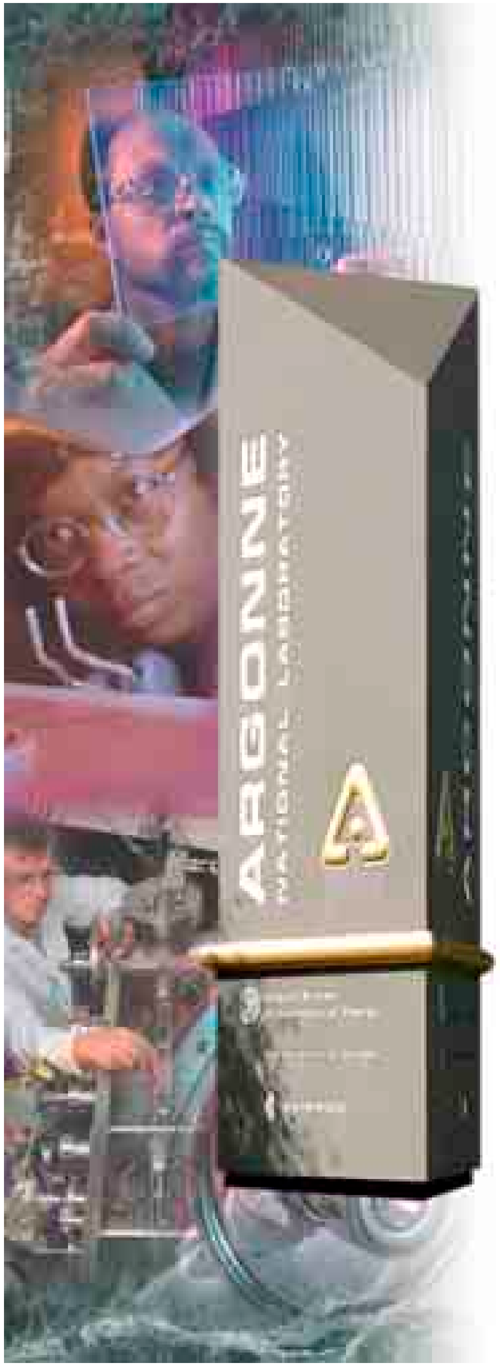

Development of Materials Resistant to Metal Dusting Degradation

K. Natesan, Z. Zeng, and D. L. Rink

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Argonne National Laboratory

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Development of Materials Resistant to Metal Dusting Degradation (CPS# 16944)

Goal: Develop metallic alloys and surface engineering of commercial alloys to mitigate metal dusting degradation and also develop a database of metal dusting degradation for chemical and petrochemical industries.

Challenge: Commercial alloys are all susceptible to metal dusting. Data are insufficient in process environments at high pressures and temperatures. New materials and mitigating approaches are needed to minimimize/eliminate metal dusting degradation.

Benefits: Recover high quality heat in the temperature range of 400-800°C. Increase productivity and reduce operating cost.

Potential End-User Applications: Hydrogen, ammonia, methanol and syngas; petroleum refineries; heat-treat industry; direct iron-ore reduction plants.

FY06 Activities: Evaluate/develop alloys in simulated process environments; Develop surface engineering and process fixes to mitigate metal dusting degradation.

Barrier-Pathway Approach

Barriers

- Insufficient metal dusting data at high pressure.
- Spinel is susceptible to attack by carbon
- How to stop the growth of metal dusting pits?

Pathways

- Built high pressure test equipment for evaluation of materials in simulated environment.
- Developed new alloys to form chromium oxide scale
- Process fixes to mitigate continued degradation

Critical Metrics

Develop alloys and surface engineering that can perform in metal dusting environments in the temperature range of 400 to 900°C

Benefits (est.)	2020
Energy Savings	**173 trillion Btu**
Cost Savings	**$220-290 million**
Carbon Reduction	**2.6 MMTCe**

