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Performance of Structural Alloys in Simulated Oxy-Fuel Environments

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Outline

- ***Background***
- ***Objectives***
- ***Materials and experimental procedure***
- ***Alloys for evaluation***
- ***Role of gas and ash environments***
- ***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***

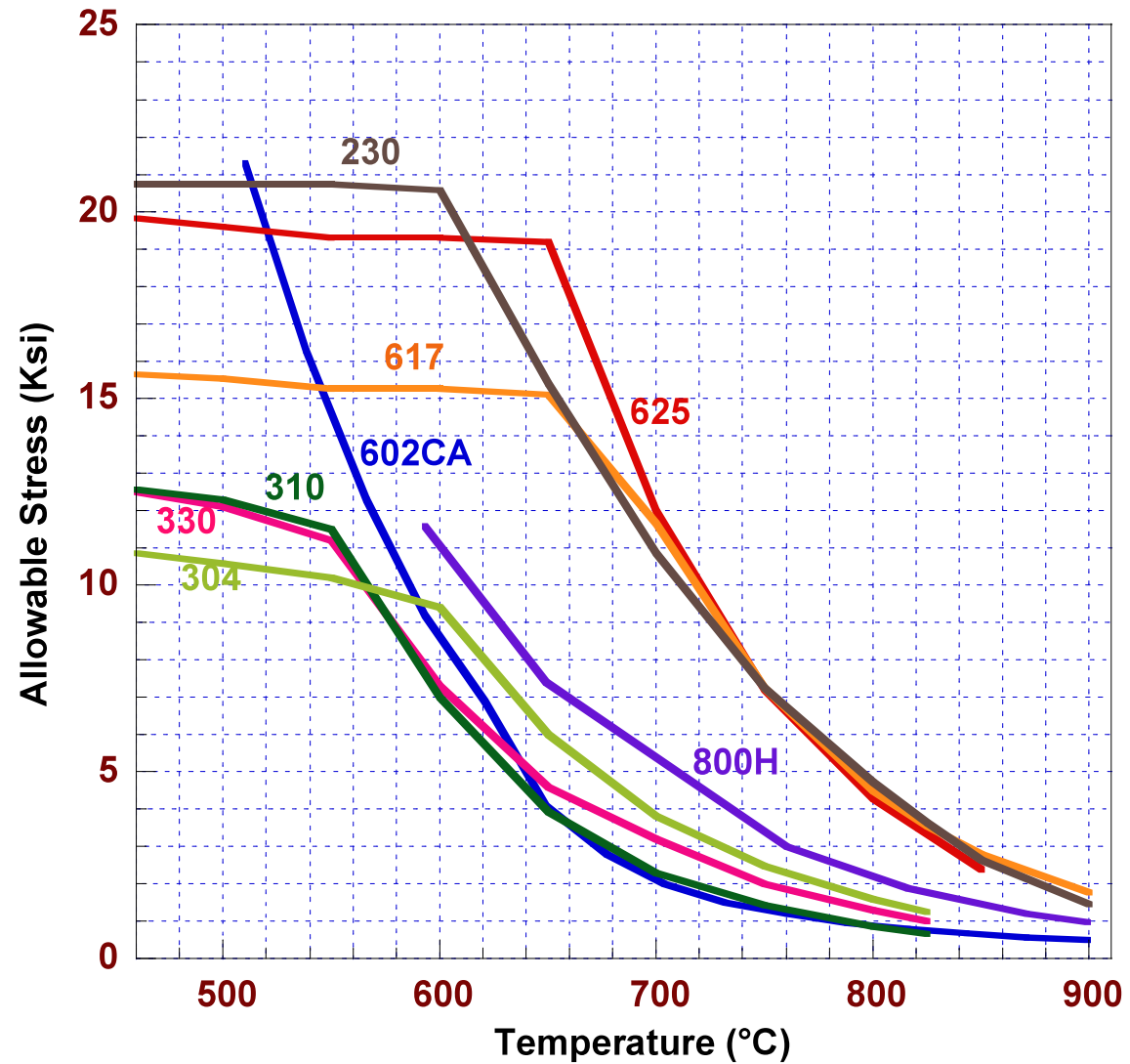
ANL Program Objectives

- **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**

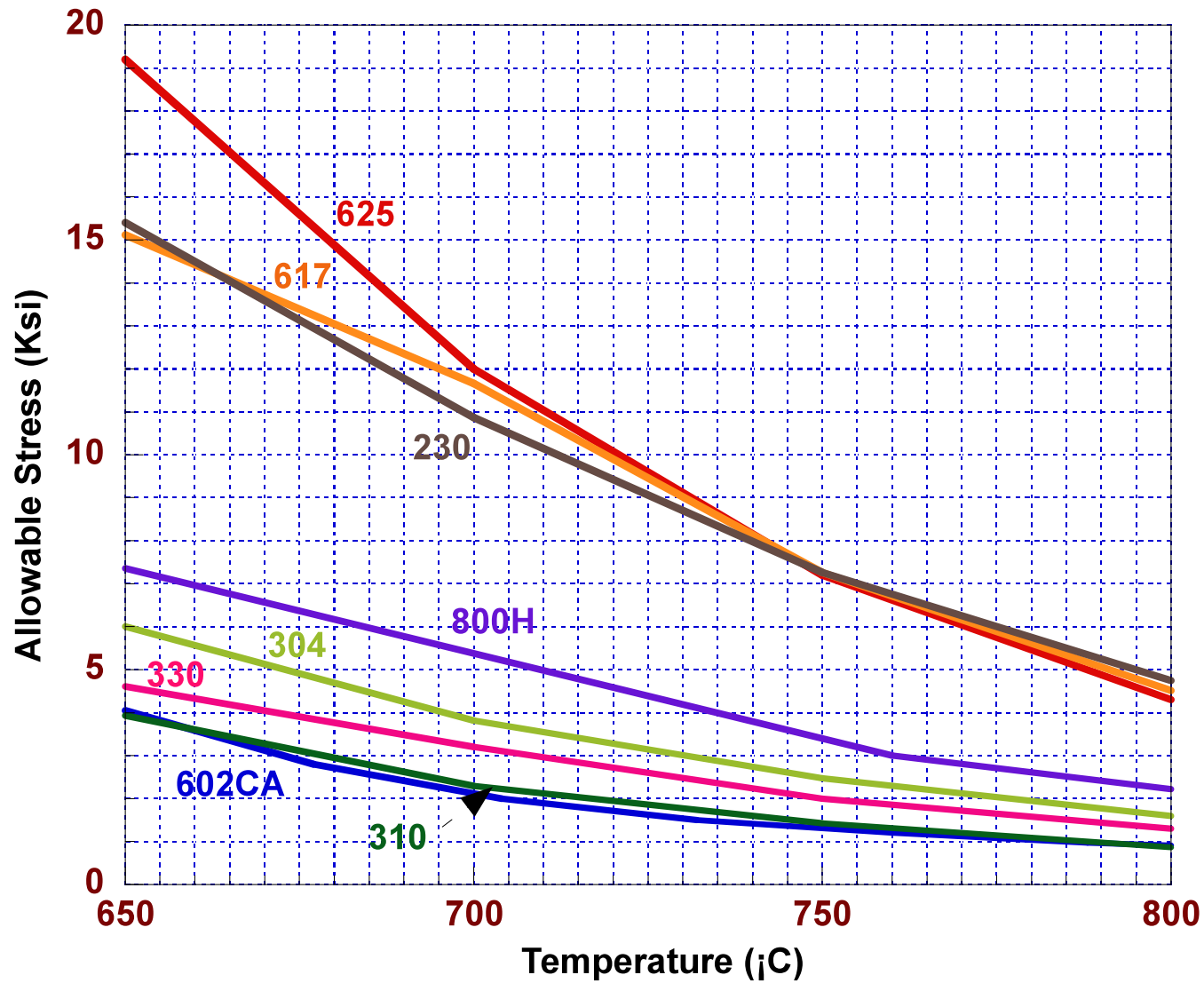
Current List of Alloys in the Study

Material	C	Cr	Ni	Mn	Si	Mo	Fe	Other
153MA	0.05	18.4	9.5	0.6	1.4	0.2	Bal	N 0.05, Nb 0.07, V 0.2
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
WASP	0.07	20.0	Bal	0.1	0.1	5	-	Al 1.4, Ti 3, Co 13.5
ANL-5	0.2	25.0	Bal	-	-	-	-	Al 3.3, Ti 0.3, Zr 0.2, Y 0.1

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: CO₂, CO₂-50% steam, oxy-fuel gas with and without steam

Deposits: Coal ash, alkali sulfates, alkali chloride

Ash mixture: 90% (SiO₂:Al₂O₃:Fe₂O₃ = 1:1:1) and 10% (Na₂SO₄:K₂SO₄ = 1:1)

