



... 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*
- *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***

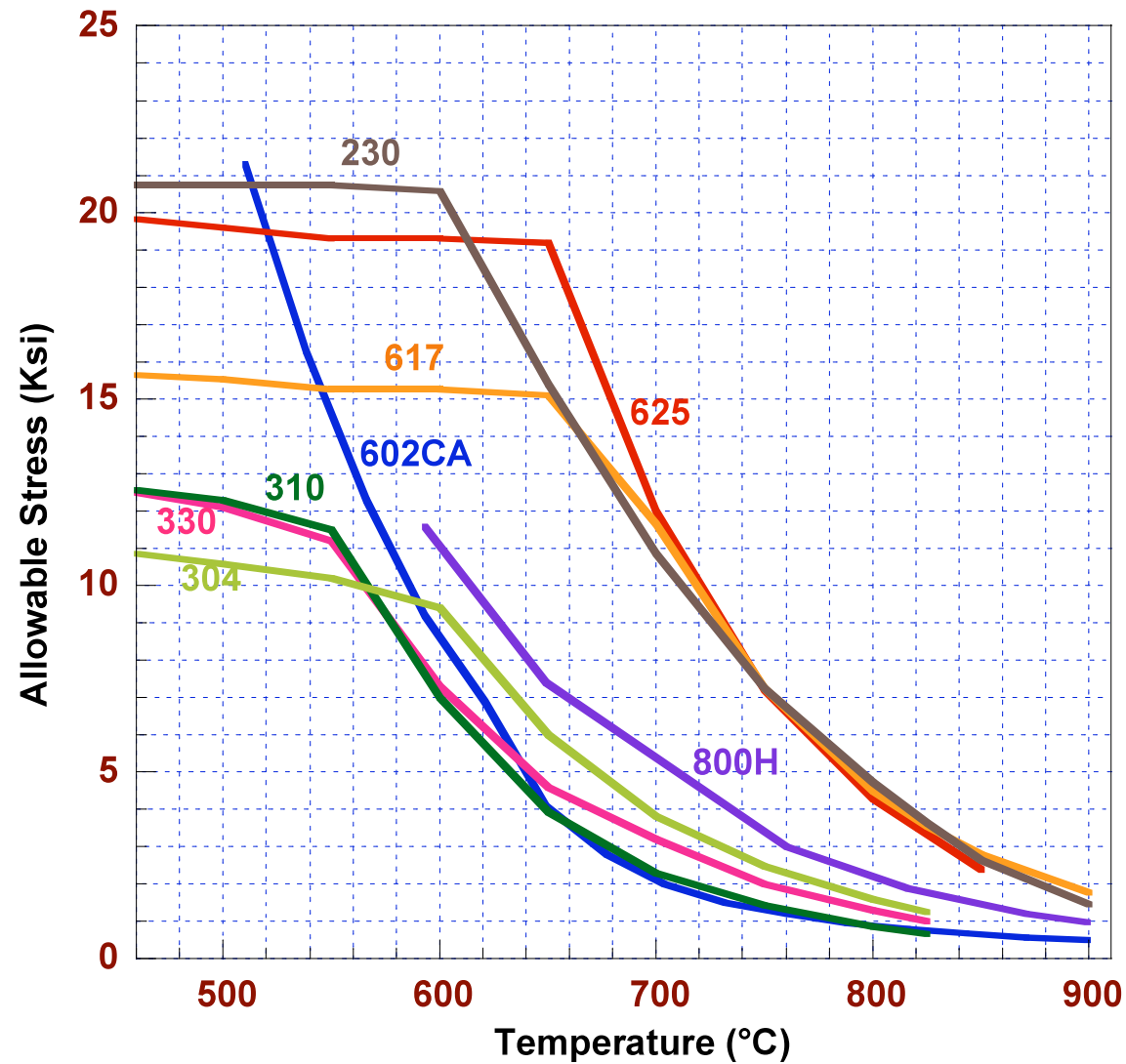
ANL Program Objectives

- **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**
- **Evaluate the effect of coal ash with trace concentrations of alkali, sulfur, and chlorine compounds on the corrosion 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**

