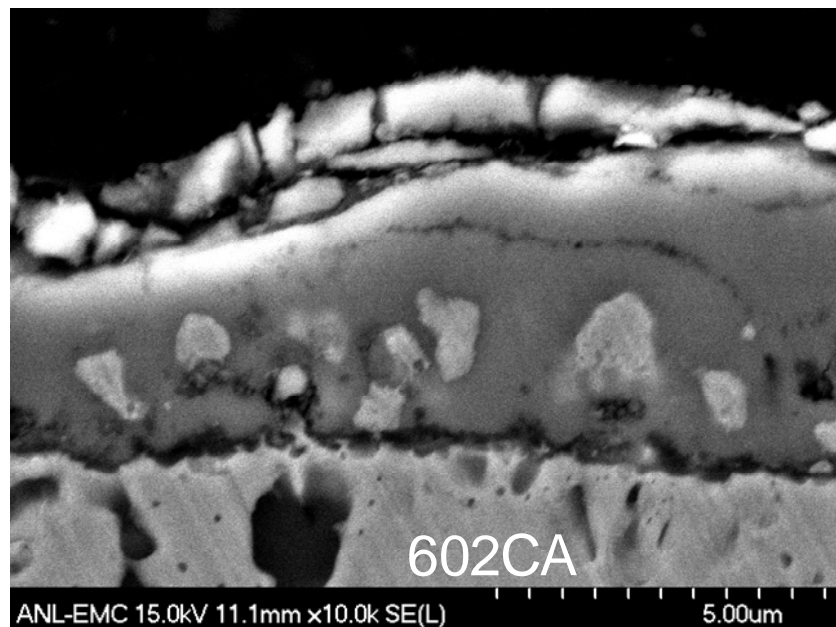
XRD at different locations of scale on the surface of Alloy 617 after 2,760-h exposure in 50%CO₂-50%Steam at 750°C



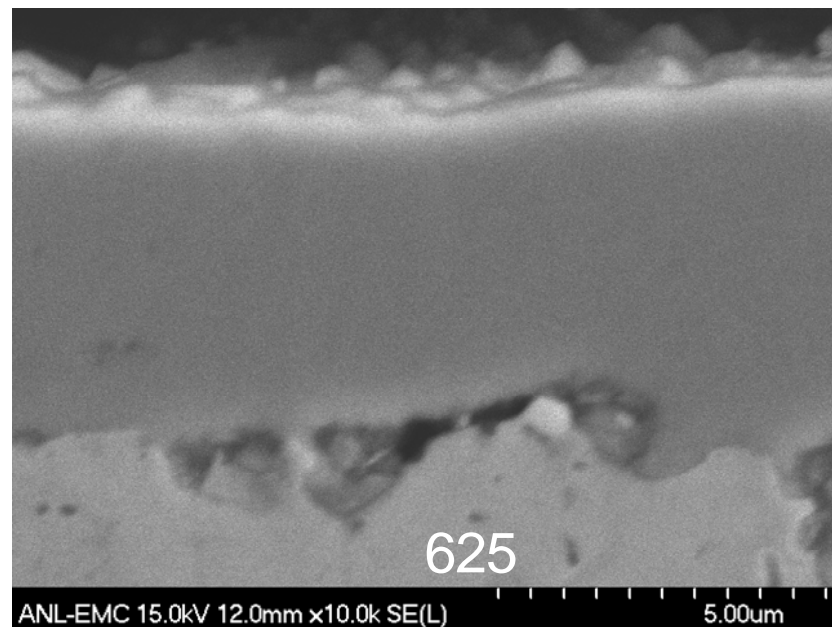
Effect of variation in p_{O_2} on scale morphology