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**

Gas Chemistry Used in Experiments

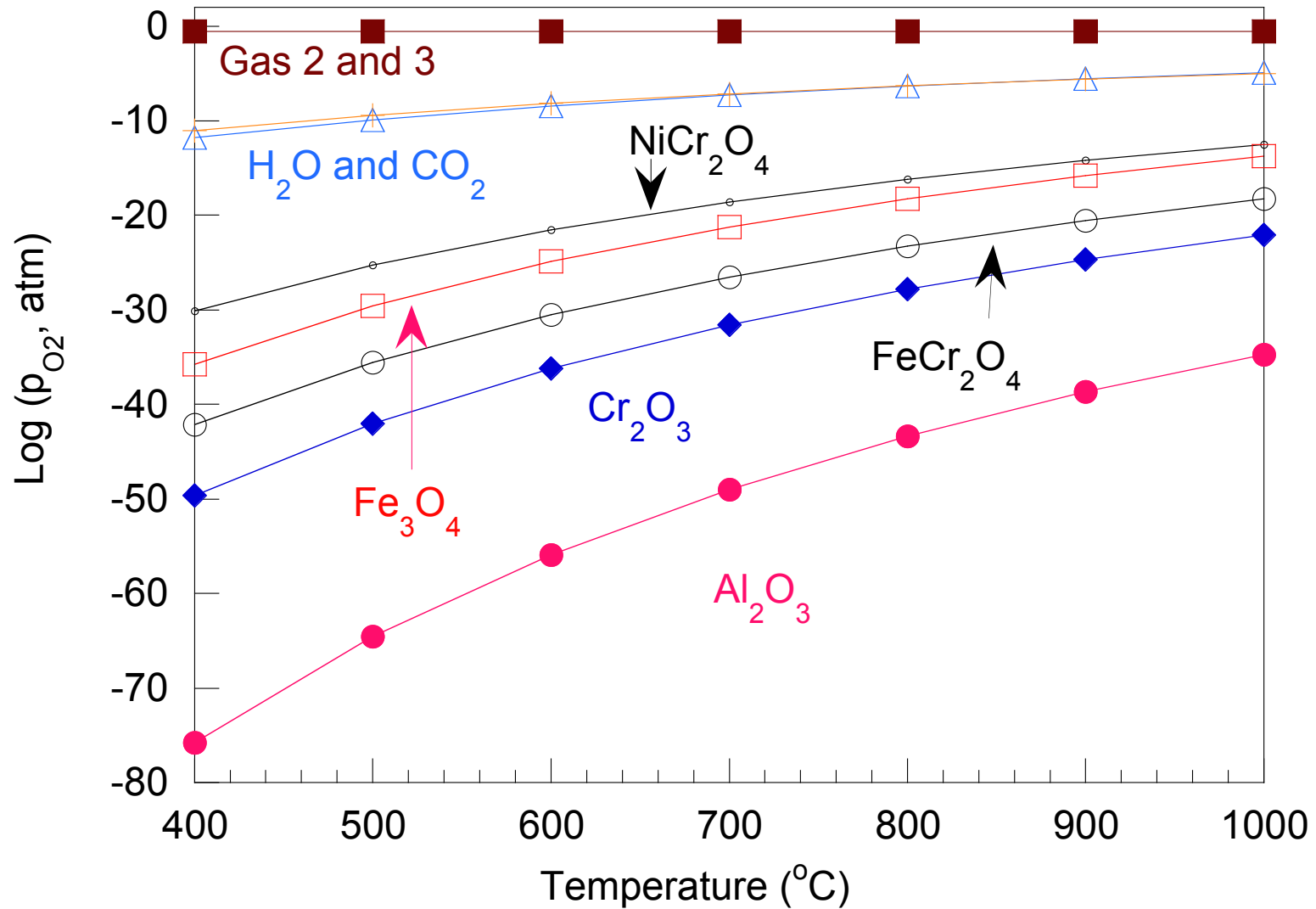
Pure CO₂

CO₂ - 50% Steam

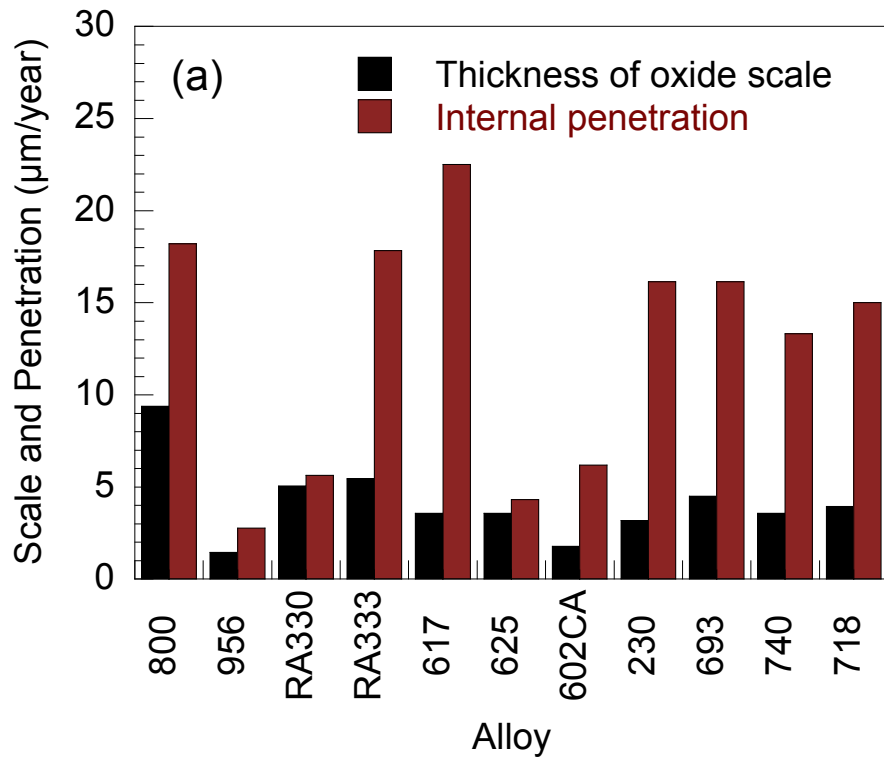
Oxy-Fuel gas mixture: 46.8% CO₂ -25.4% H₂O – 26.8% O₂ – 0.99% SO₂

Gas mixture without steam: 72.2% CO₂ – 26.8% O₂ – 0.99% SO₂

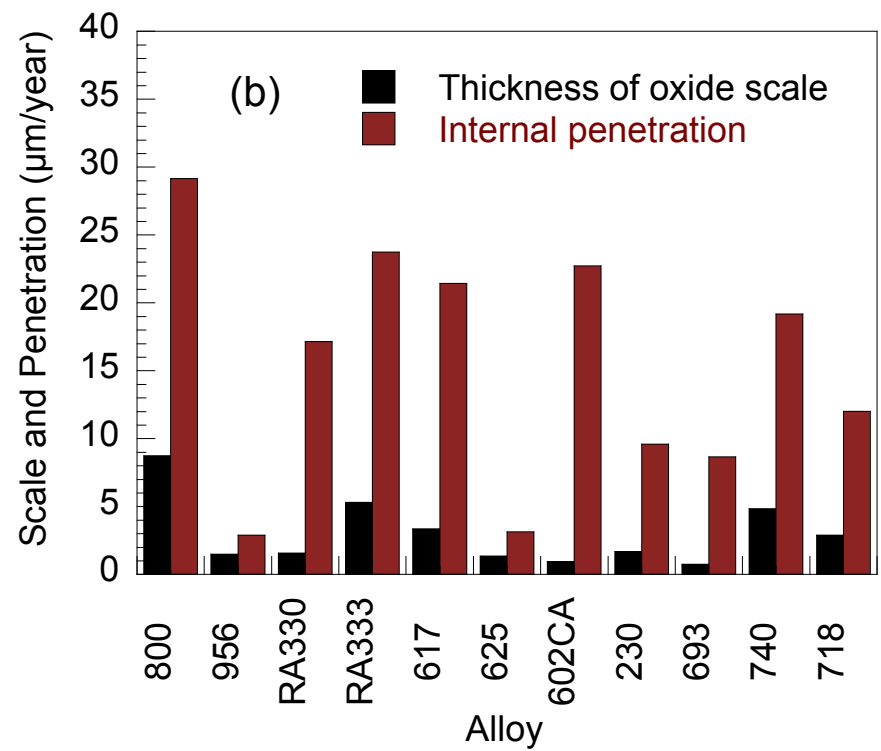
Thermodynamic Stability of Oxide Phases in the Scale