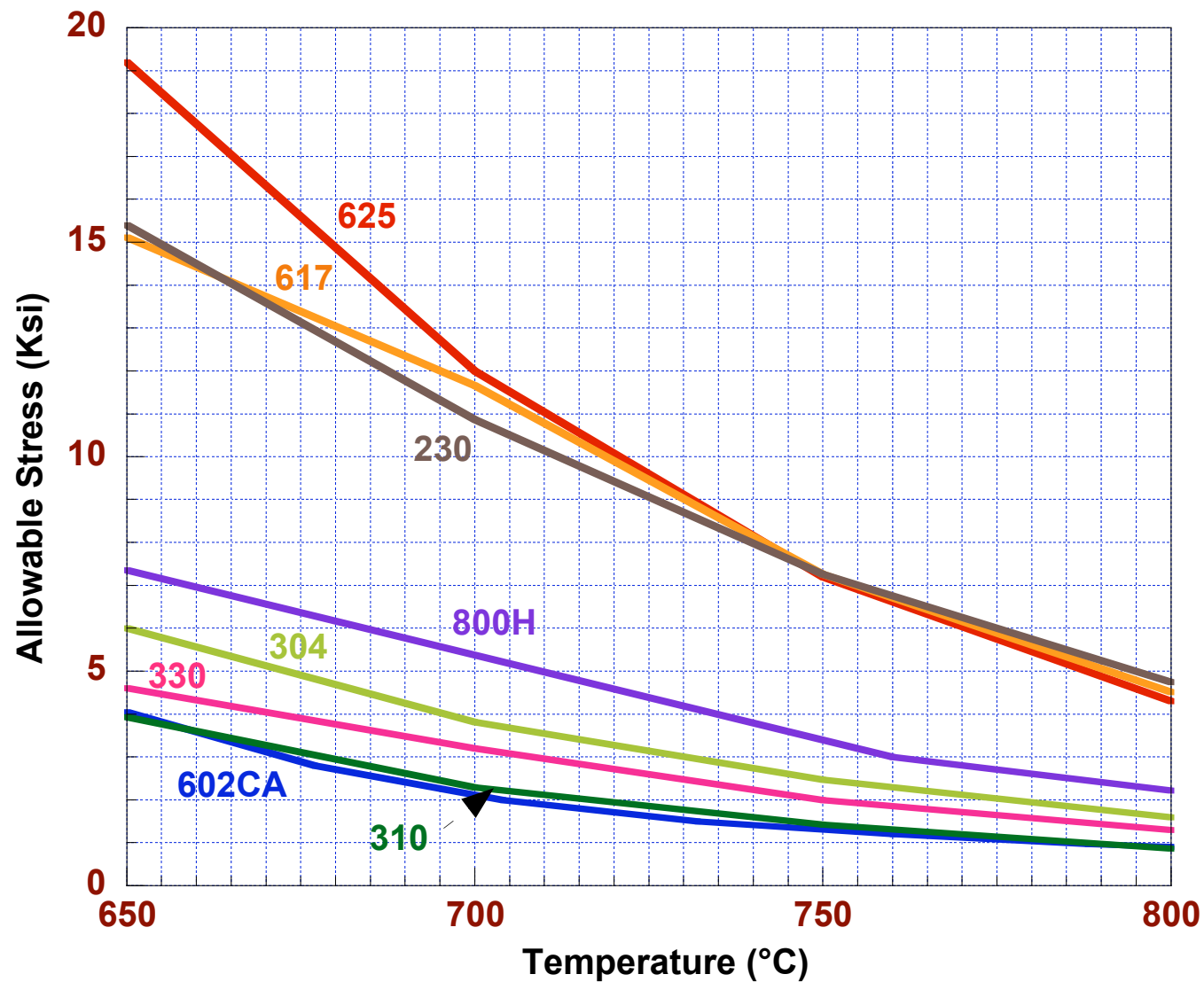
Current List of Alloys in the Study

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

ASME Code Allowable Stress Values



ASME Code Allowable Stress Values at 650-800°C



Laboratory Test Details

Key variables: Temperature, time, alloy composition

Materials: Fe- and Ni-base alloys, coatings

Environment: Pure CO₂ and CO₂-steam mixtures

Deposits: Coal ash, alkalis, sulfur, chlorine

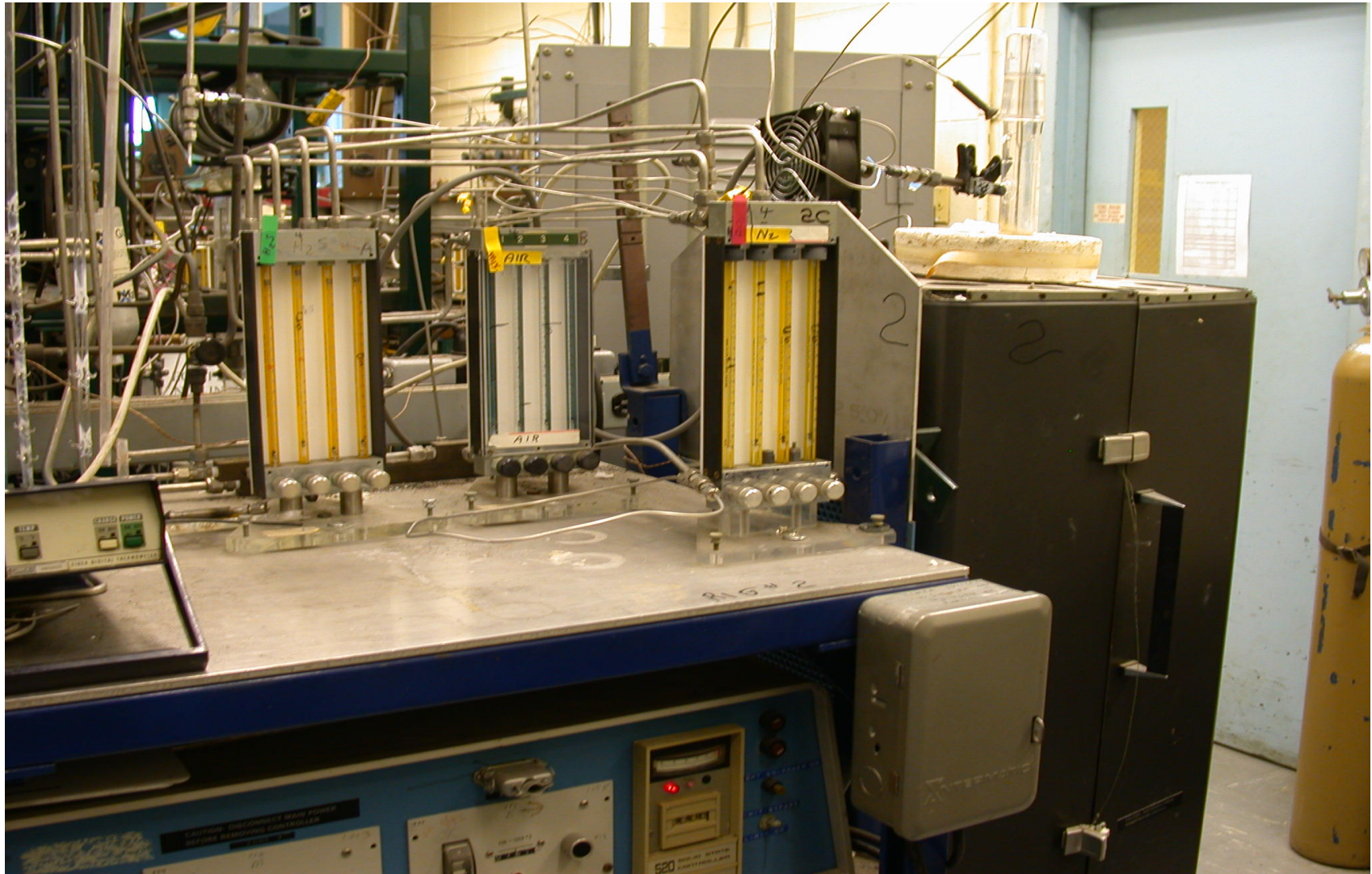
Test temperature range: 650-1000°C

Test times: up to 10,000 h

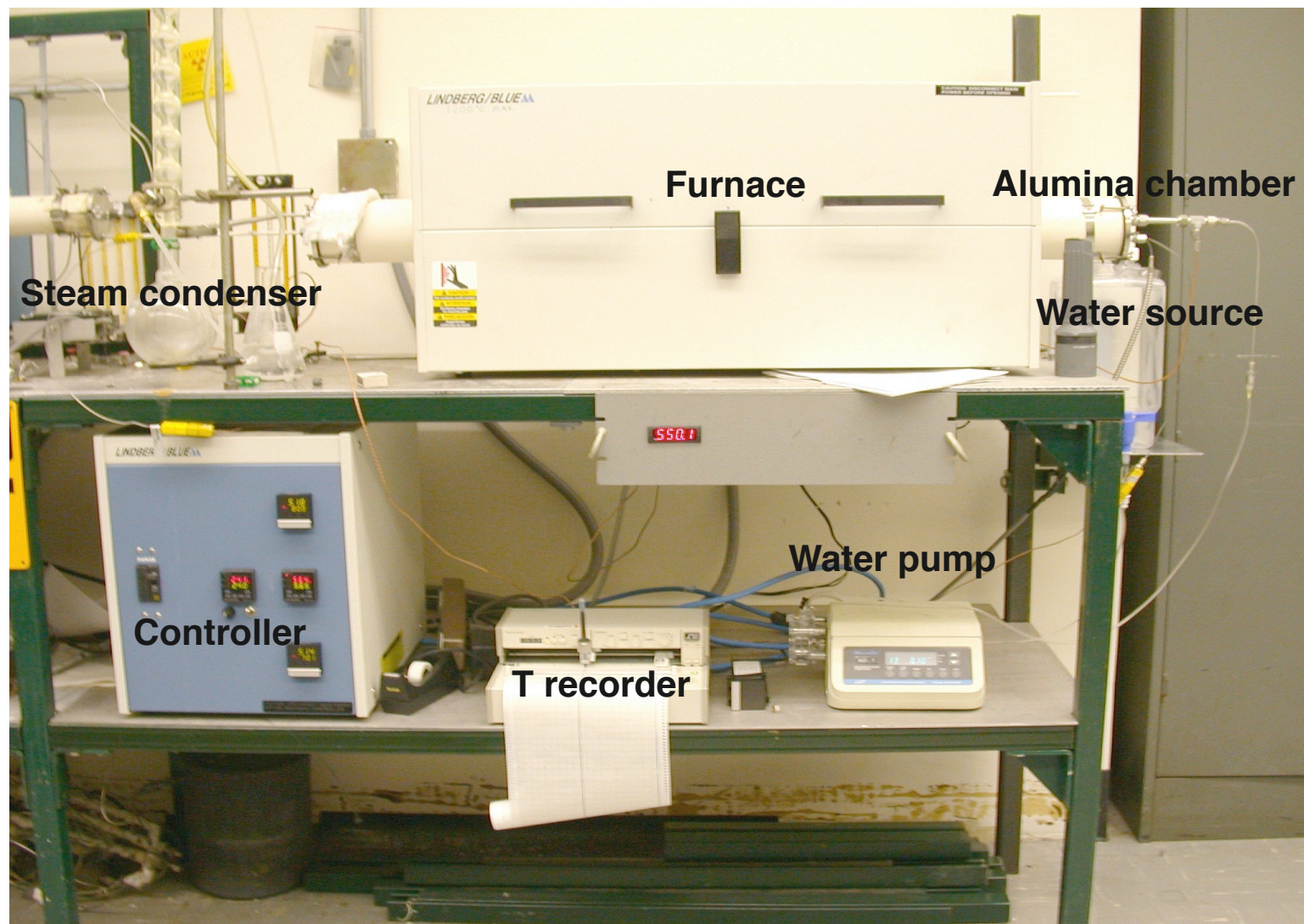
Specimen evaluation:

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

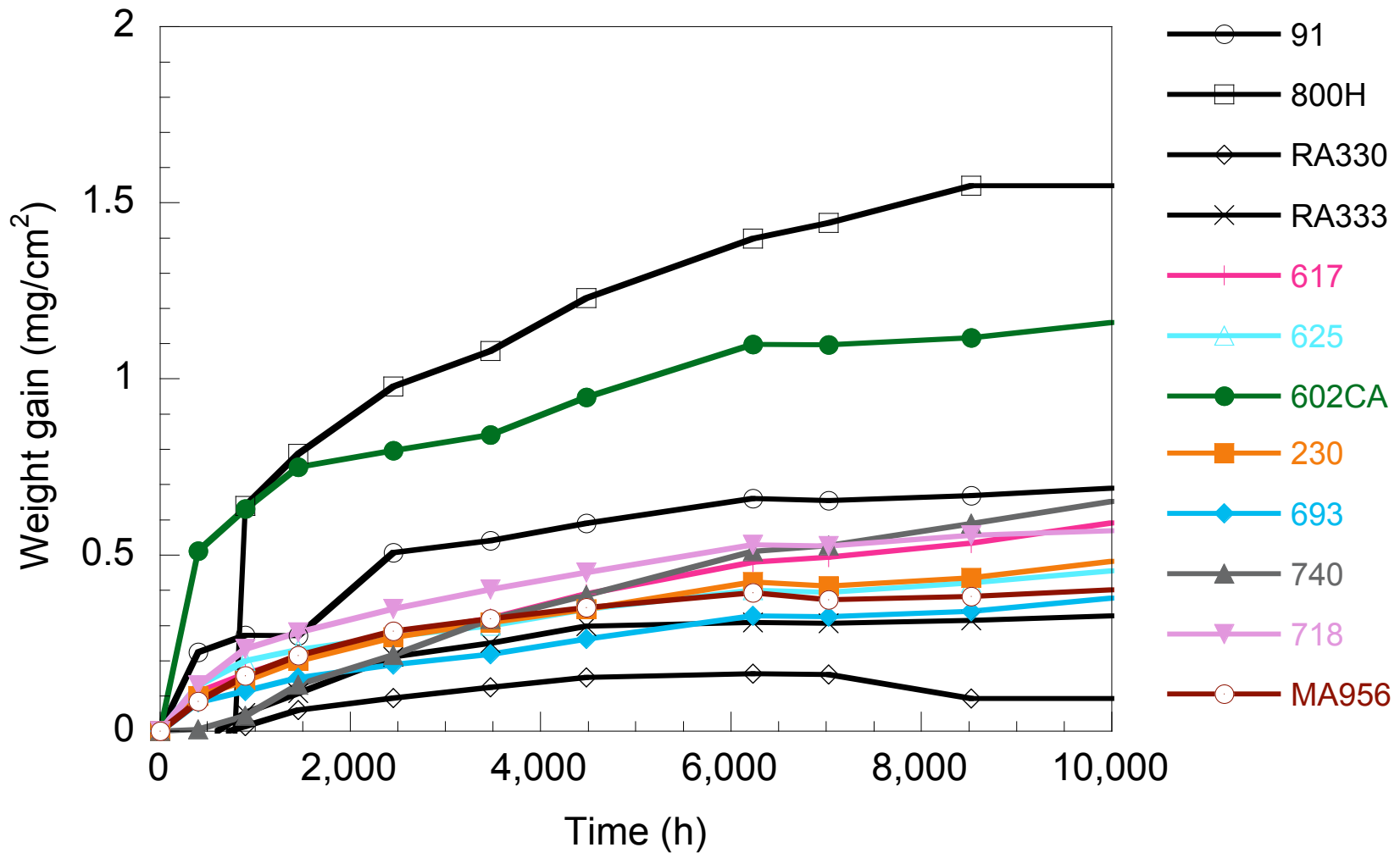
CO₂ Exposure Test Facility



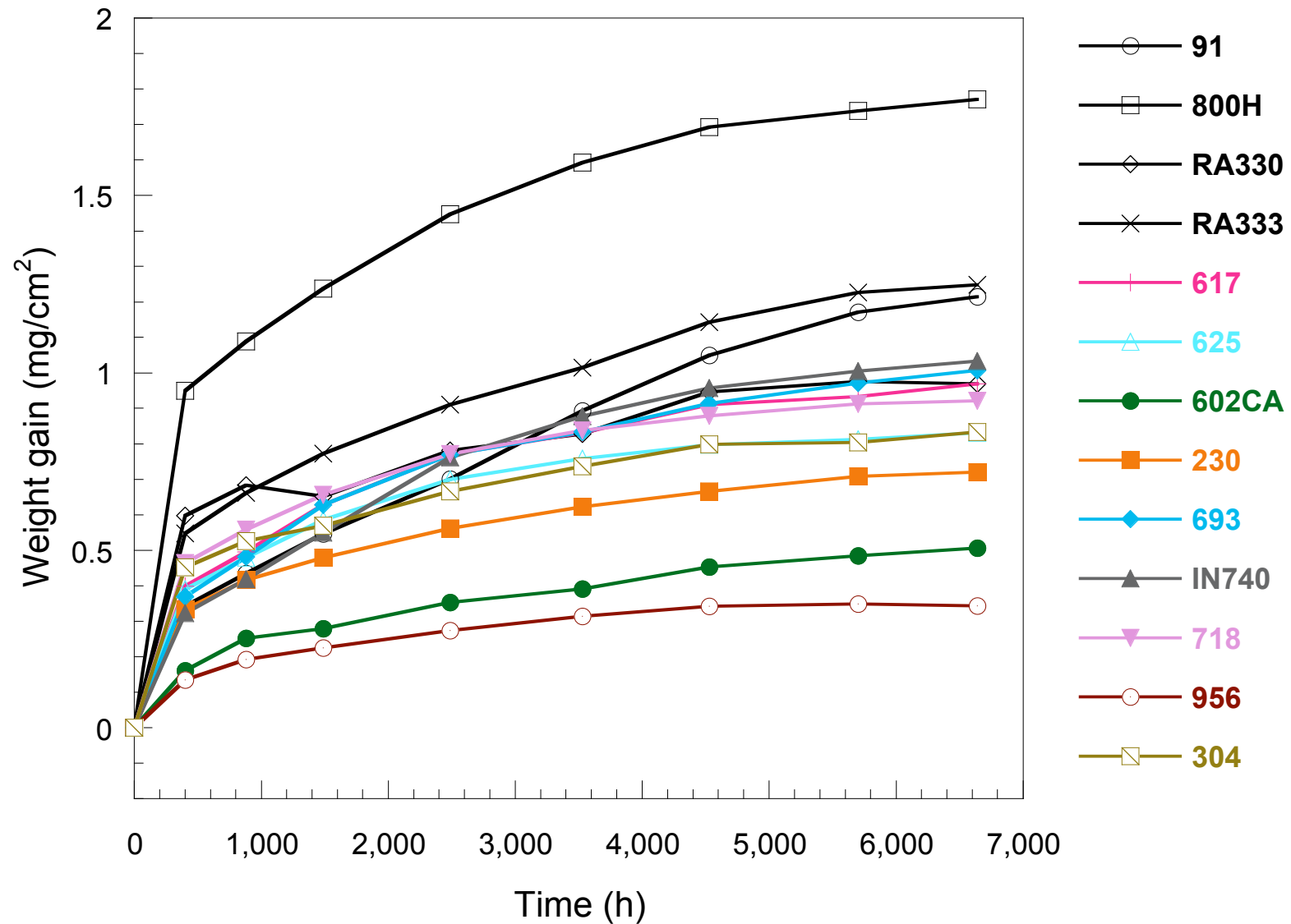
CO₂-Steam Exposure Test Facility



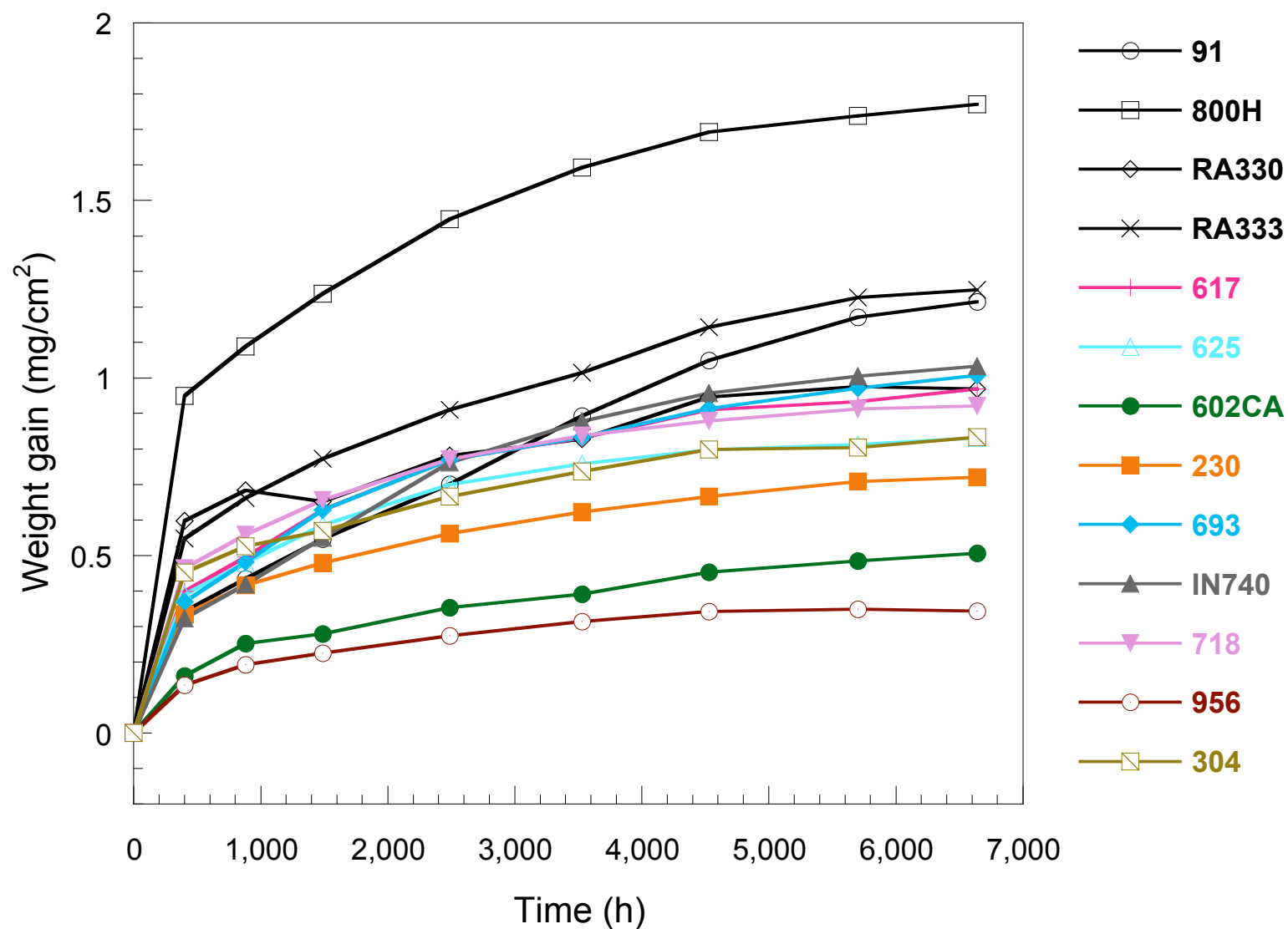
Oxidation Performance in Pure CO₂ at 750°C



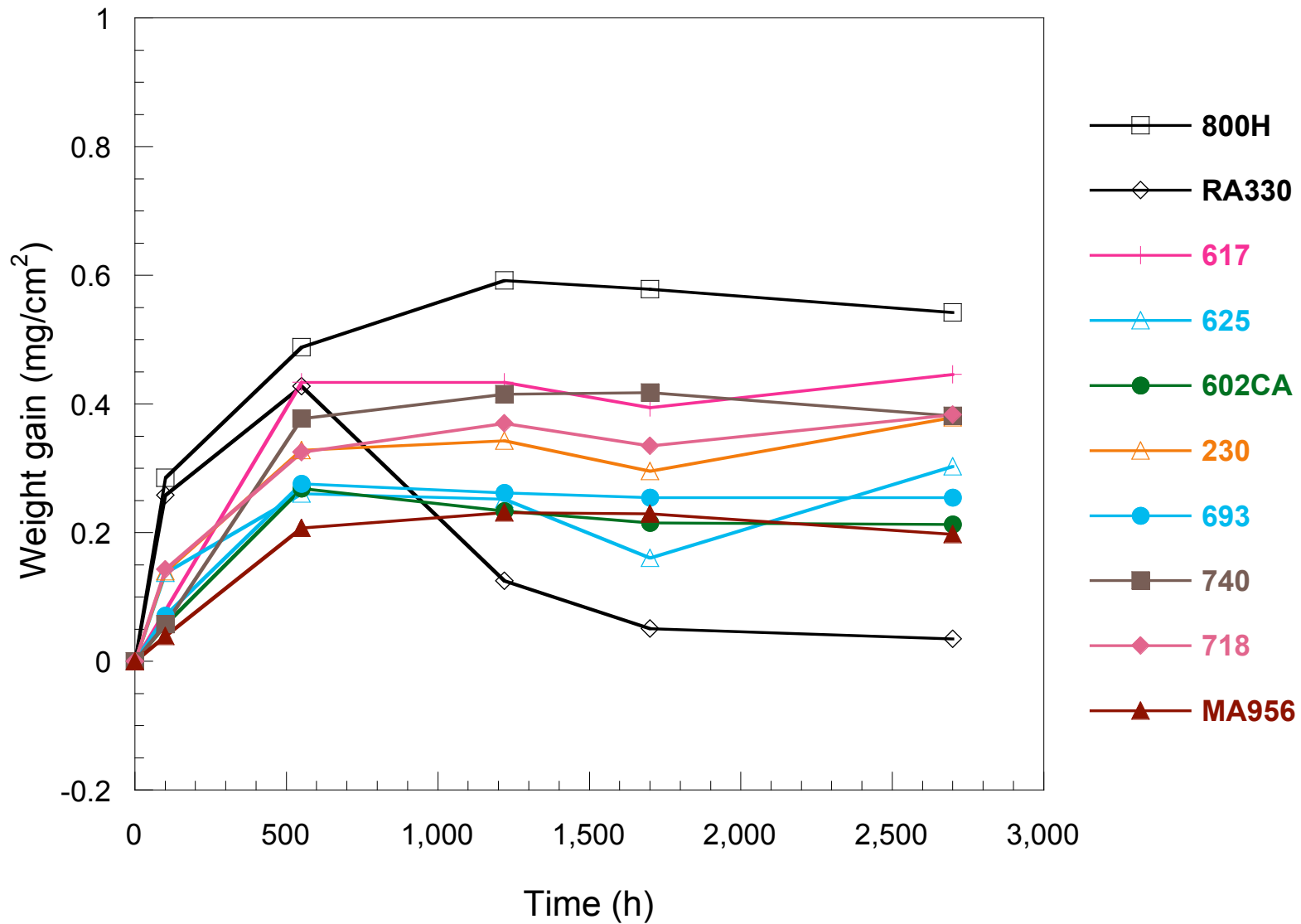
Oxidation Performance in 50% CO₂- 50% H₂O at 750°C



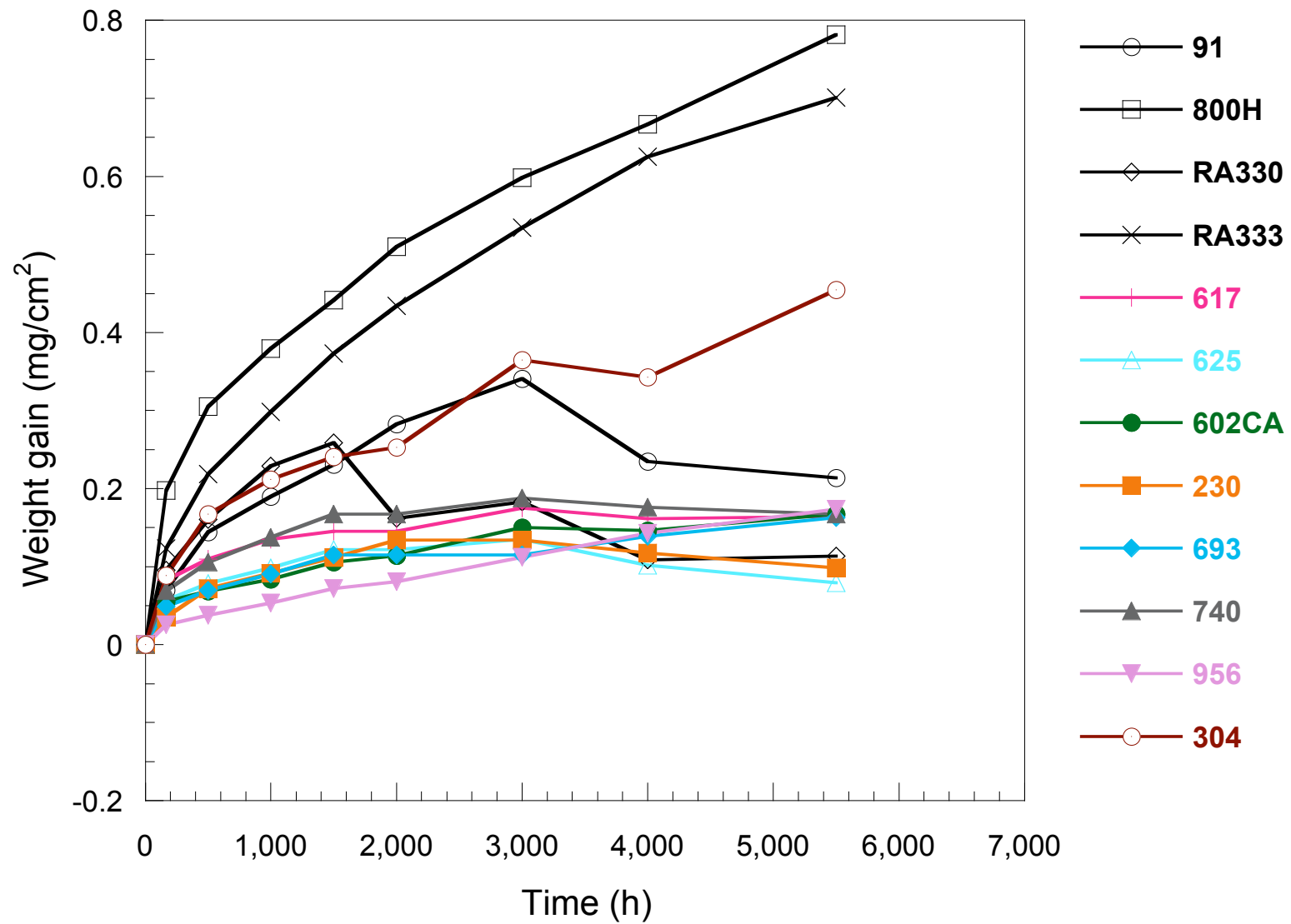
Oxidation Performance in 50% CO₂-50% H₂O at 750°C