Chemical Industry Participants

- Materials Technology Institute of the Chemical Process Industries
- Air Products and Chemicals Inc.
- ConocoPhilips
- Haldor Topsoe
- DuPont Chemical Company
- Haynes International
- Special Metals
- Krupp VDM
- Sandvik Steel
- Spectrum Metals (Rolled Alloys)

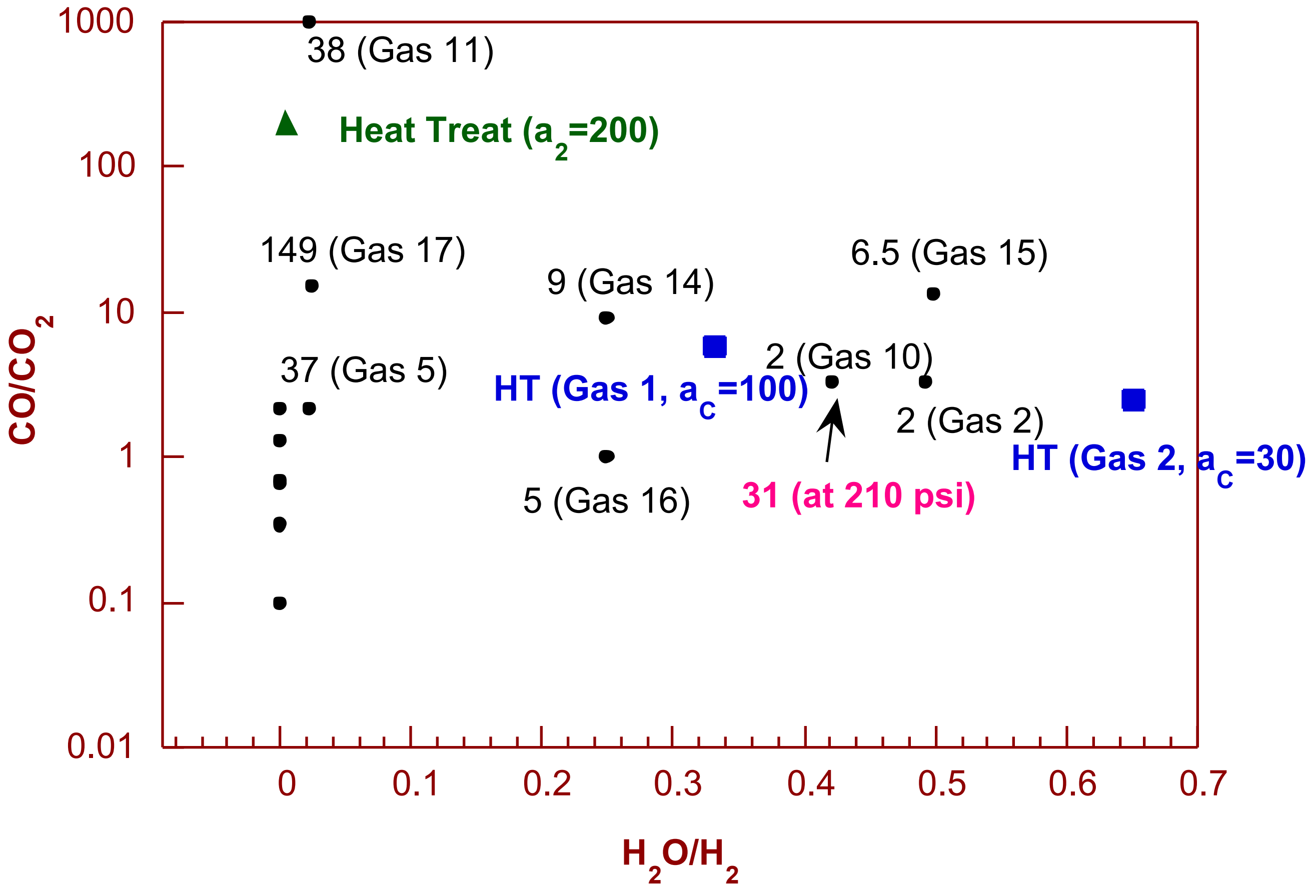
Outline of Presentation

- **Key tasks in the project**
- **Materials and Experimental Procedure**
- **Performance of Ni-base Alloys at high pressure**
- **Details on degradation of alloys**
  - **pit size, pit depth, pit distribution**
  - **pit growth rate**
  - **correlation between pitting and weight loss**
- **Project Summary**