Scaling and Alloy Penetration Rates at 750°C

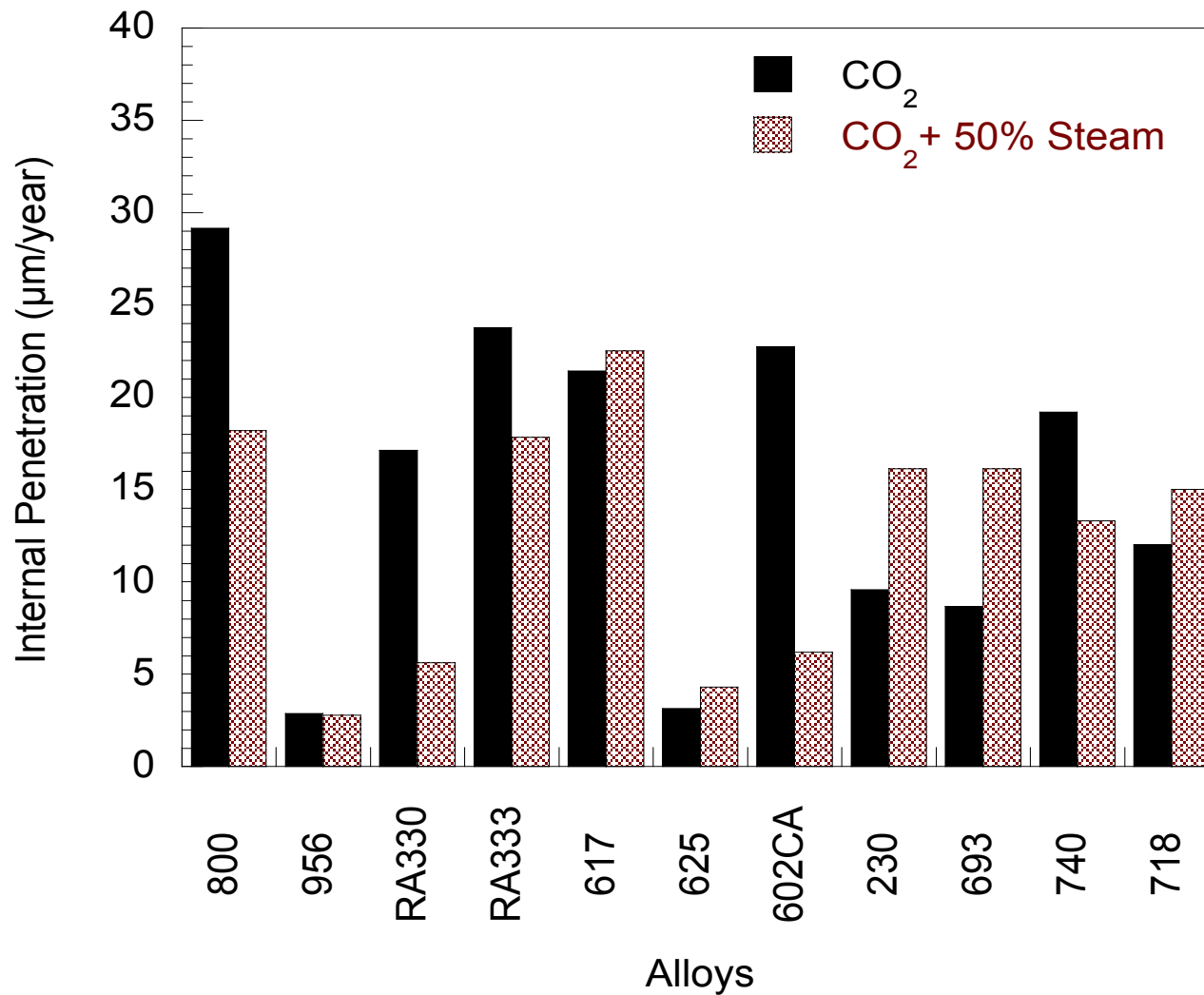


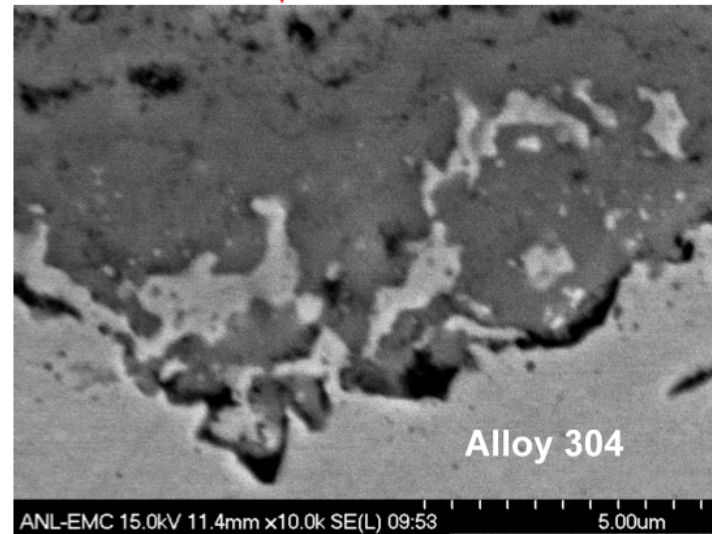
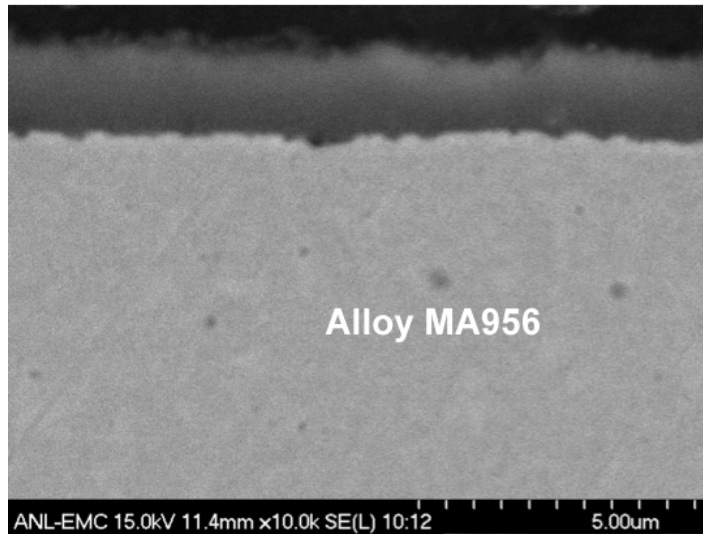
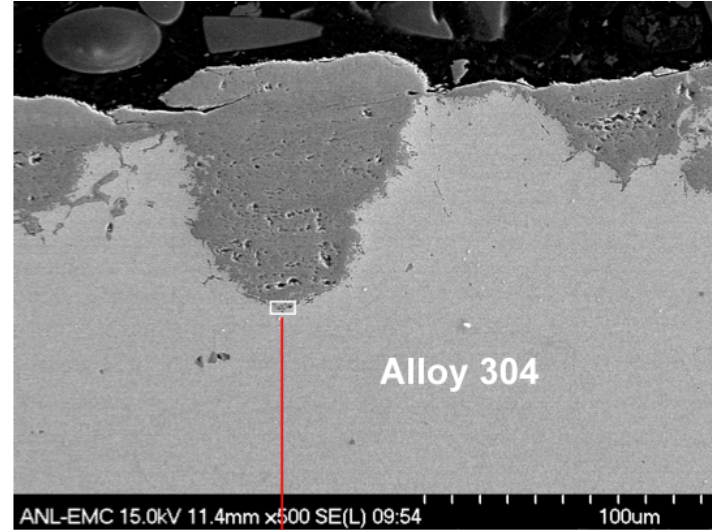
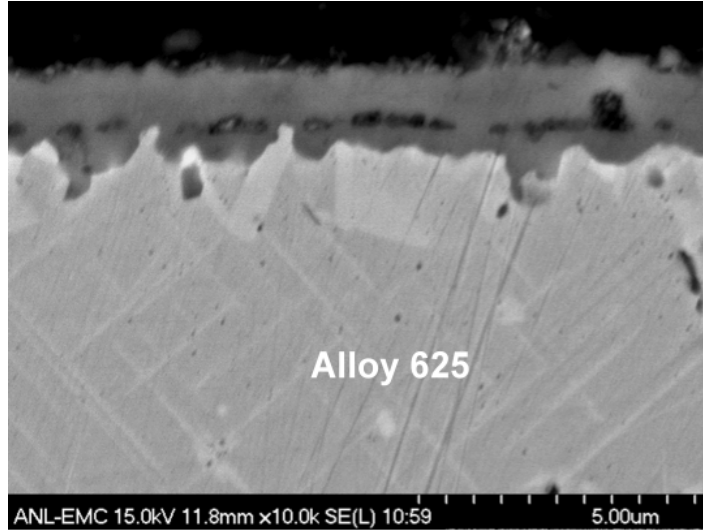
CO₂-50% steam



100% CO₂

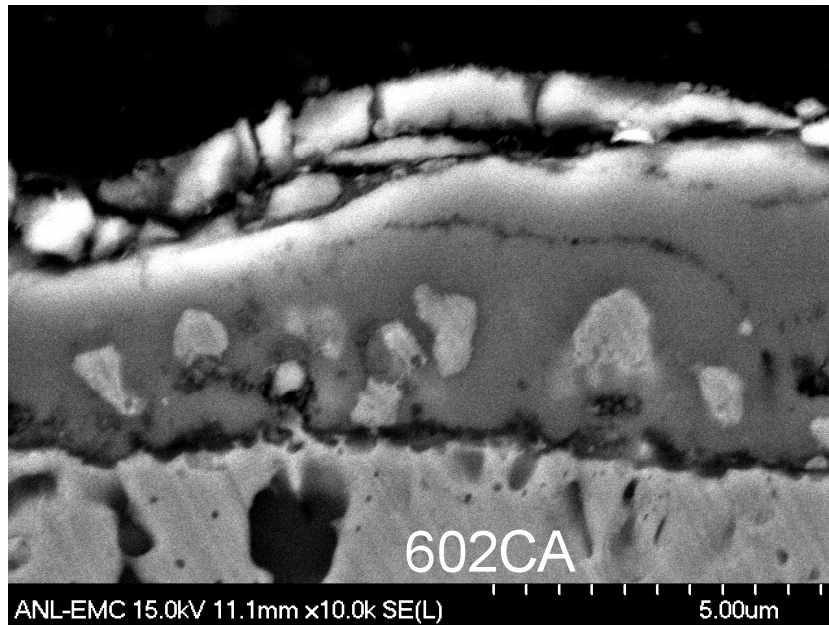
Alloy Penetration Rates in CO₂ and in CO₂-50% Steam at 750°C