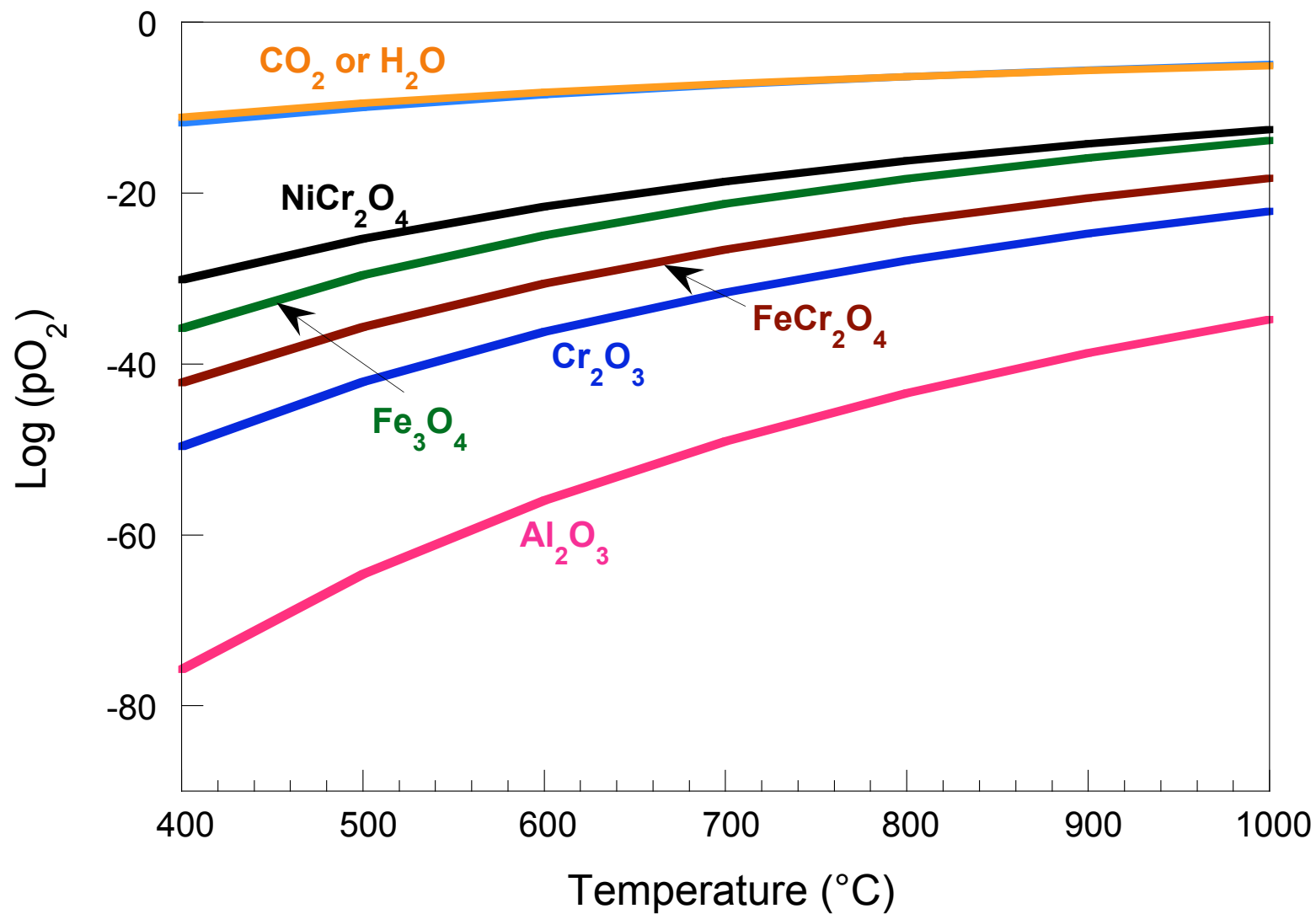
Oxidation Performance in Pure Steam at 725°C



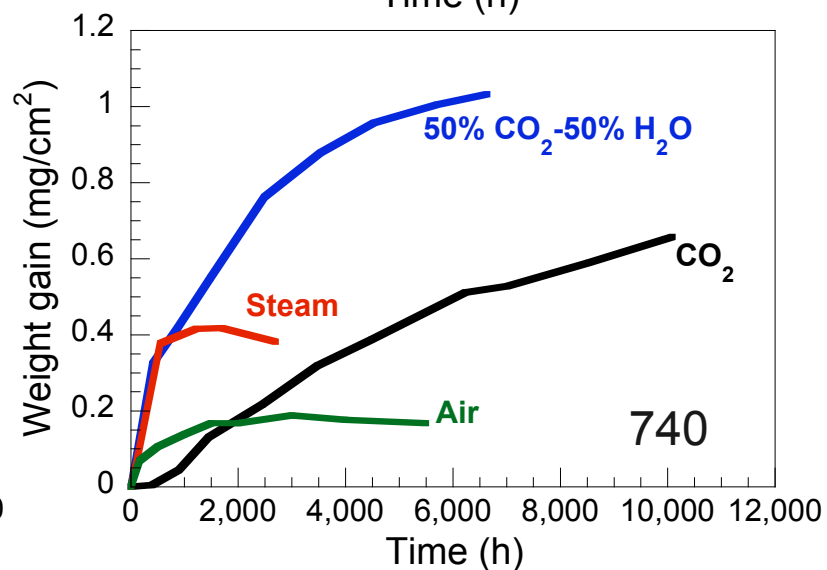
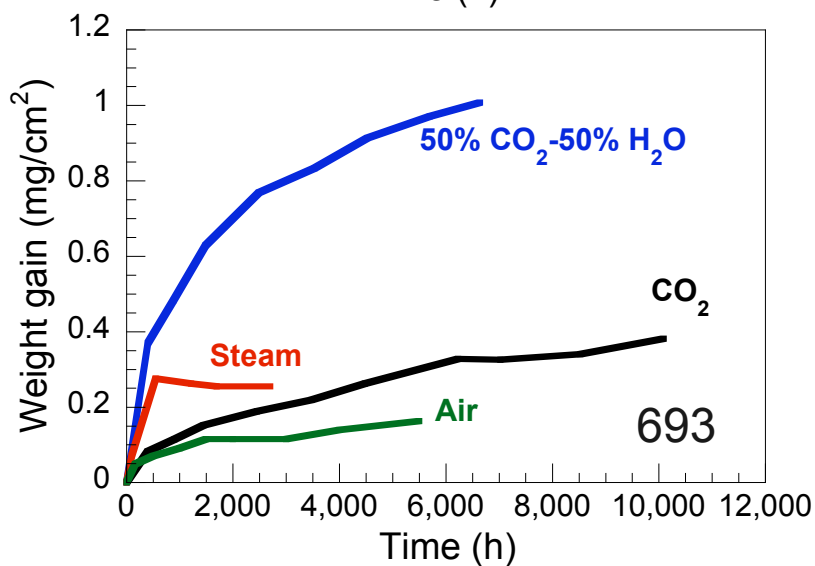
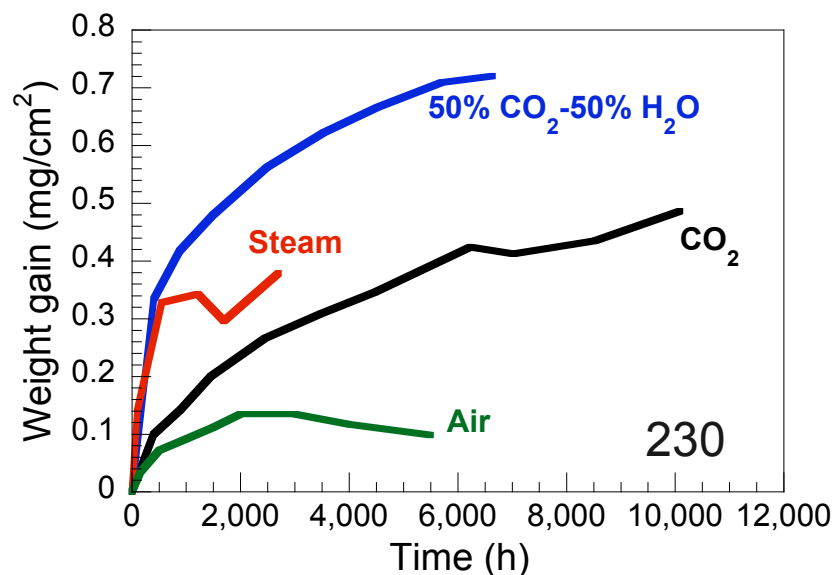
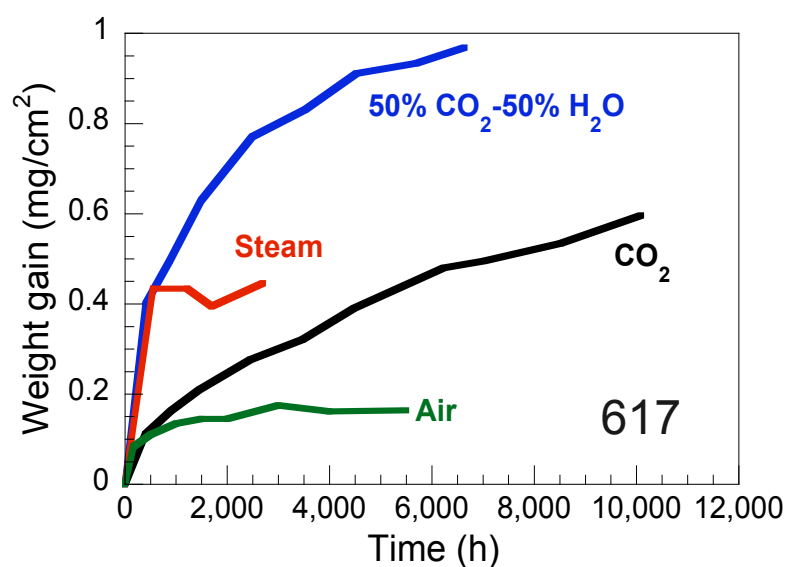
Oxidation Performance in Air at 750°C