Key Tasks

- Experimentally determine degradation rates (pit size, pit depth, pit density, growth rate, etc.) for Fe- and Ni-base alloys in simulated metal dusting environments
- Develop surface engineering approaches for structural alloys to minimize coking and to mitigate degradation via metal dusting
- Establish the key parameters (such as T, P, gas chemistry, alloy chemistry etc.) that are responsible for metal dusting initiation and propagation
- Procure weldments of selected Fe- and Ni-base alloys and conduct tests on them in simulated metal dusting environments
- Modify and/or develop alloys with improved resistance to metal dusting degradation at temperatures between 400 and 900°C

Gas Chemistry and Carbon Activity in Experimental Runs



Run 59: Data discussed today; HT (Gas 1): Test in progress; Heat Treat: Test in progress

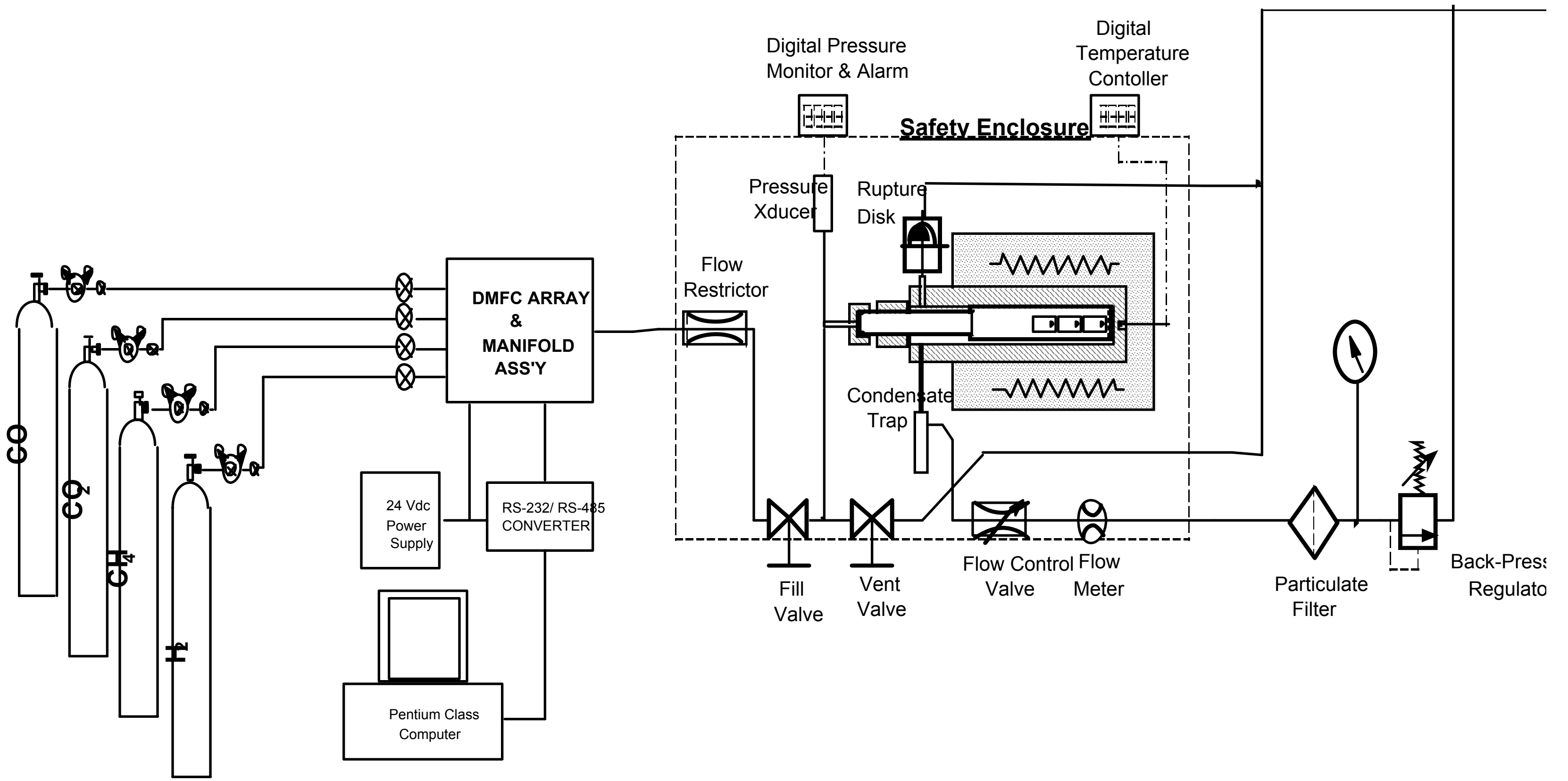
Ni-base alloys selected for tests at high pressure