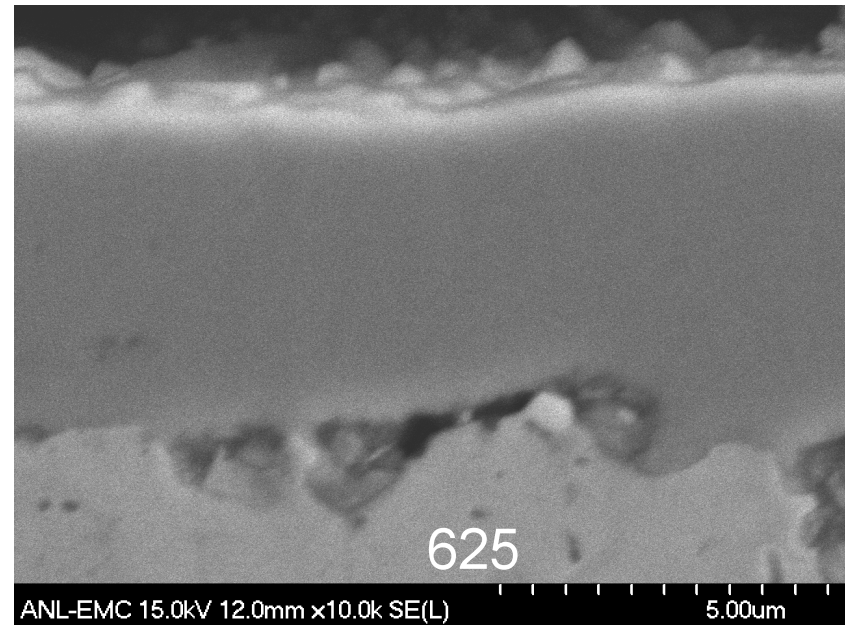


Pure CO₂ at 750°C for 10,090 h

Effect of Fe content in alloy on the oxidation scale morphology

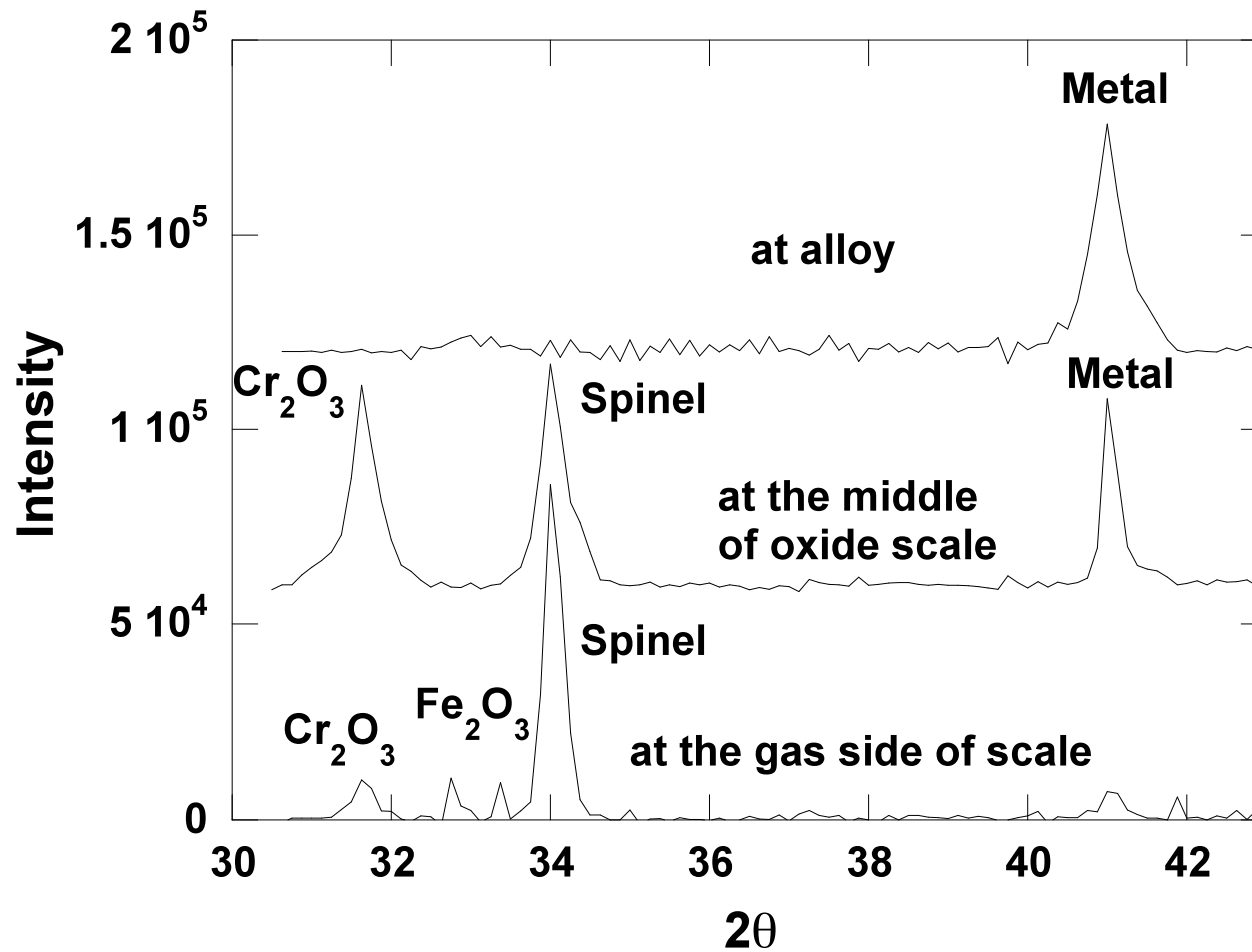


9.3 wt.% Fe

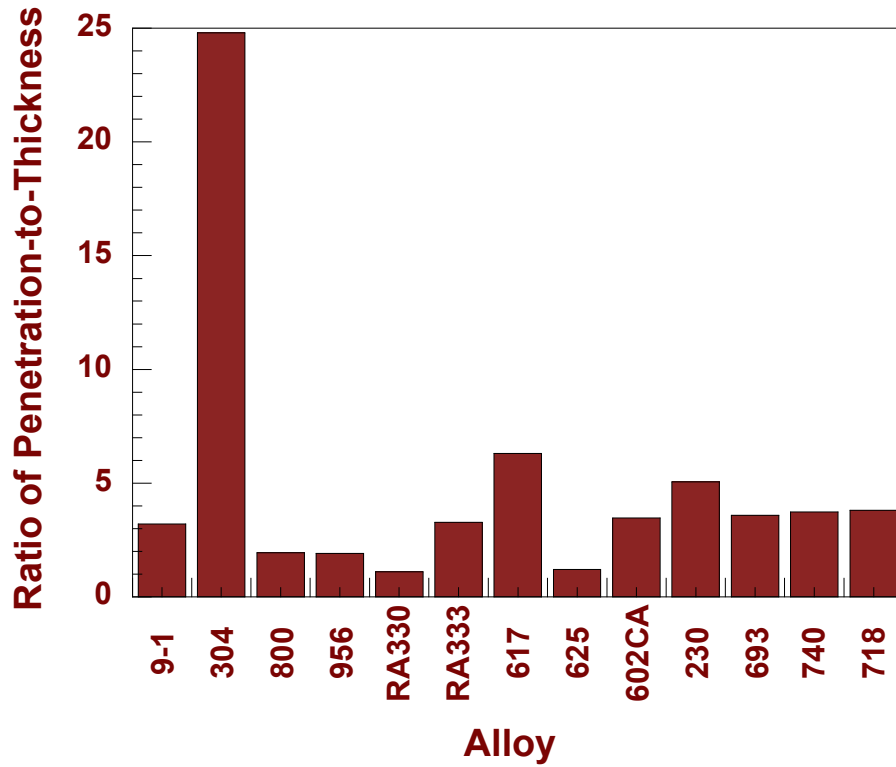


2.5 wt.% Fe

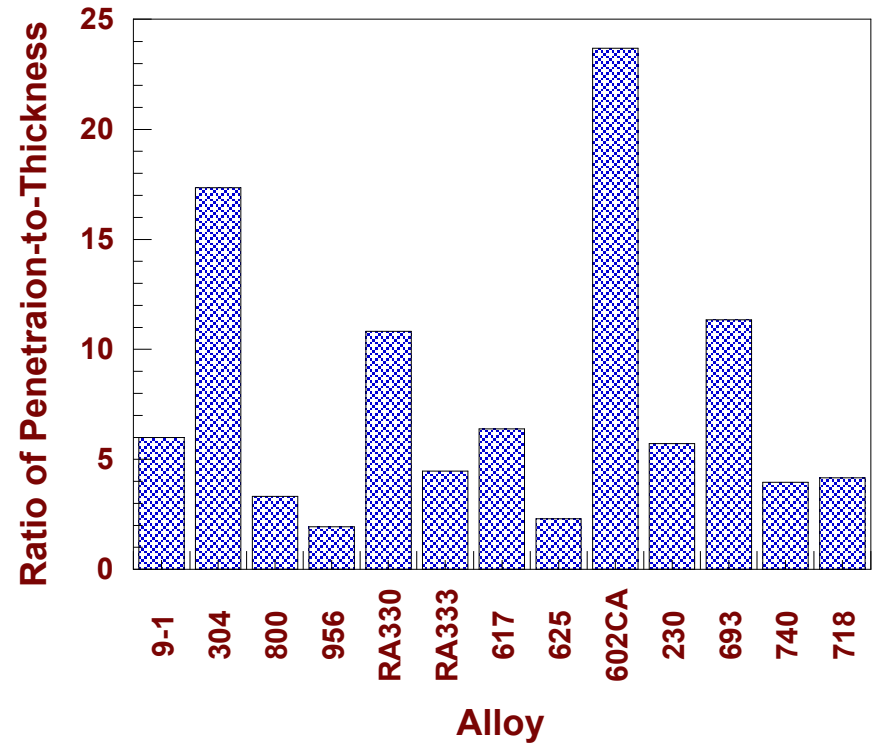
XRD at different locations of scale on the surface of Alloy 617 after 2,760-h exposure in 50%CO₂-50%Steam at 750°C