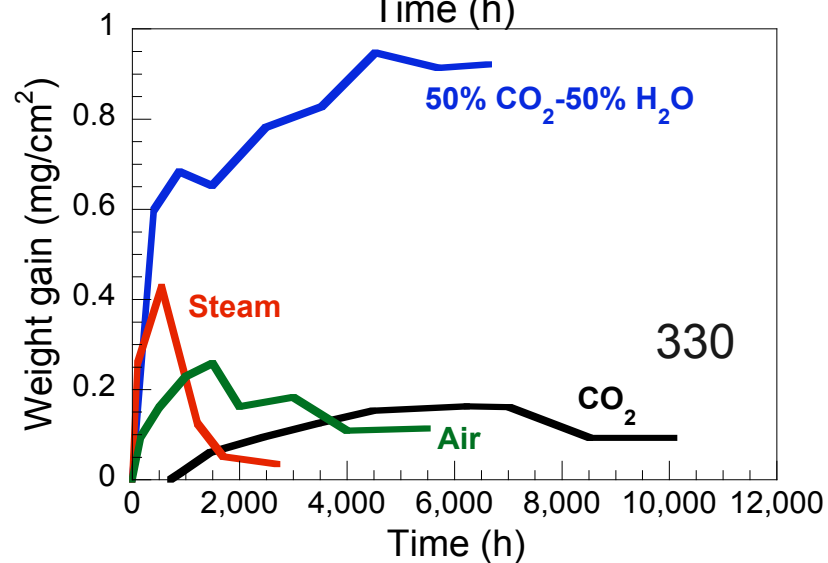
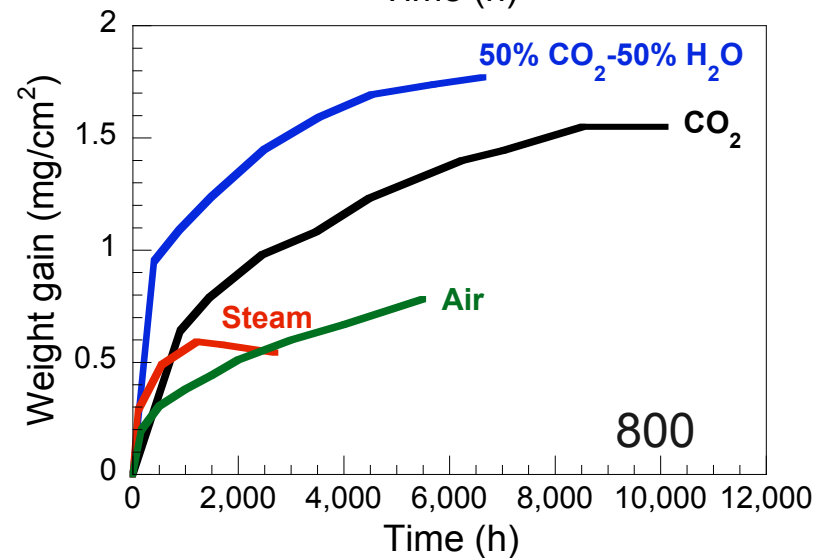
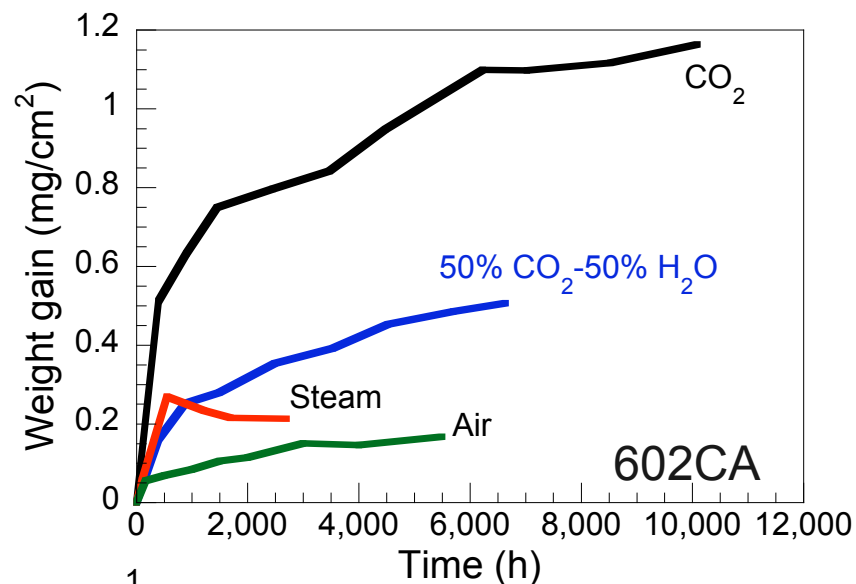
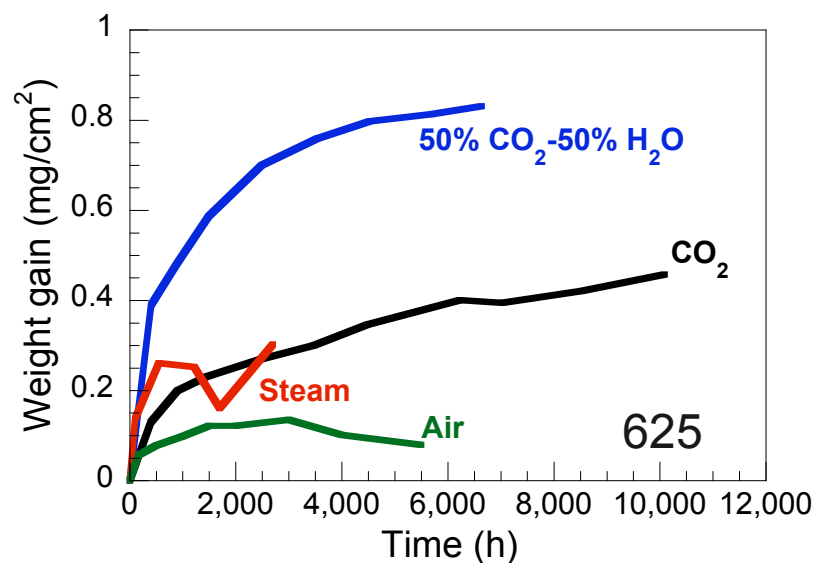
Thermodynamic Stability of Oxide Phases in the Scale