Alloy	Cr	Ni	Si	Mo	Al	Fe	Other
601	21.9	Bal	0.2	0.1	1.4	14.5	Ti 0.3, Nb 0.1
690	27.2	Bal	0.1	0.1	0.2	10.2	Ti 0.3
617	21.6	53.6	0.1	9.5	1.2	0.9	Co 12.5, Ti 0.3
602CA	25.1	Bal	0.1	-	2.3	9.3	Ti 0.13, Zr 0.19, Y 0.09
214	15.9	Bal	0.1	0.5	3.7	2.5	Zr 0.01, Y 0.006
45TM	27.4	46.4	2.7	-	-	26.7	RE 0.07
HR 160	28.0	Bal	2.8	0.1	0.2	4.0	Co 30.0
693	28.9	Bal	0.04	0.13	3.3	5.9	Ti 0.4, Nb 0.7, Zr 0.03

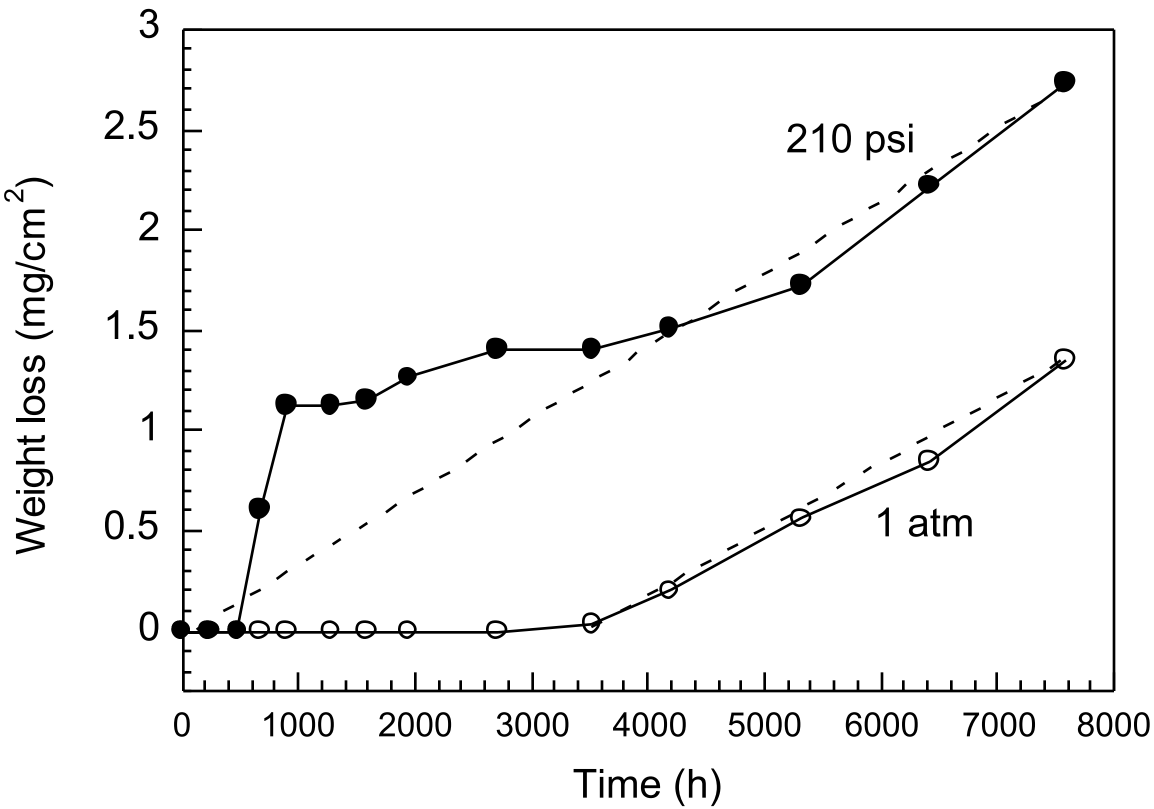
Gas Chemistry Conditions in H_2 reformer and in Run 59