Ratio of Alloy Penetration to Scale Thickness at 750°C

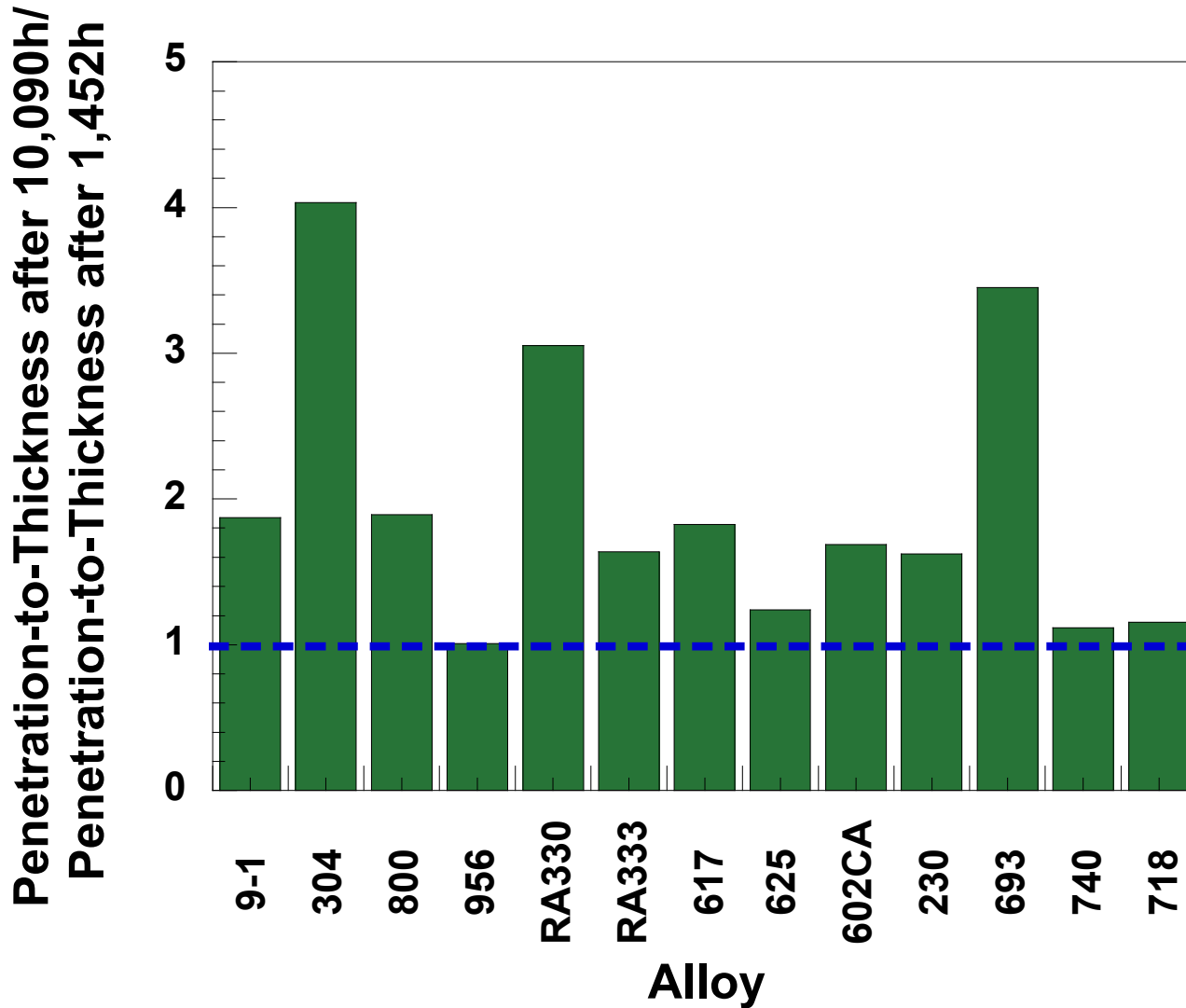


50%CO₂-50%Steam

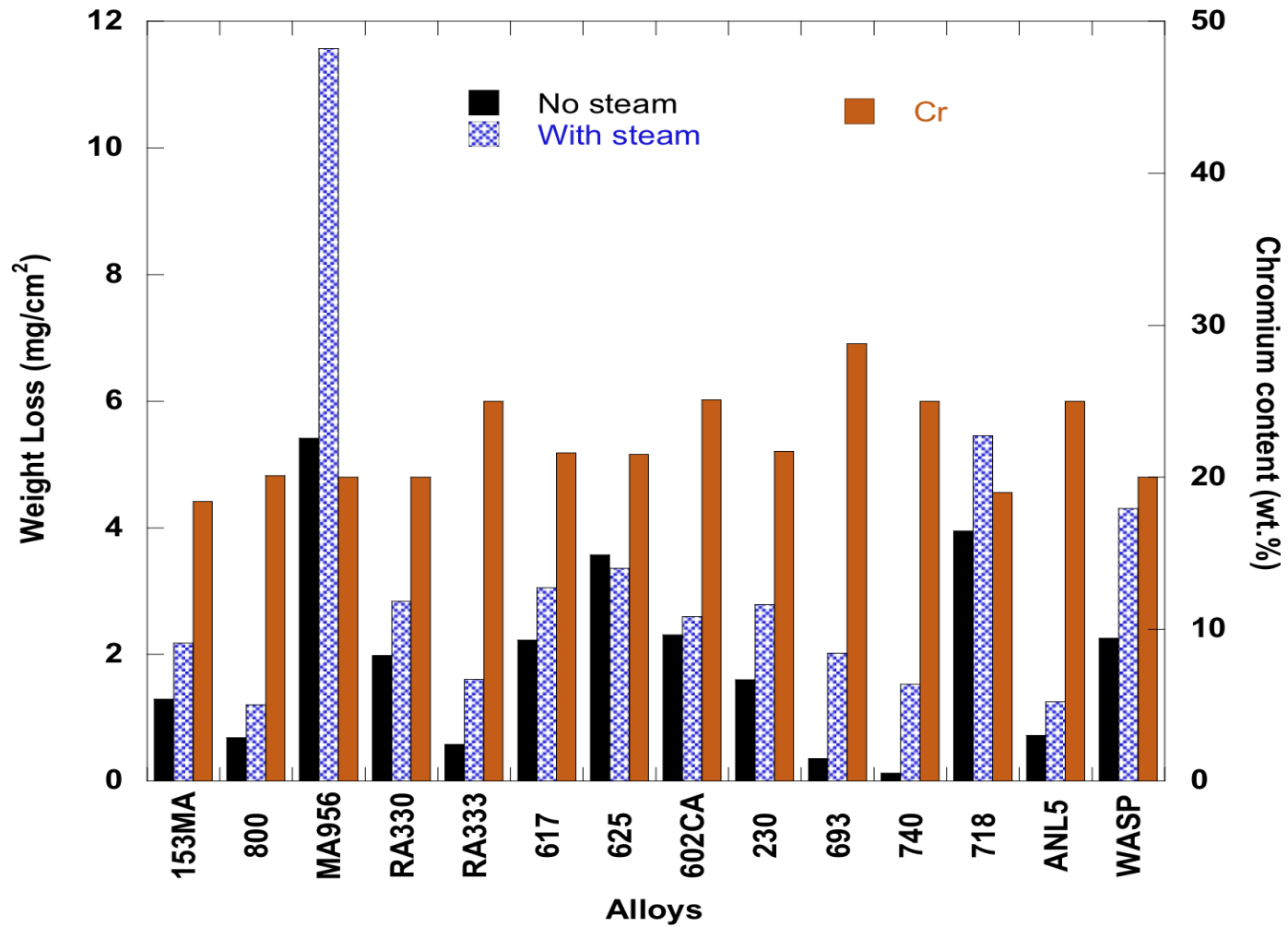


Pure CO₂

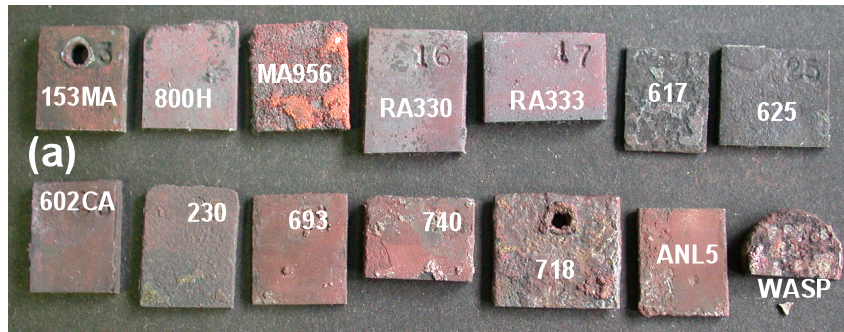
Effect of Exposure time on the Ratio of Alloy Penetration to scale Thickness in Pure CO₂ at 750°C