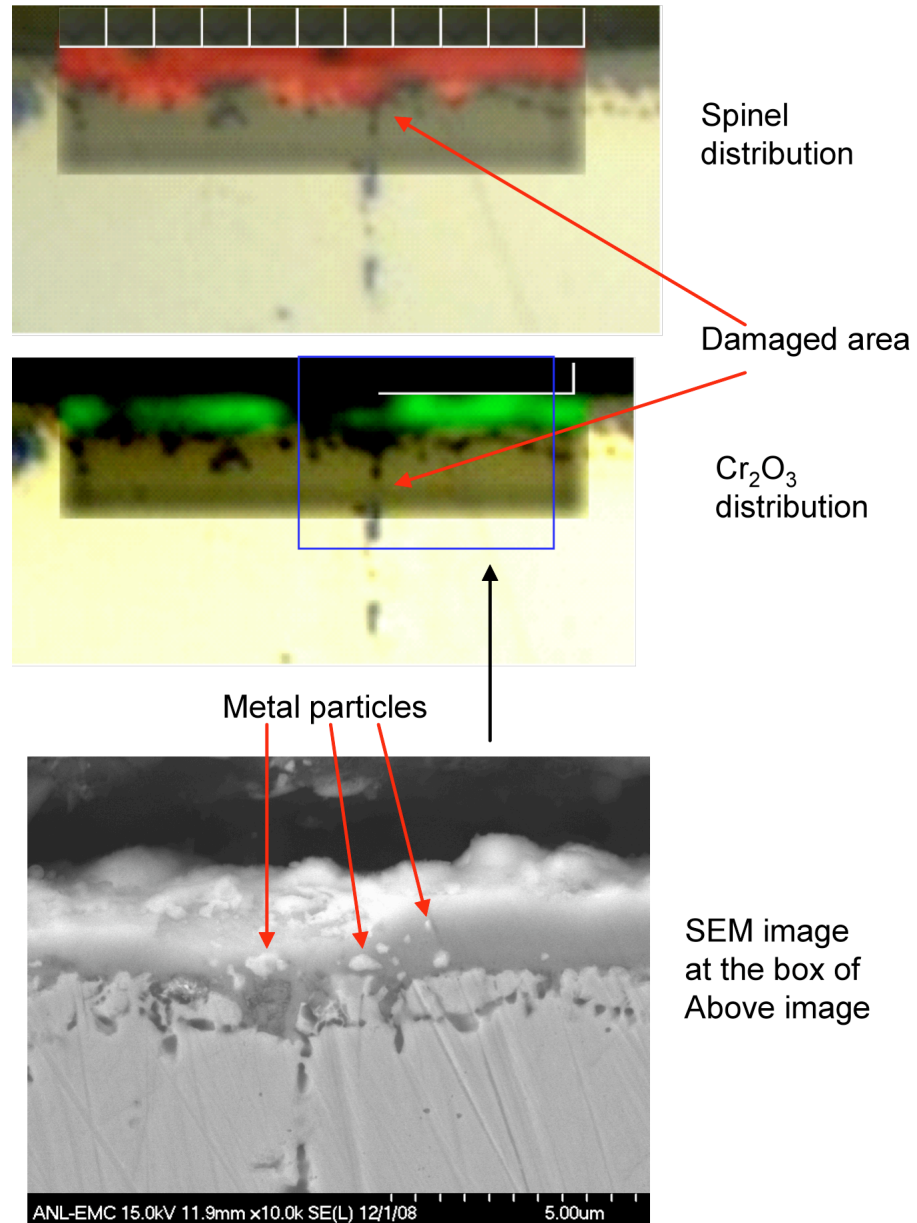


Oxidation Performance in Various Environments at 750°C

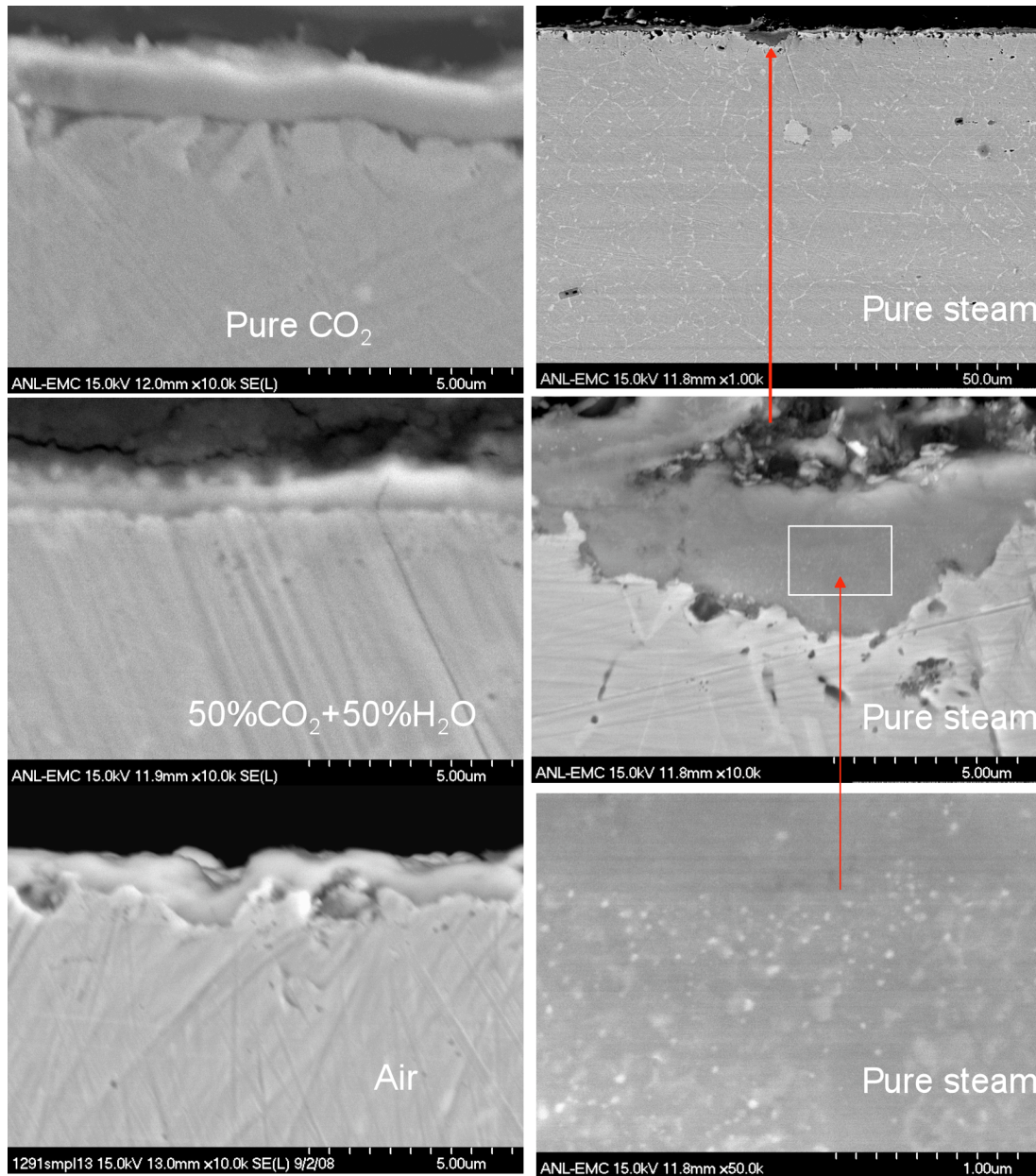


Oxidation Performance in Various Environments at 750°C

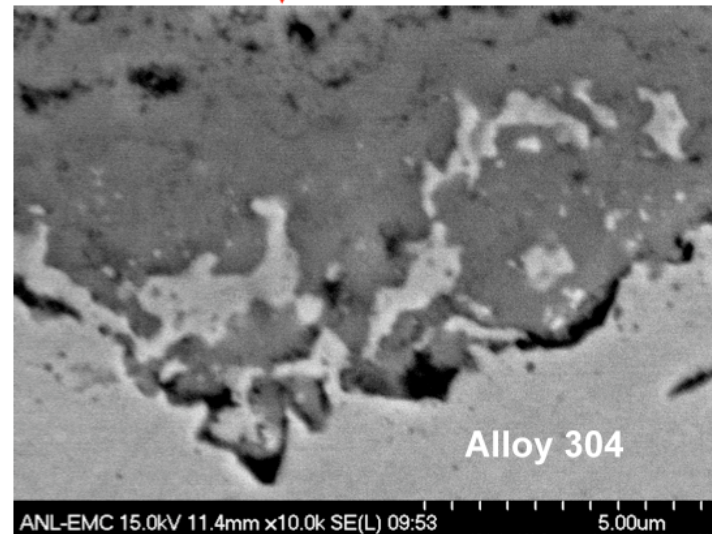
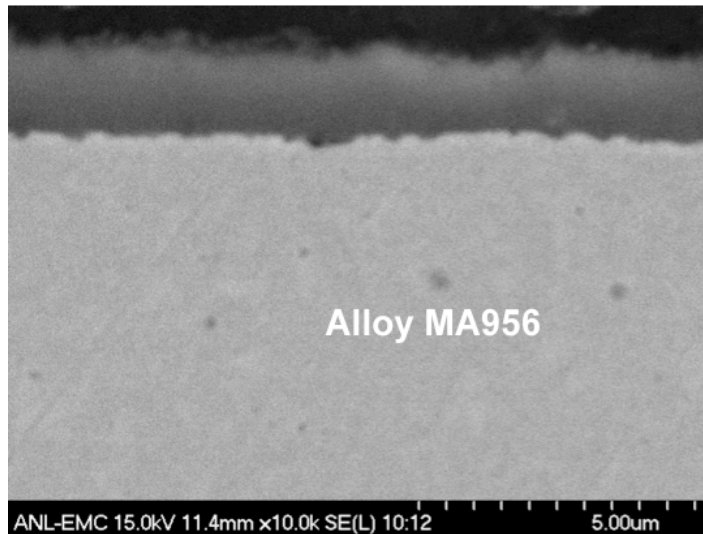
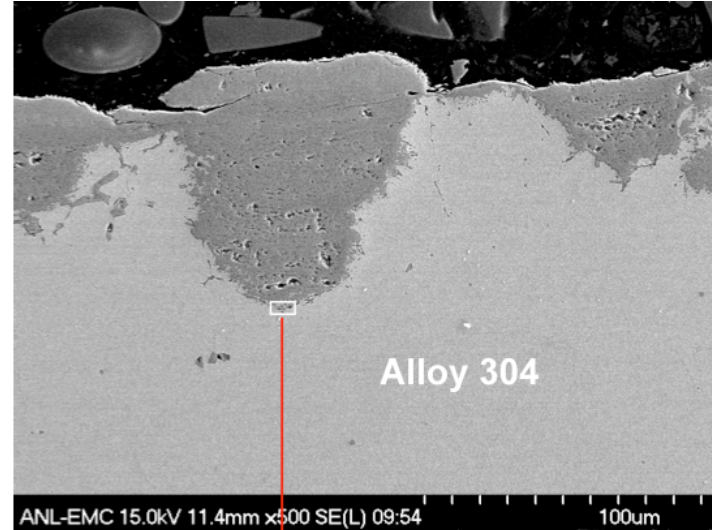
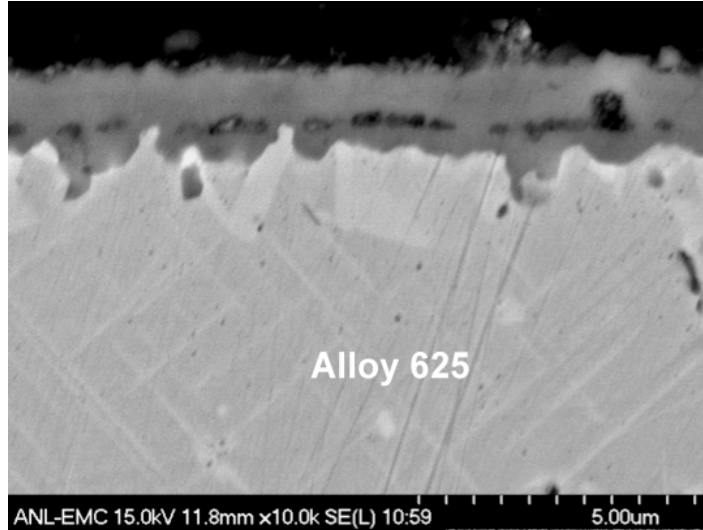