Effect of Fe content in alloy on the oxidation scale morphology

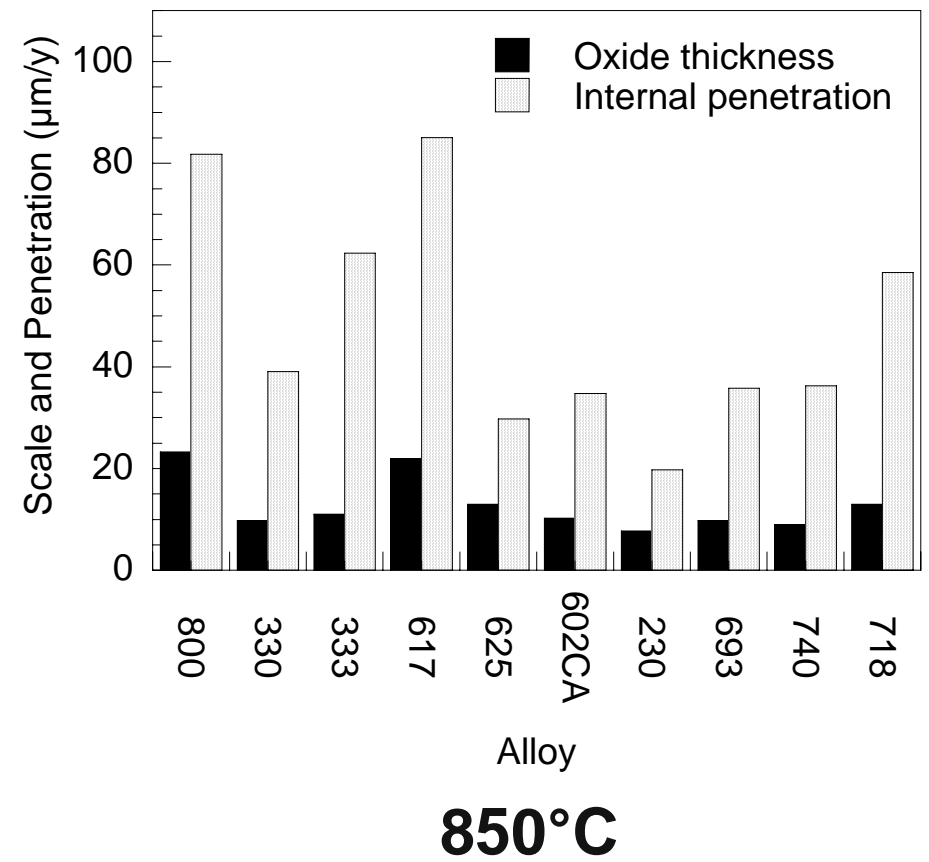
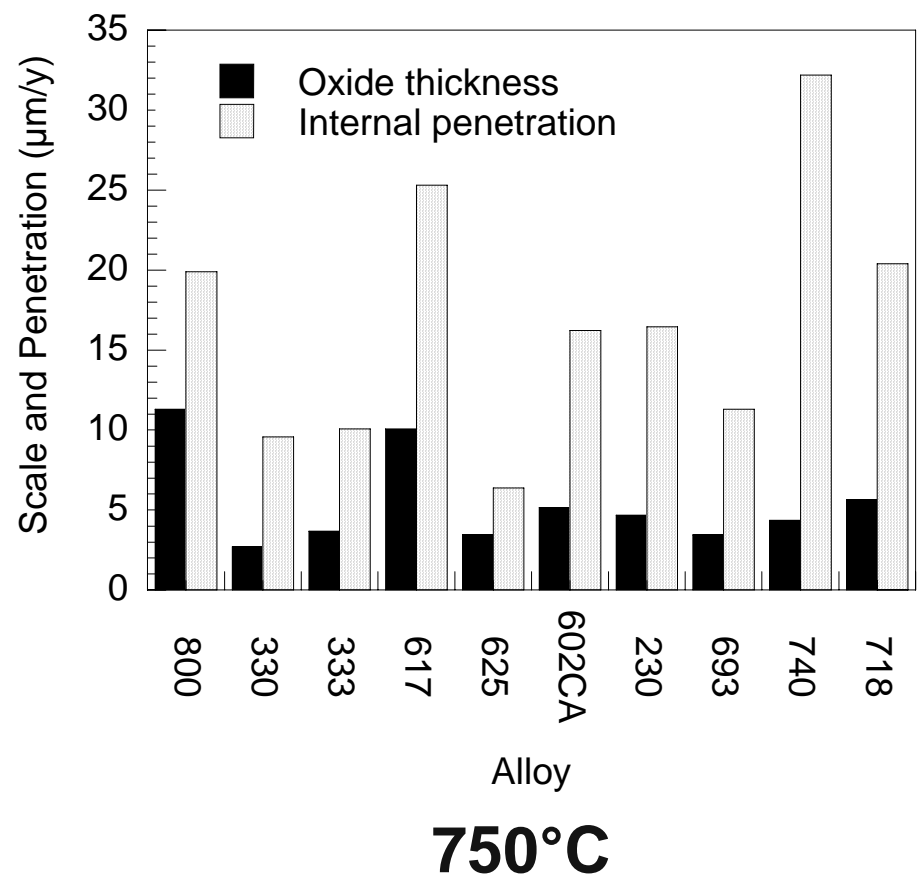