	Composition in mole %	
Gas species	Hydrogen reformer environment	Laboratory-simulated environment (Run 59)
CH_4	1.1	0
CO	18	18.4
	5.6	5.7
	52	53.4
	23	22.5
	-	-
	-	-
		1685 (918)
Maximum pressure, psia (atm)	215 (14.6)	-
Temperature and pressure in ANL experiment	-	1100°F, 210 psia (593°C, 14.3 atm)
Carbon activity at 1100°F, 210 psia	30	31

System for High Pressure Tests

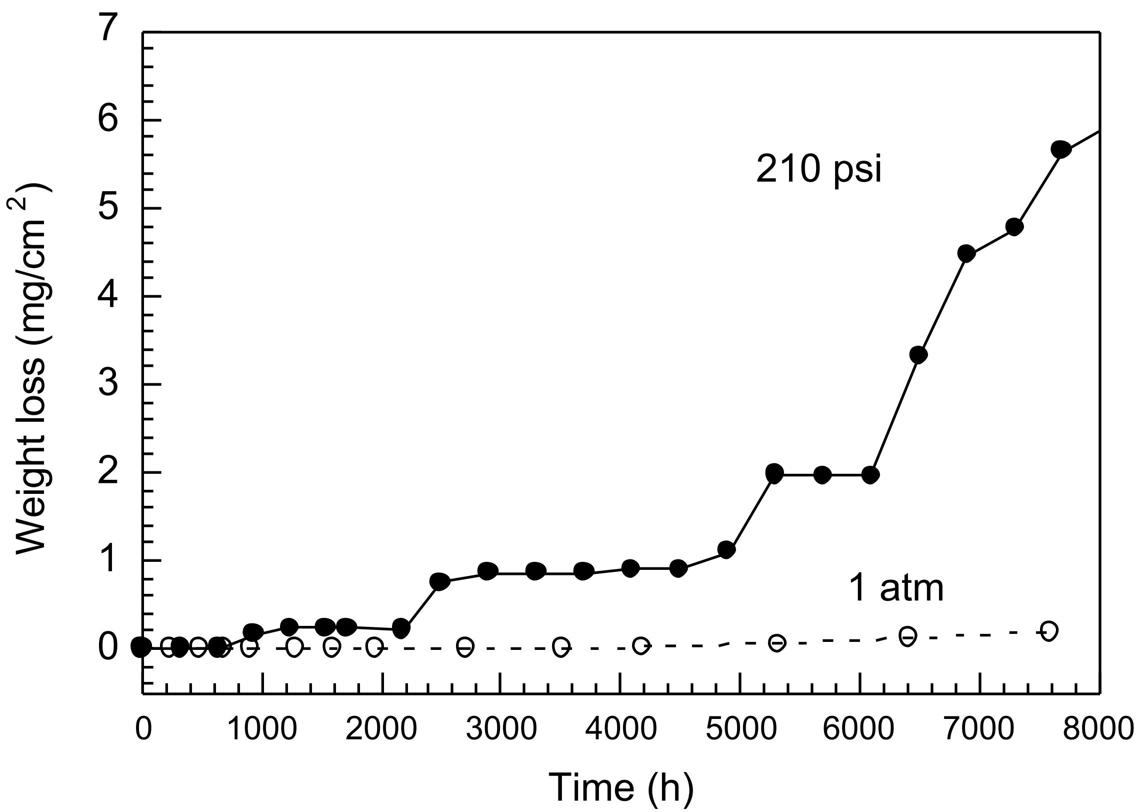


Weight loss of Alloy 601 in gases with similar carbon activity but at different pressure