Alloy 617

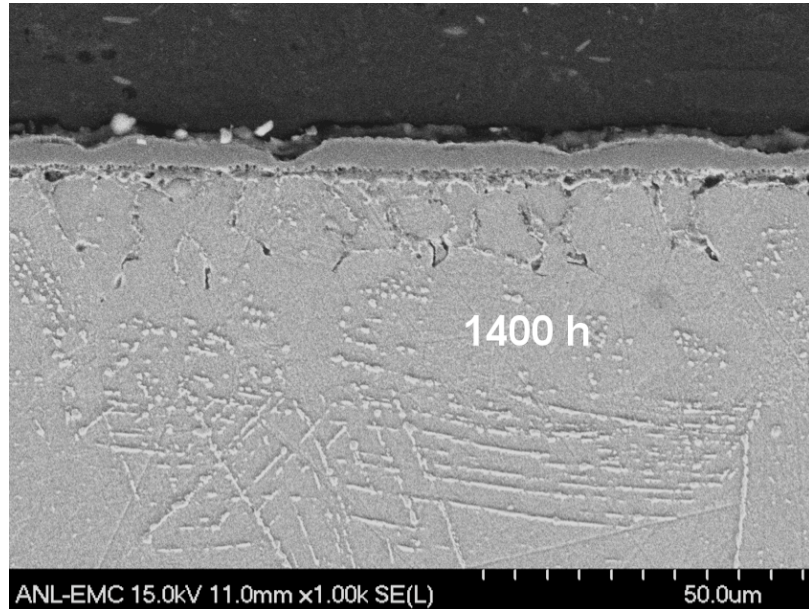


Alloy 625

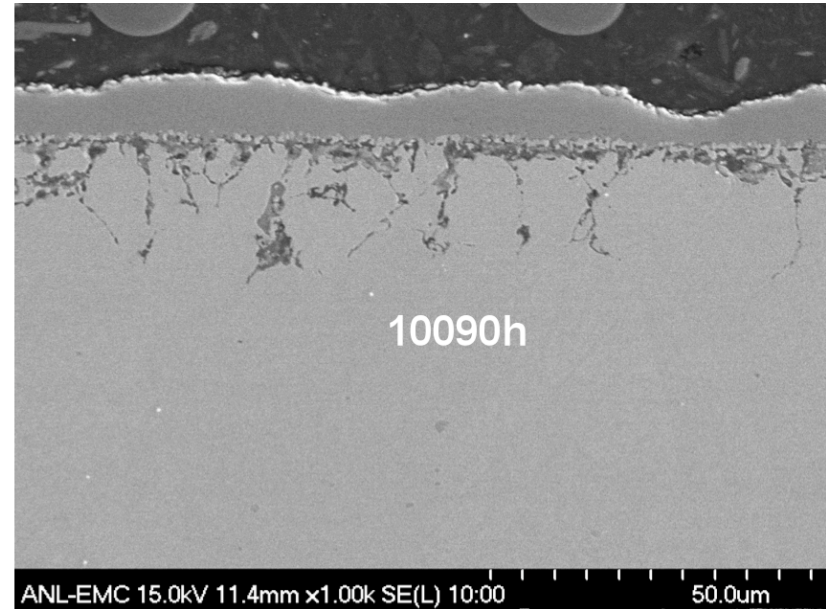


Pure CO₂ at 750°C for 10,090 h

Alloy 800 exposed to Pure CO₂ at 750°C

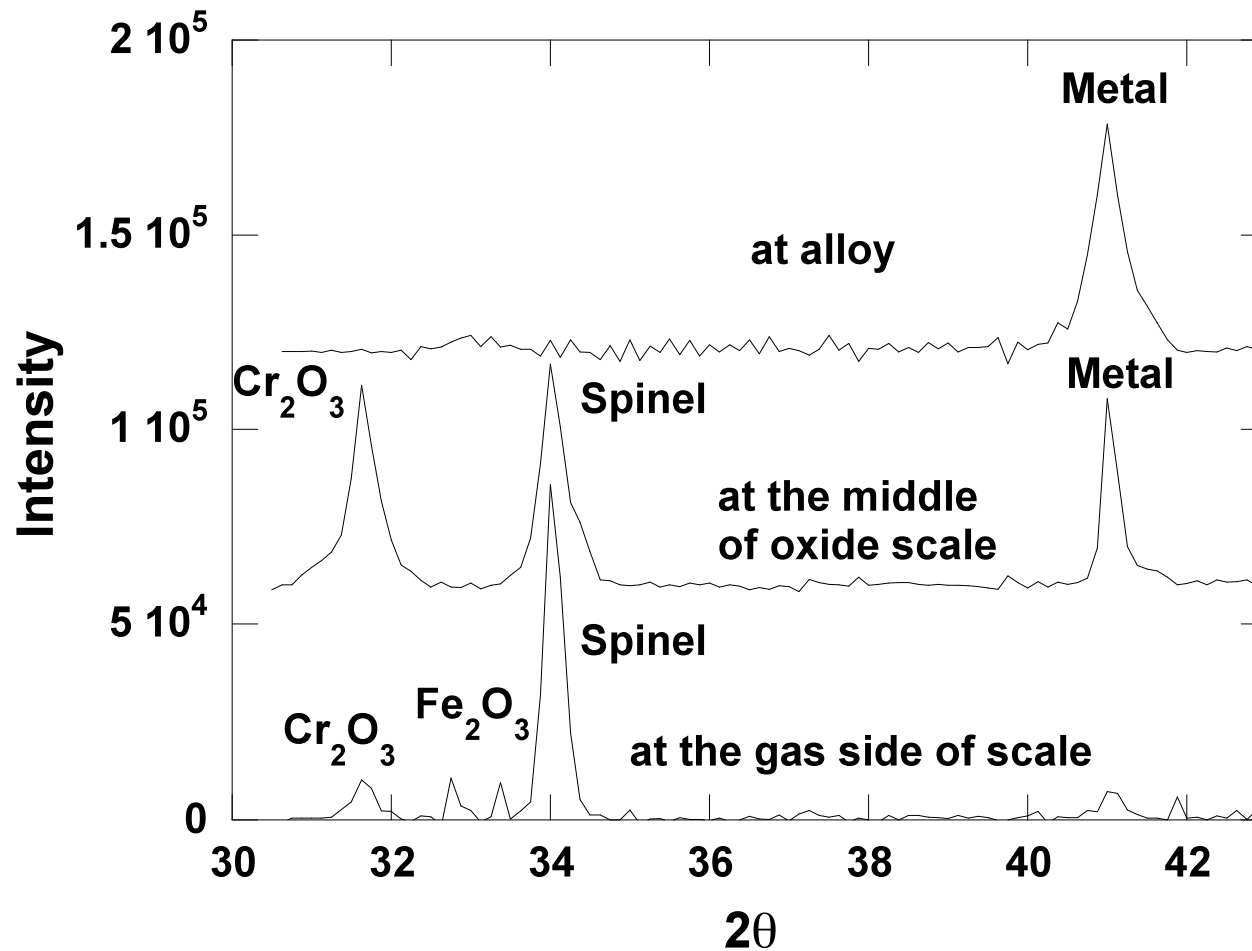


1452 h

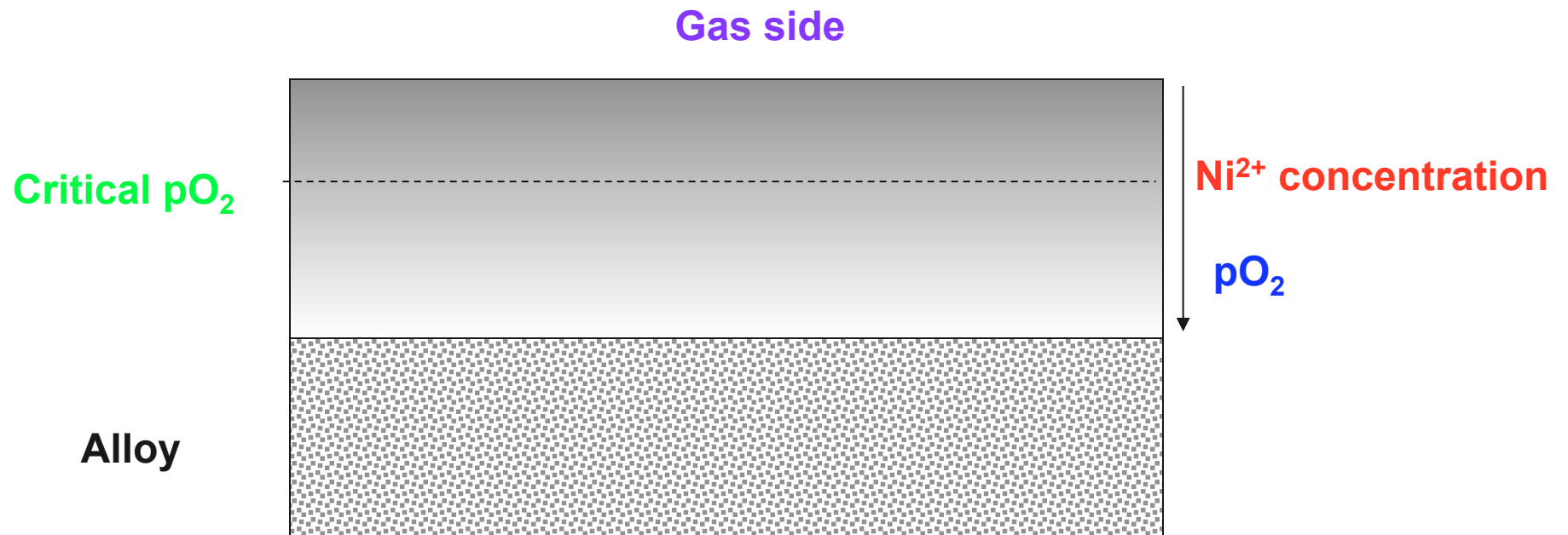


10,090 h

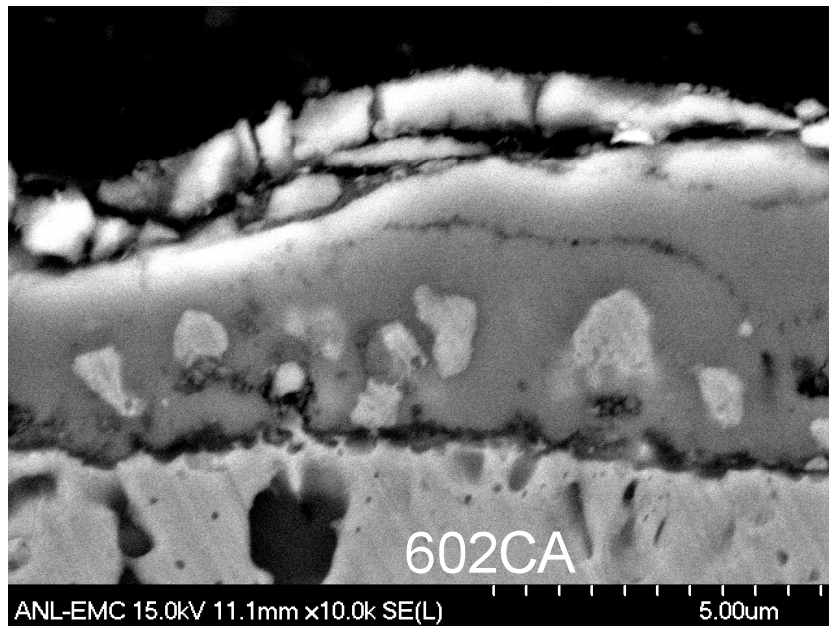
***XRD at different locations of scale on the surface of Alloy 617
after 2,760-h exposure in 50%CO₂-50%Steam at 750°C***



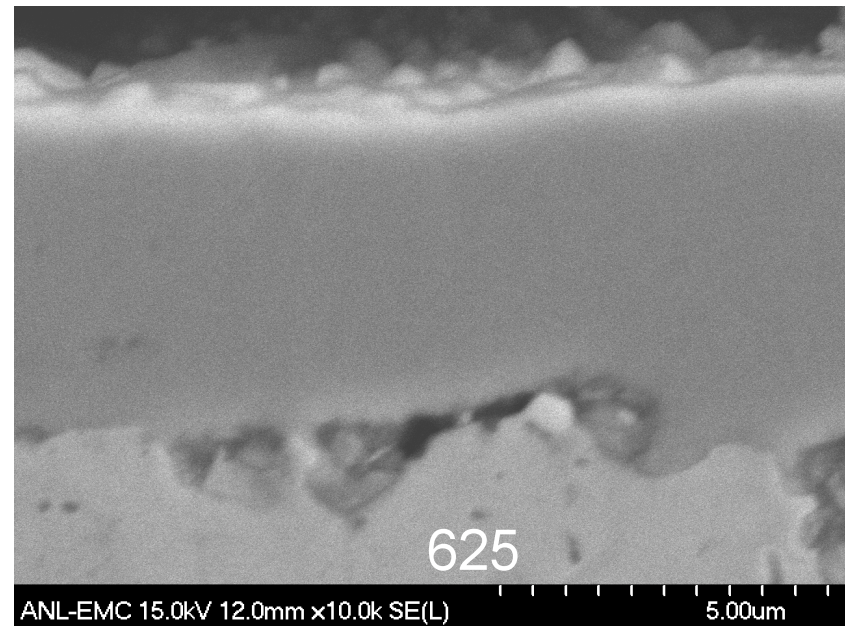
Effect of variation in p_{O_2} on scale morphology