9.3 wt.% Fe

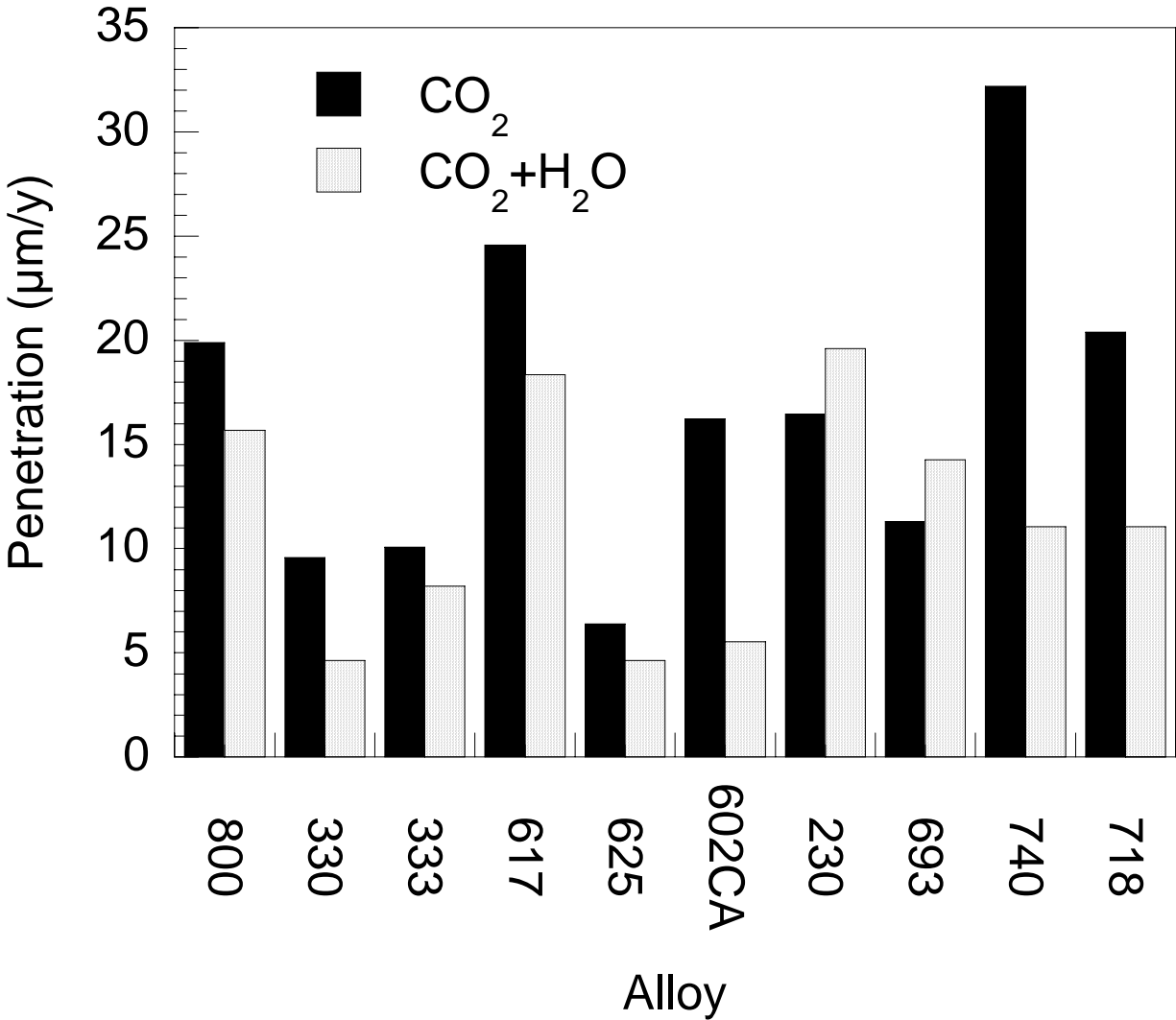


2.5 wt.% Fe

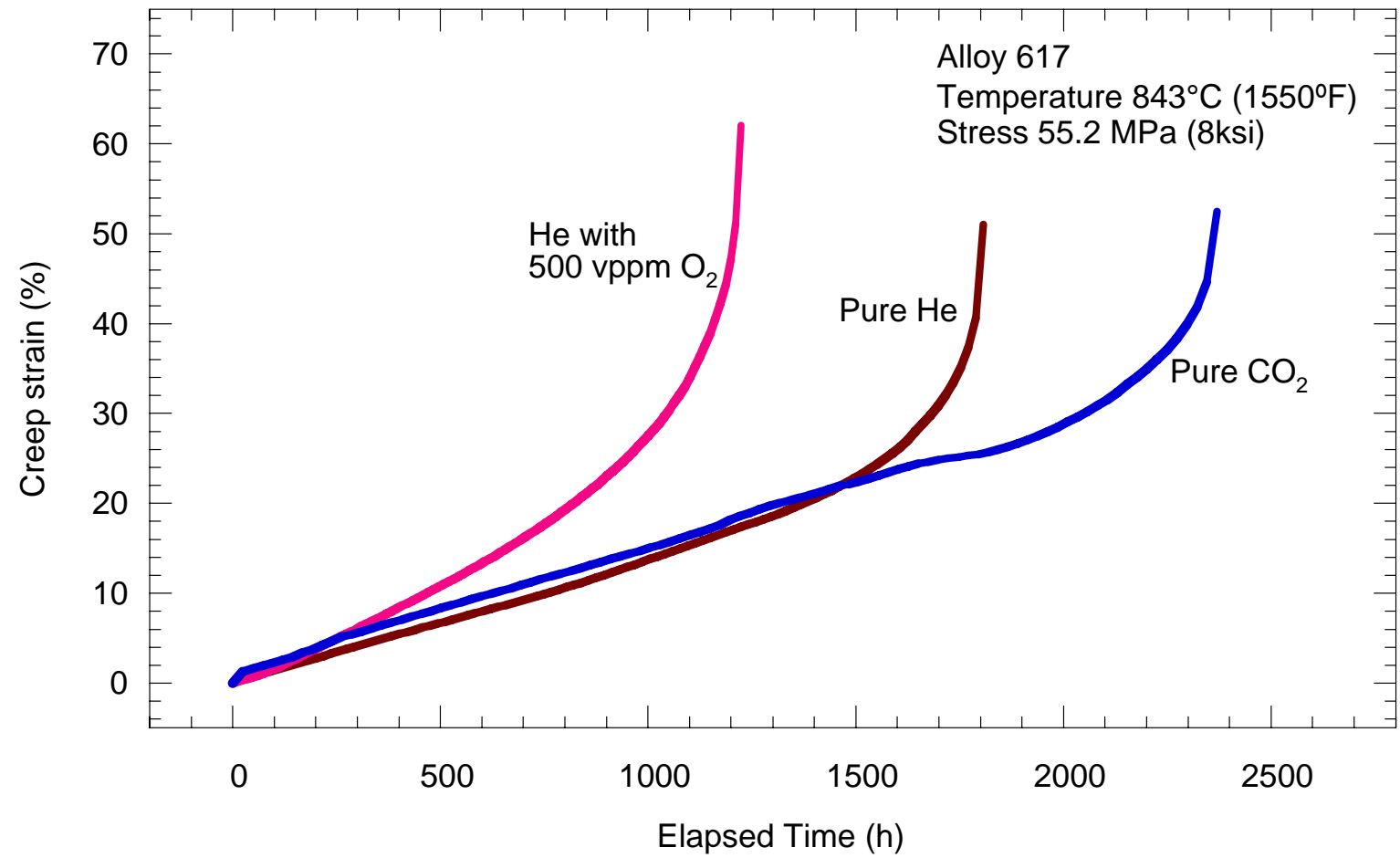
Scale growth and penetration rates in pure CO₂ (Parabolic kinetics)