Effect of chromium content on the corrosion rates in CO₂



Photograph of Specimens Exposed to Ash

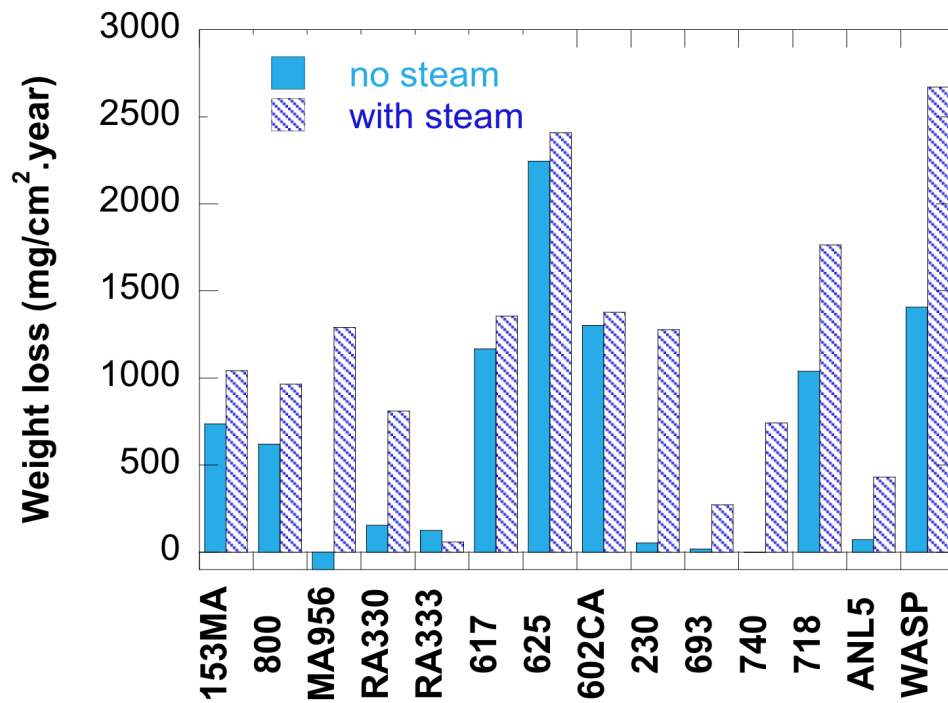


600 h at 750°C in ash
and Gas with steam

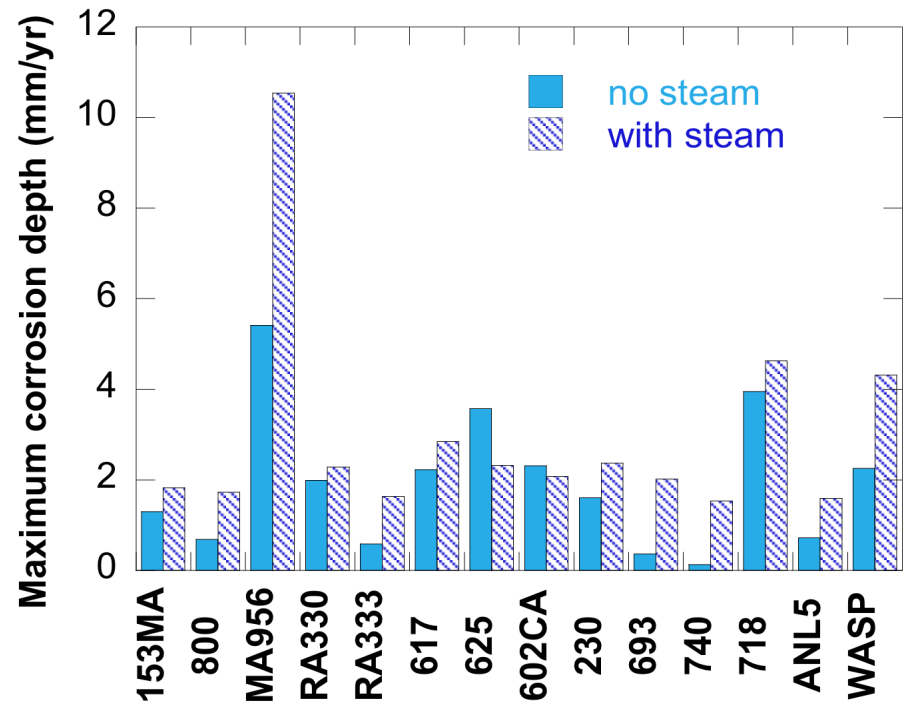


600 h at 750°C in ash
and Gas without steam

Weight loss and corrosion depth after exposure at 750°C in oxy-fuel environment containing ash