Effect of Fe content in alloy on the oxidation scale morphology

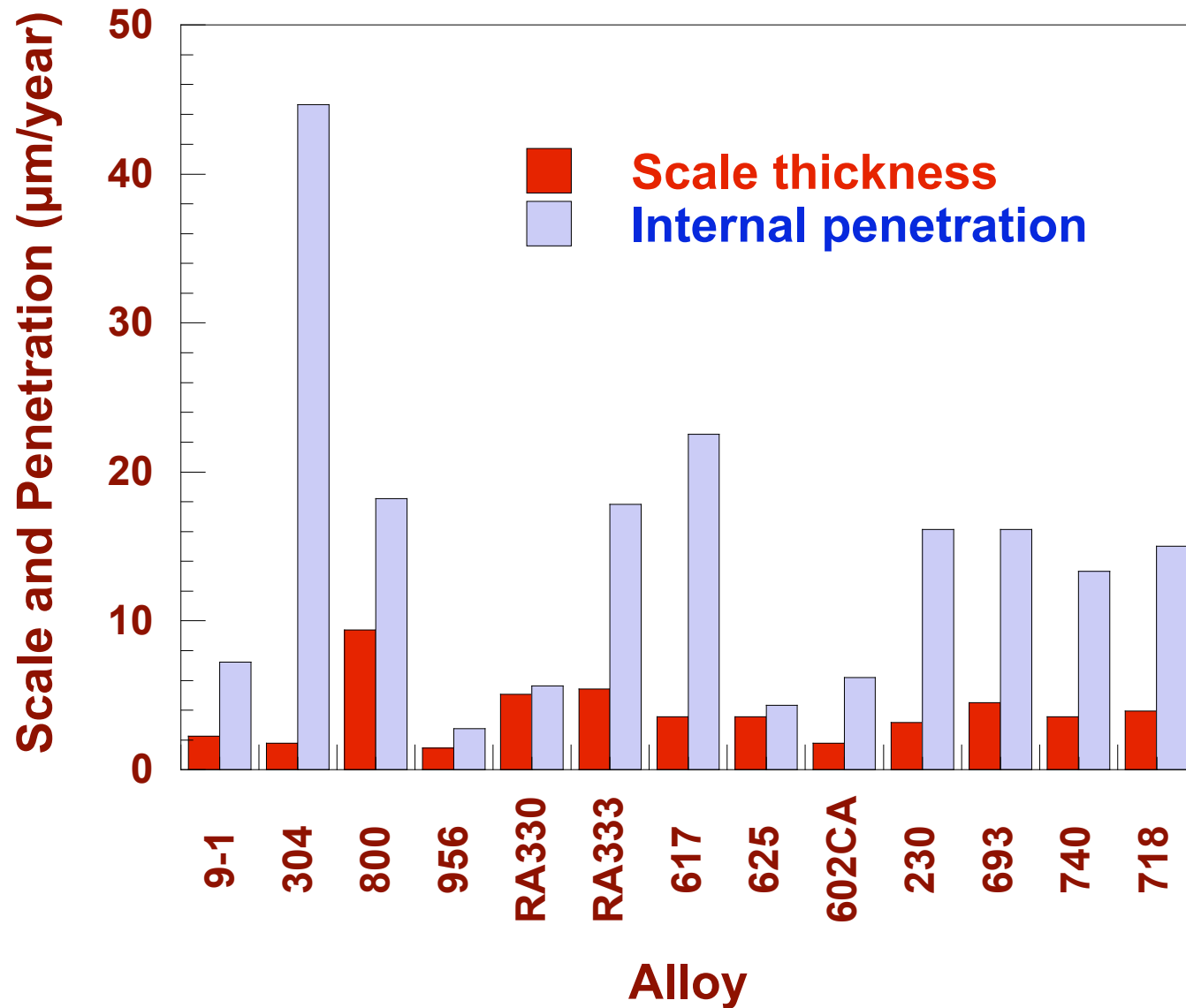


9.3 wt.% Fe

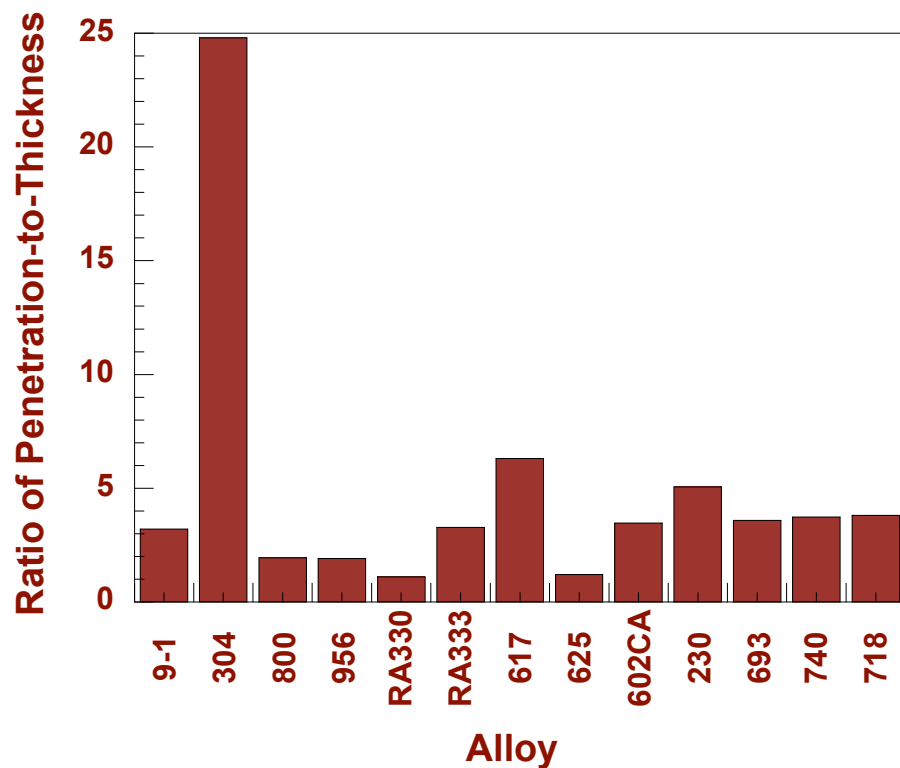


2.5 wt.% Fe

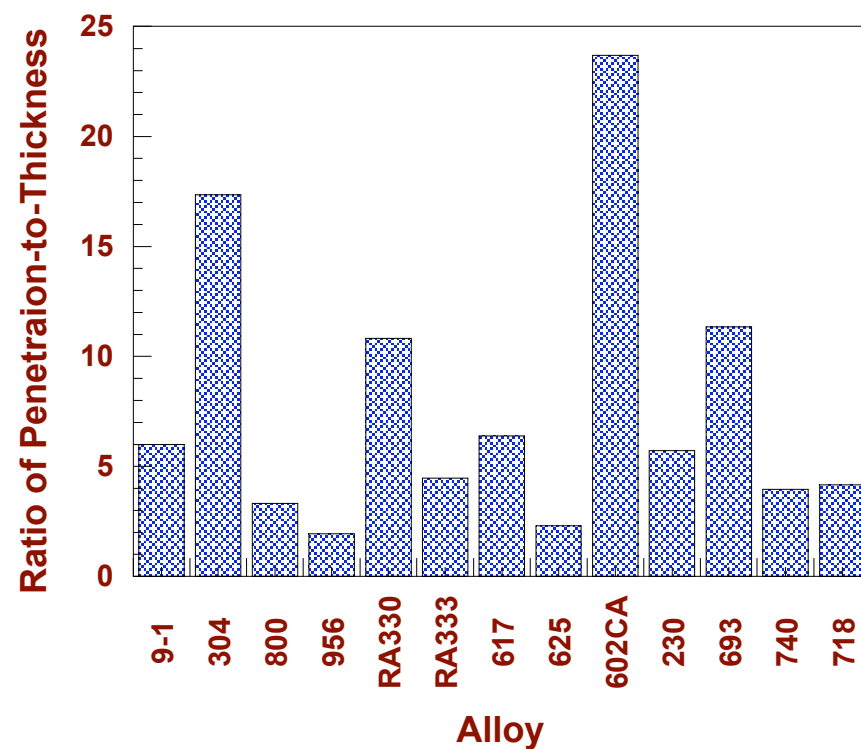
Scaling and Alloy Penetration Rates at 750°C in 50%CO₂-50%Steam



Ratio of Alloy Penetration to Scale Thickness at 750°C

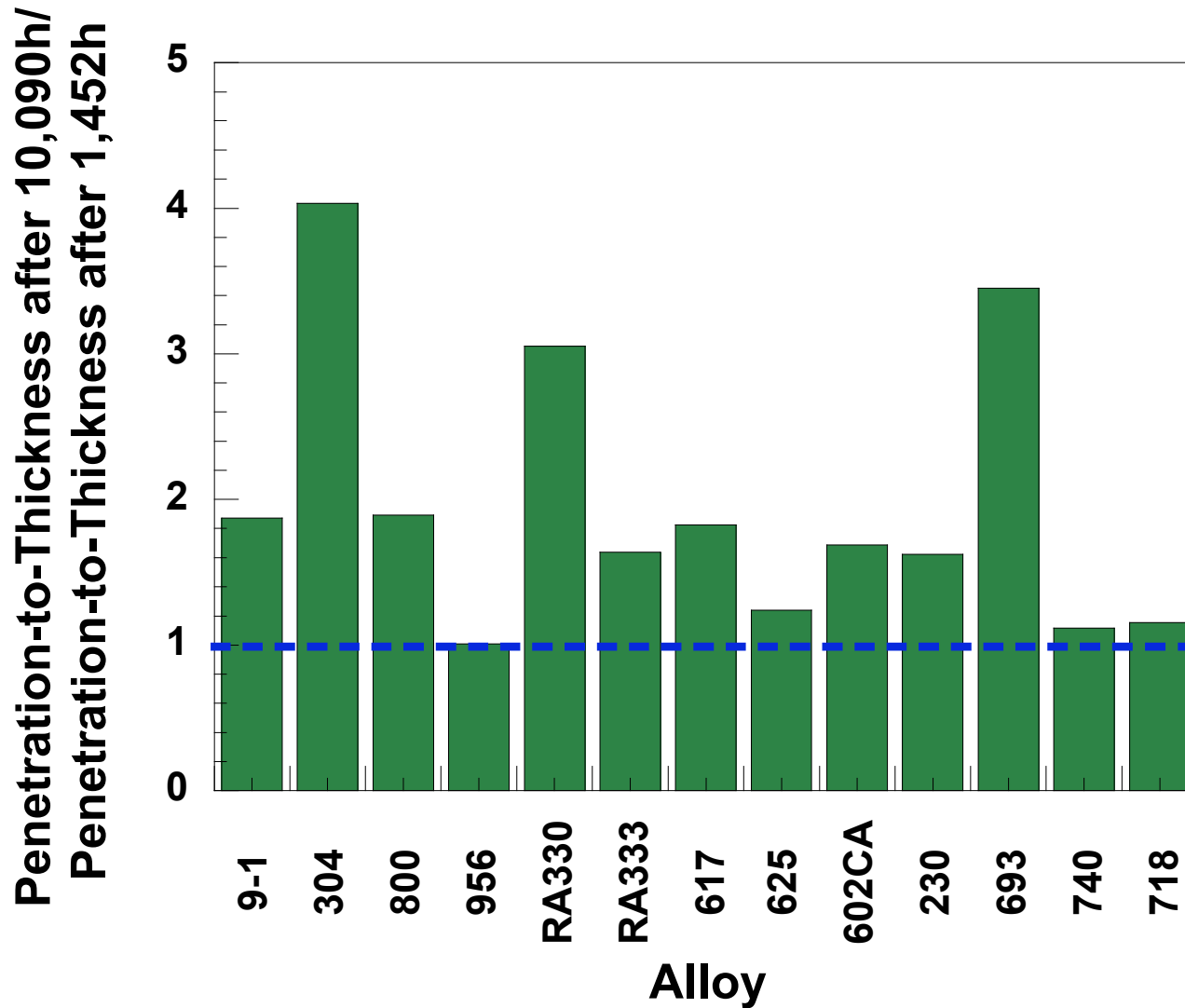


50%CO₂-50%Steam



Pure CO₂

Effect of Exposure time on the Ratio of Alloy Penetration to scale Thickness in Pure CO₂ at 750°C



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 believe the corrosion rates in these environments are acceptable for service. However, the effect on mechanical properties is not established.**
- **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**
- **At present, we are conducting tests in oxy-fuel environments with coal ash, alkali sulfates, and alkali chlorides. The integrity of the scales in resisting S, Cl, and coal ash attack will dictate the use of these alloys.**