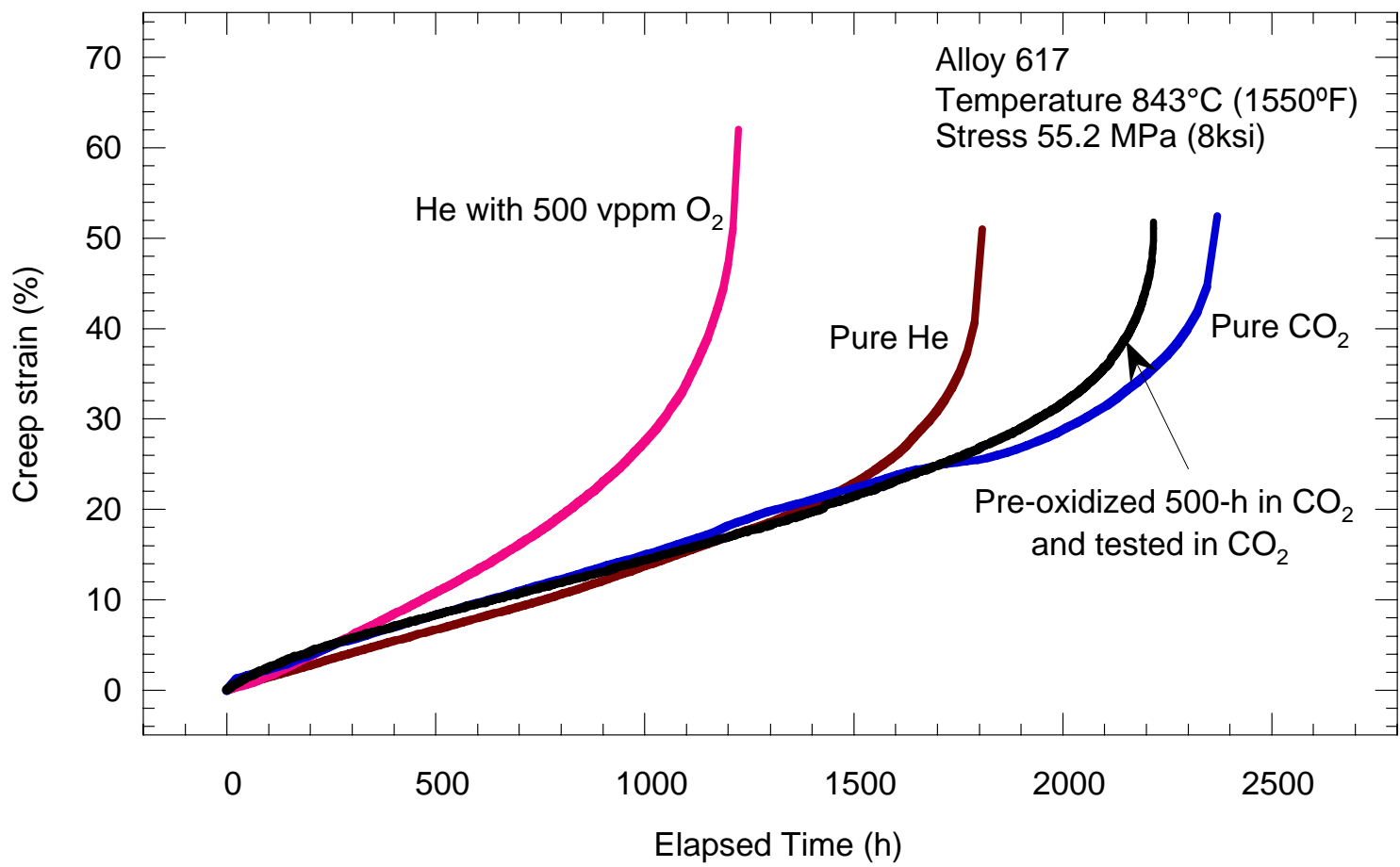
Alloy penetration rates at 750°C in CO₂ and in 50%CO₂-50%Steam