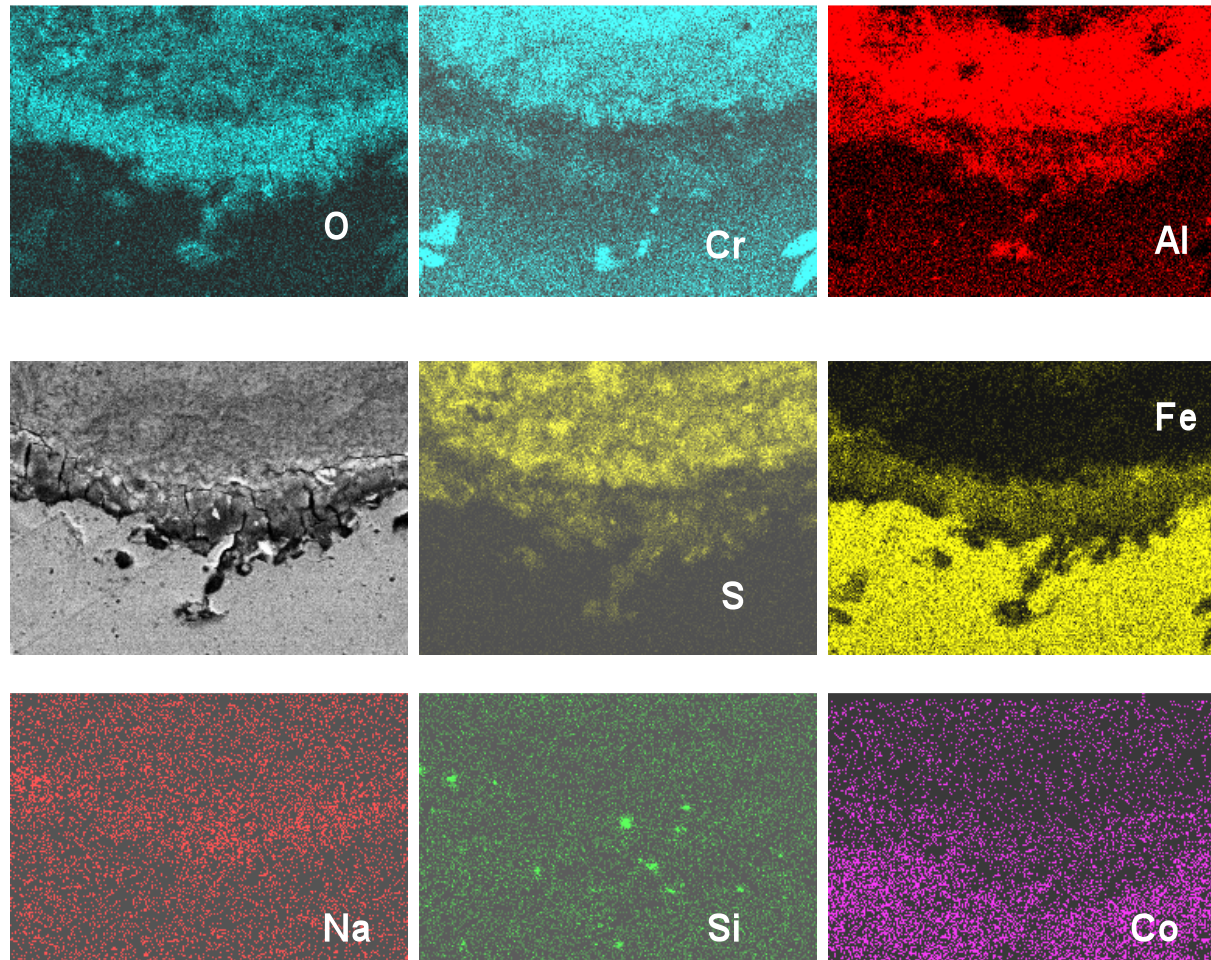


Weight loss



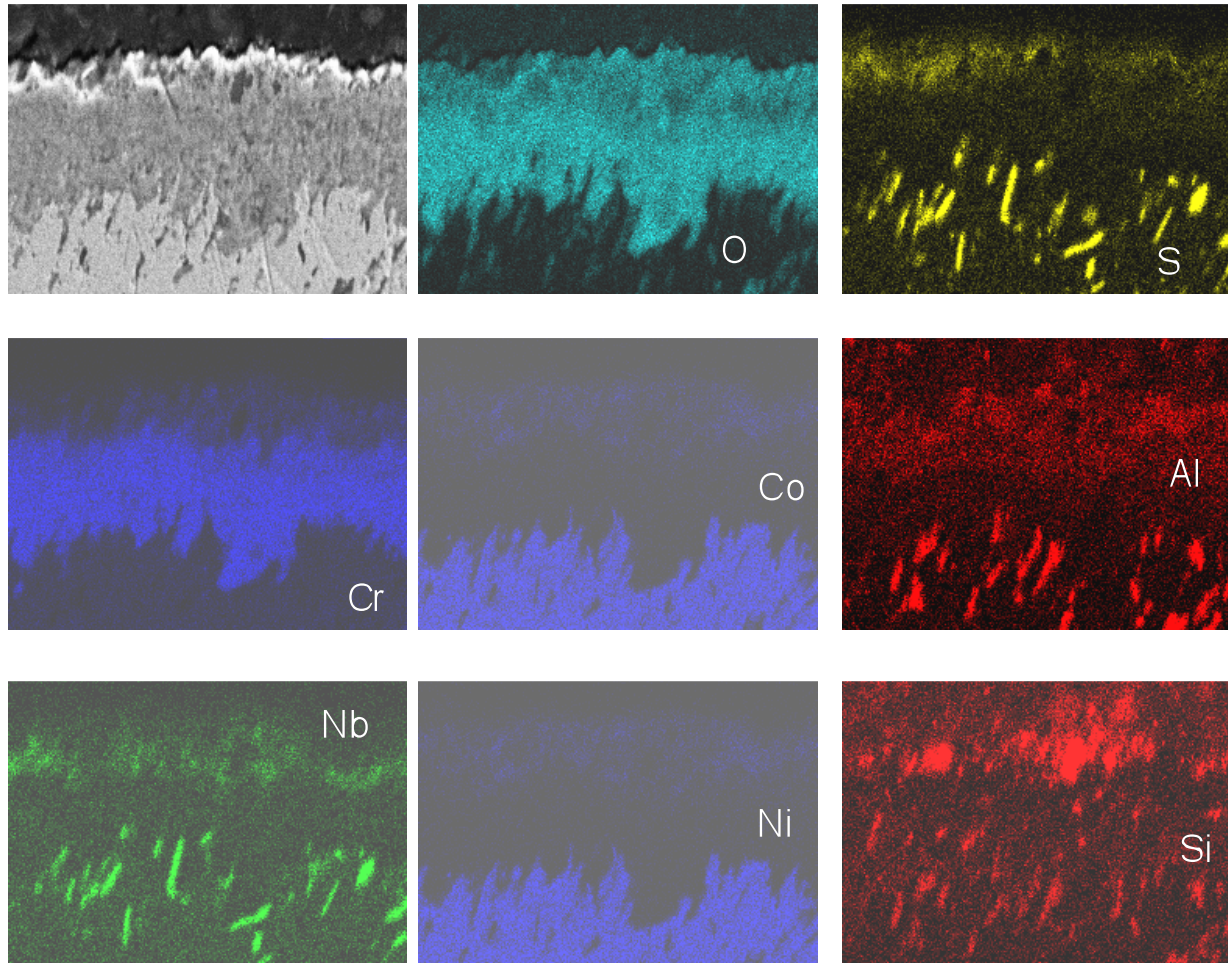
Corrosion depth

EDX Analysis of MA956 Exposed to Ash



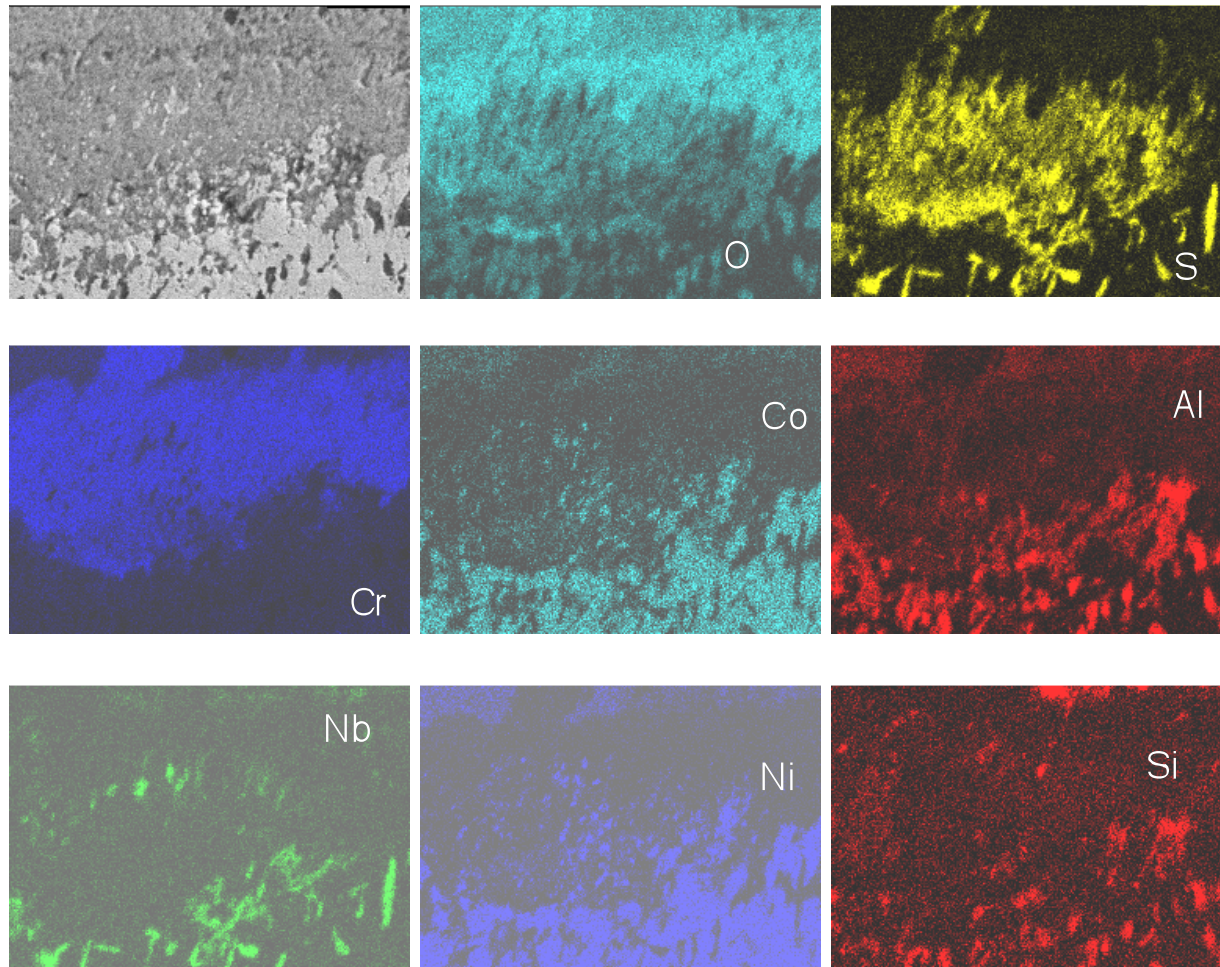
MA956 after 1200-h exposure to ash and Gas without steam at 750°C