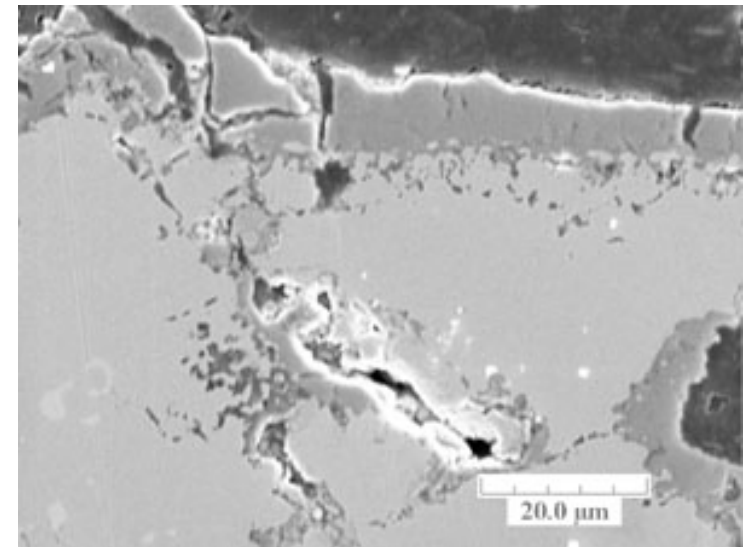
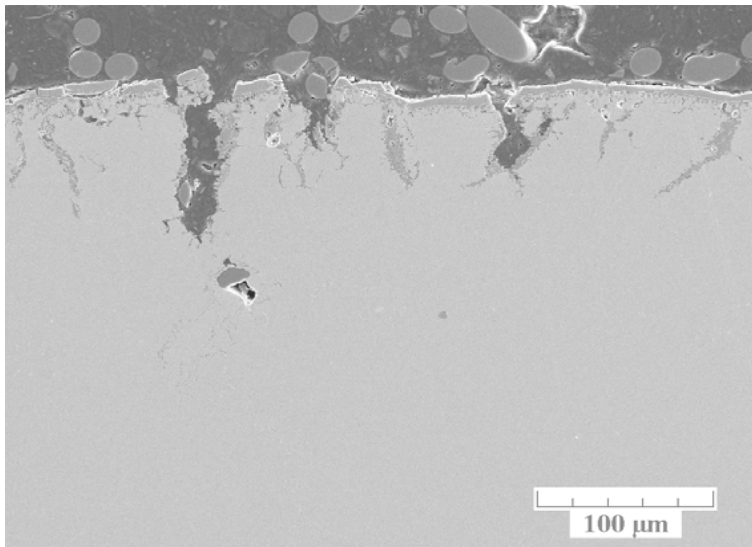
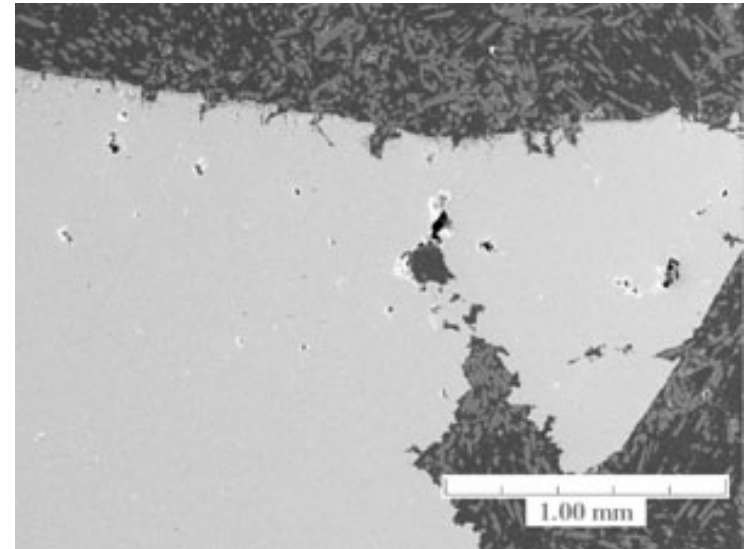
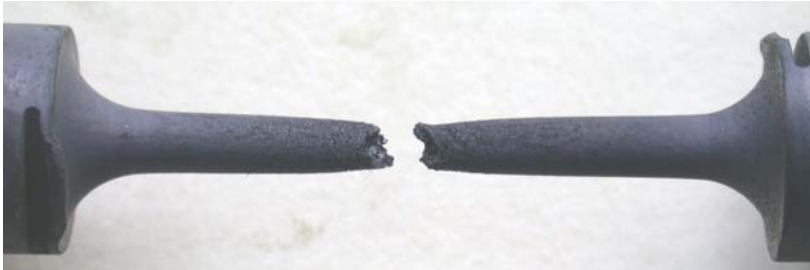
Creep performance of Alloy 617 at 843°C in several environments



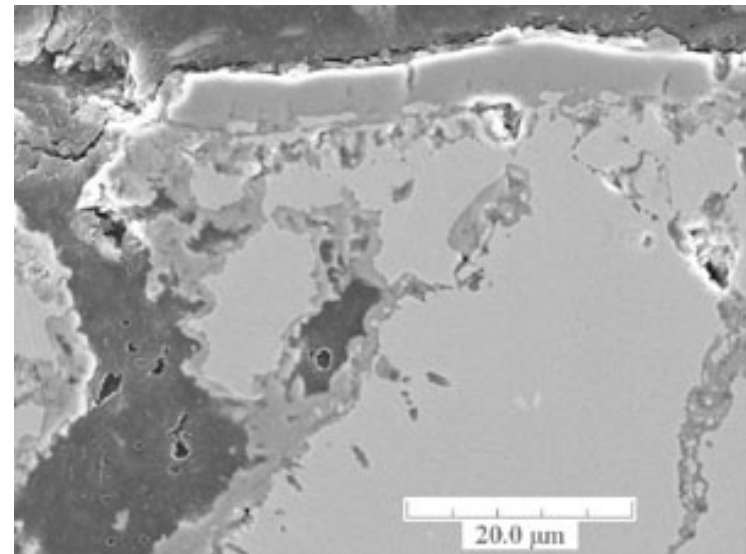
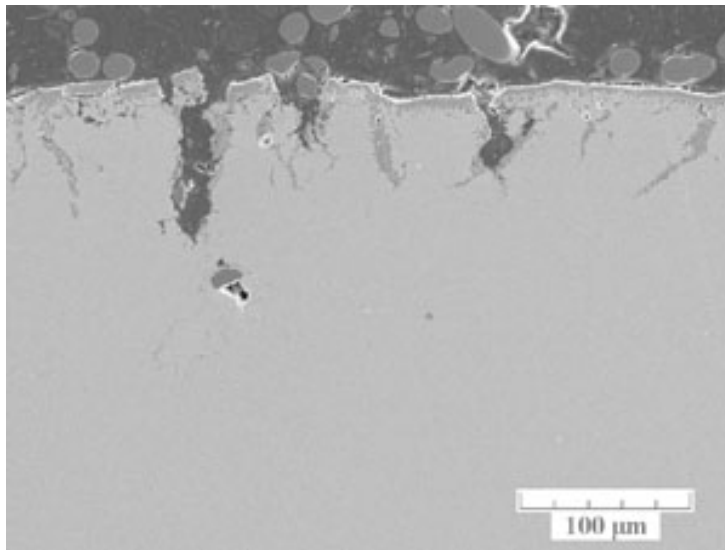
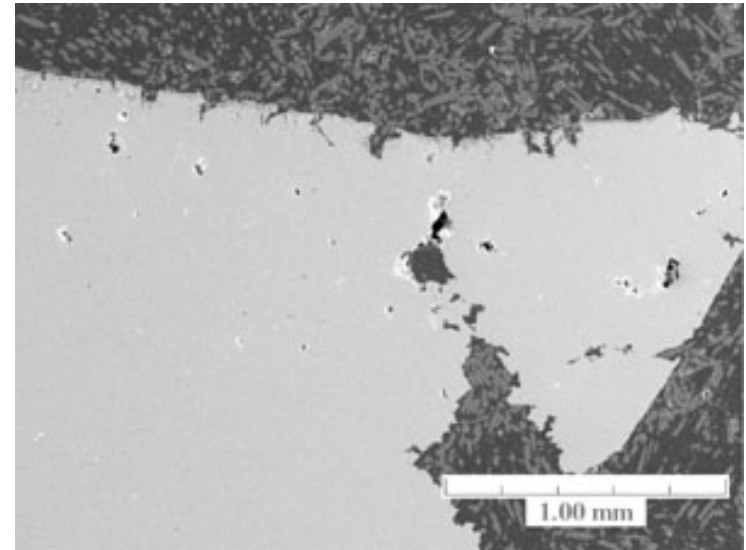
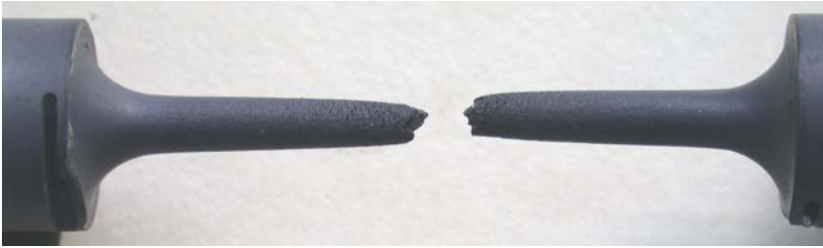
Creep performance of pre-oxidized Alloy 617 at 843°C