EDX Analysis of Alloy 740 Exposed to Ash



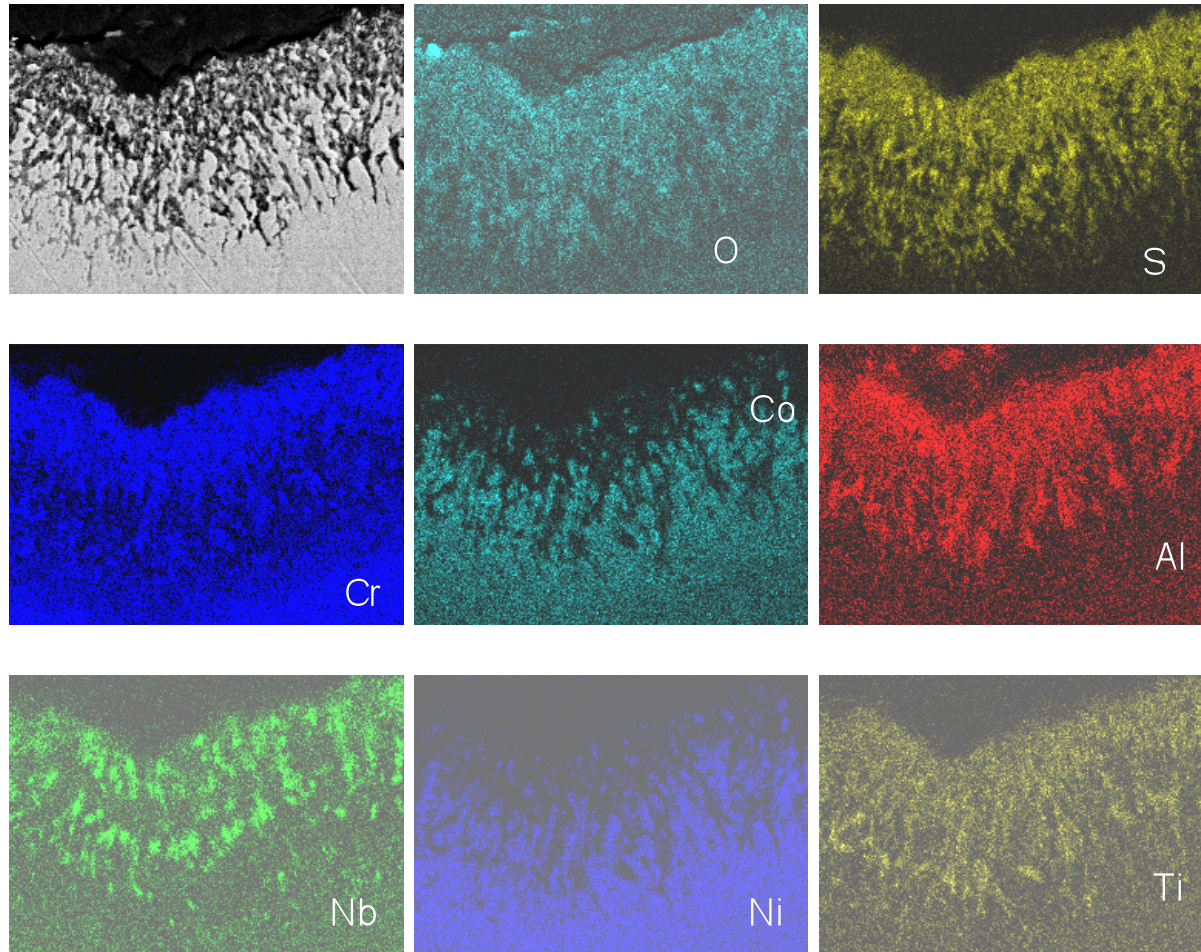
Alloy 740 **non-pit area**, after 1200-h exposure to ash
and Gas without steam at 750°C

EDX Analysis of Alloy 740 Exposed to Ash



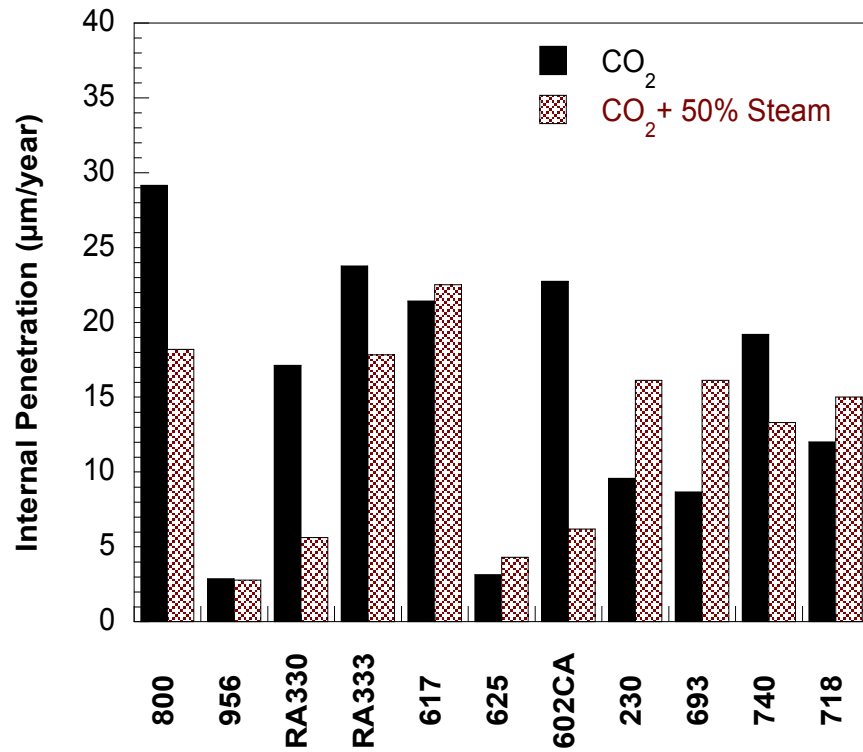
Alloy 740 **pit area**, after 1200-h exposure to ash and Gas without steam at 750°C

EDX Analysis of Alloy 740 Exposed to Ash

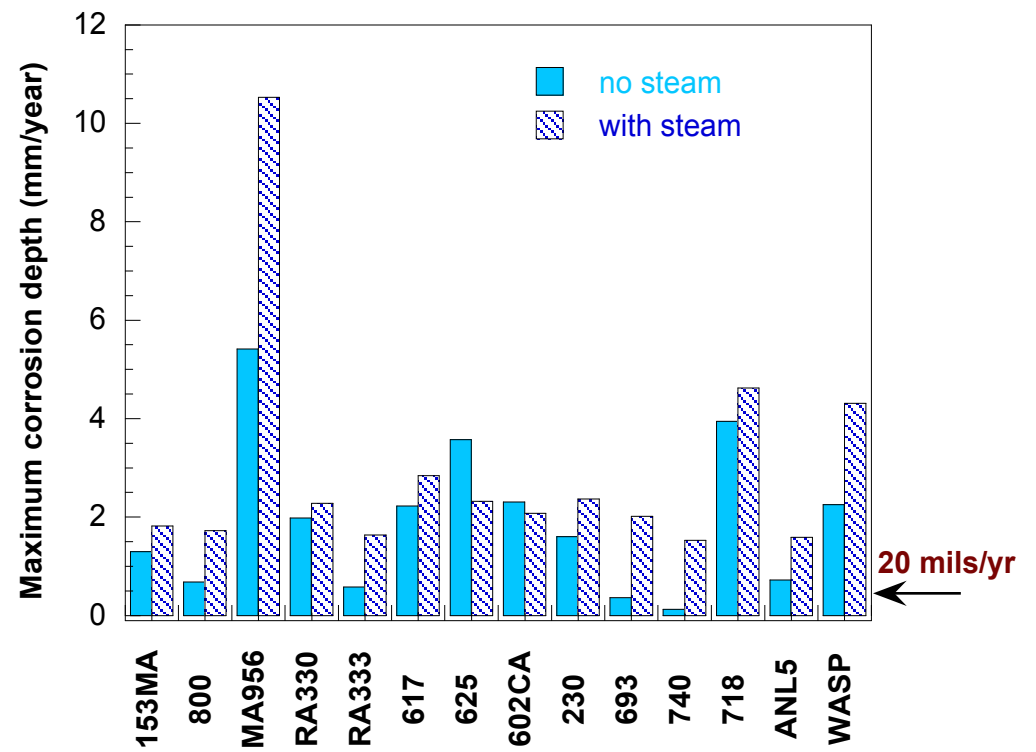


Alloy 740, after 1200-h exposure to ash and Gas with steam at 750°C

Alloy Penetration Rates With and Without Ash at 750°C



Without ash



With ash

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 (in the absence of sulfur) 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 may occur.**
- **The presence of ash (with alkali sulfates) coupled with steam in the gas environment accelerates corrosion of all structural alloys.**
- **Ash-test results show that in the absence of steam, Alloys 800H, 333, 693, 740, and ANL5 exhibit acceptable performance.**
- **In the presence of steam, all the alloys exhibit corrosion rates ≥ 2 mm/year, based on linear kinetics.**

Project Accomplishments

- **Establish materials performance window for alloys for service in oxy-fuel systems using eastern and western coals**
- **We have completed the study in ash simulating eastern coal ash and a report will be issued in September 2010. Experiments will continue, to assess the role of western coal ash and alkali chlorides.**
- **Continue corrosion evaluation of advanced Fe- and Ni-base alloys in the presence of alkali sulfate/alkali chloride in simulated fireside combustion environments.**
- **We have completed the testing and analysis and a summary report on the results will be issued later this calendar year. Additional testing is in progress.**
- **Continue corrosion evaluation of turbine materials in CO₂ plus steam environments.**
- **This effort will be initiated late 2010 and continued beyond 2010.**

Future Plans for the ANL Research Project

- **Complete corrosion evaluation of structural alloys in oxy-fuel environments containing ash, alkali sulfates, and alkali chlorides. This includes a range of coal ash chemistry and gas environments at temperatures up to 750°C.**
- **Experimentation to mitigate corrosion of structural alloys in both advanced steam-cycle and oxy-fuel combustion systems**
 - **Conventional coatings**
 - **Ash additives**
 - **Alloy surface modification using nano-structures**