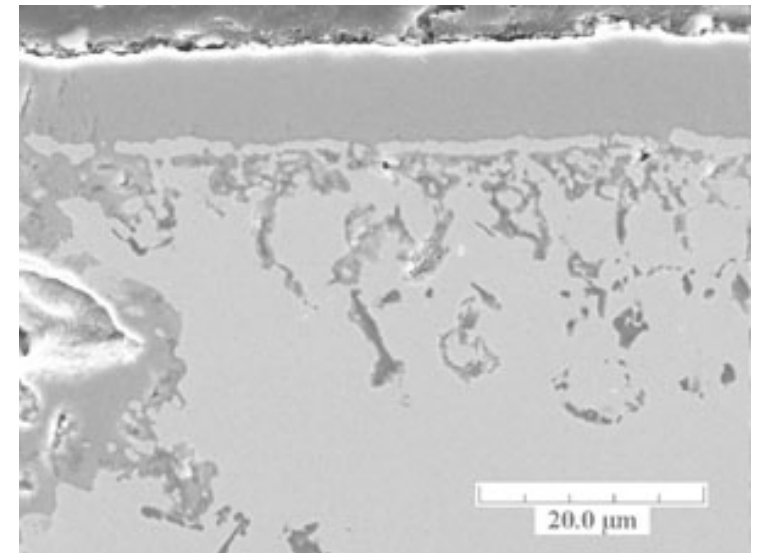
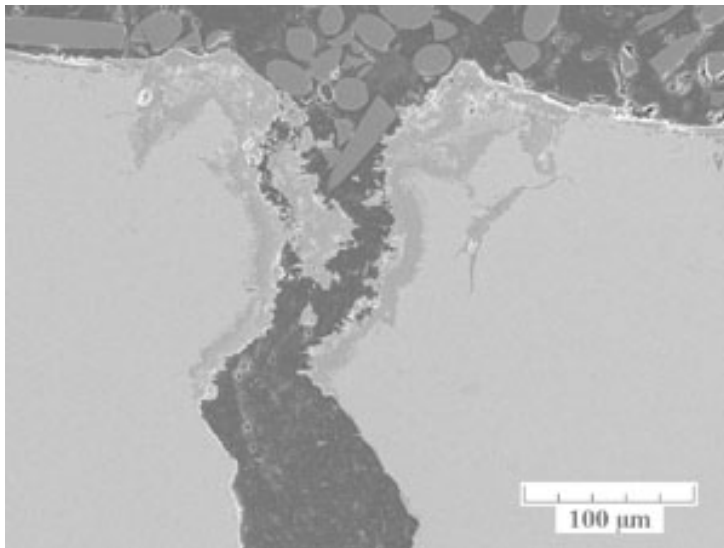
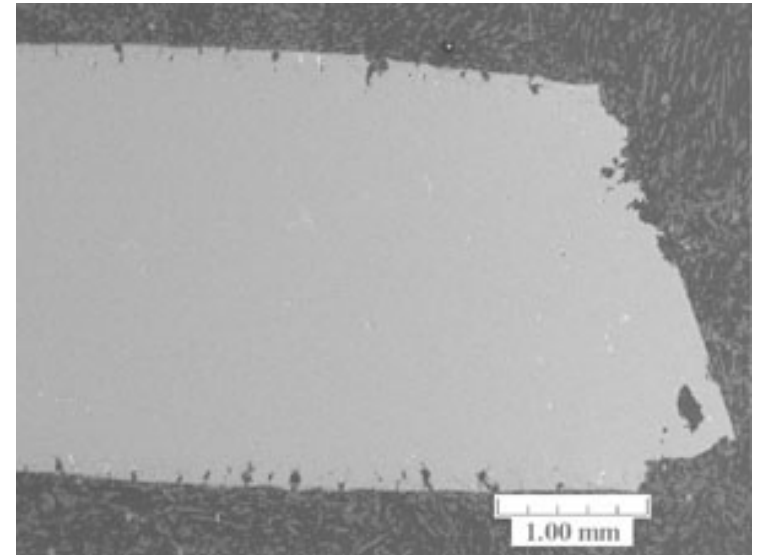
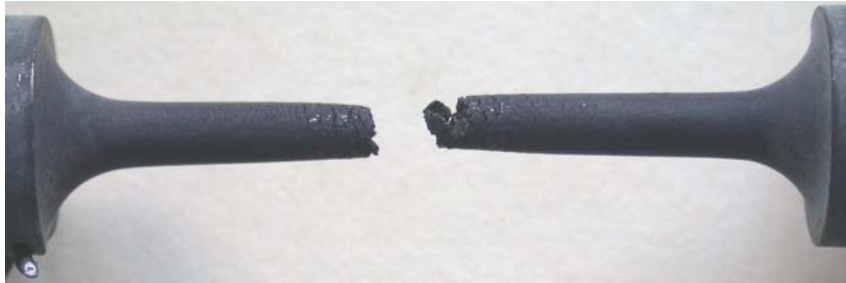
***Alloy 617, 843°C, CO₂ environment
Applied stress 55.2 MPa
Rupture life 2,369 h***



***Alloy 617, 843°C, CO₂ environment
Applied stress 68.95 MPa
Rupture life 543.6 h***



**Alloy 617, Preoxidized 500 h in CO₂,
843°C, tested in CO₂ environment
Applied stress 55.2 MPa
Rupture life 2,217.6 h**



Project Summary

- **We have conducted a study to evaluate the oxidation performance of structural alloys in CO₂ and CO₂-steam environments at temperatures up to 1000°C**
- **We will incorporate additional gas-turbine alloys as they become available**
- **Results indicate that the oxide scales that develop on the alloys are not that protective and internal carburization of the substrate can occur**
- **The formation of nano-particles of metals such as Fe, Ni, and Co can act as continuous channels for the transport of carbon through the oxide scale**
- **Preliminary results on creep of Alloy 617 in pure CO₂ environment showed very little effect on the properties such as creep rupture strain and creep rupture life**