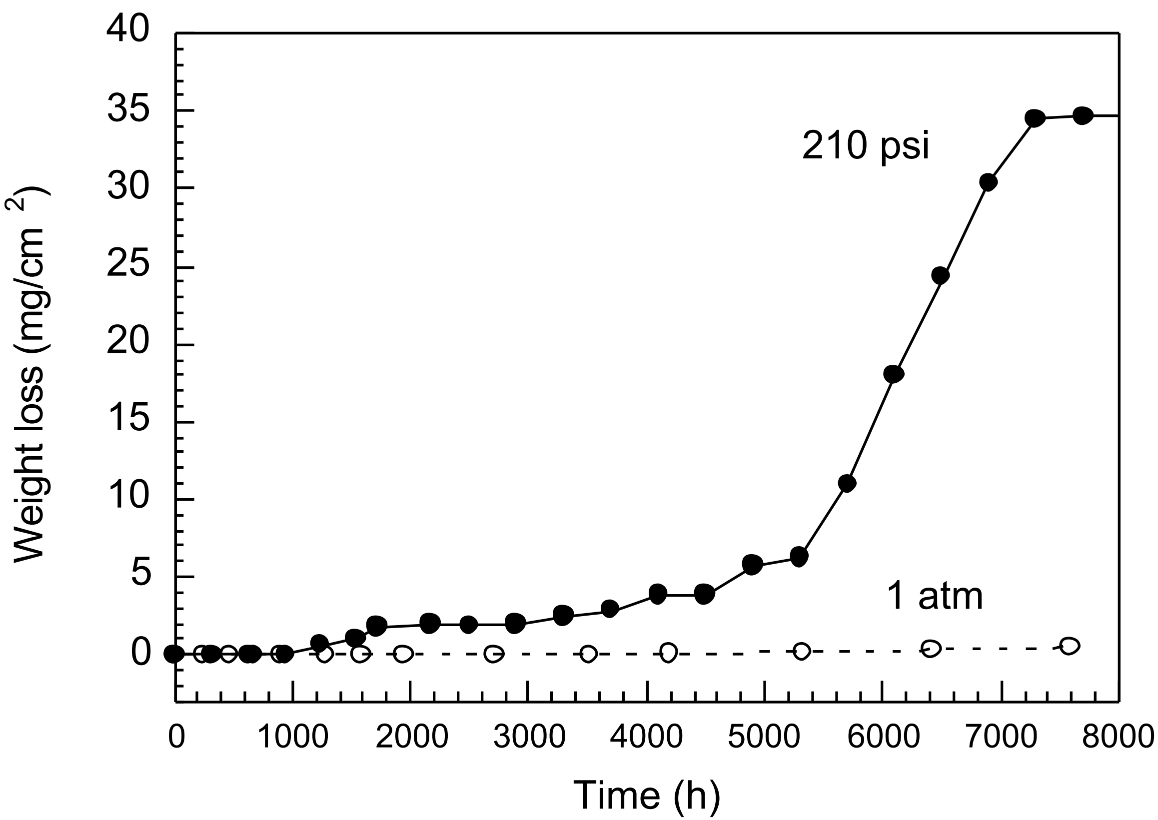
Alloy 601 in Gas 10 (53.4%H_2, 18.4%CO, 5.7%CO_2 and 22.5%H_2O) at 210 psi and Gas 11 (79.5%H_2, 18.2%CO, and 2.3%H_2O) at 1 atm and 593°C.

Weight loss of Alloy 690 in gases with similar carbon activity but at different pressure



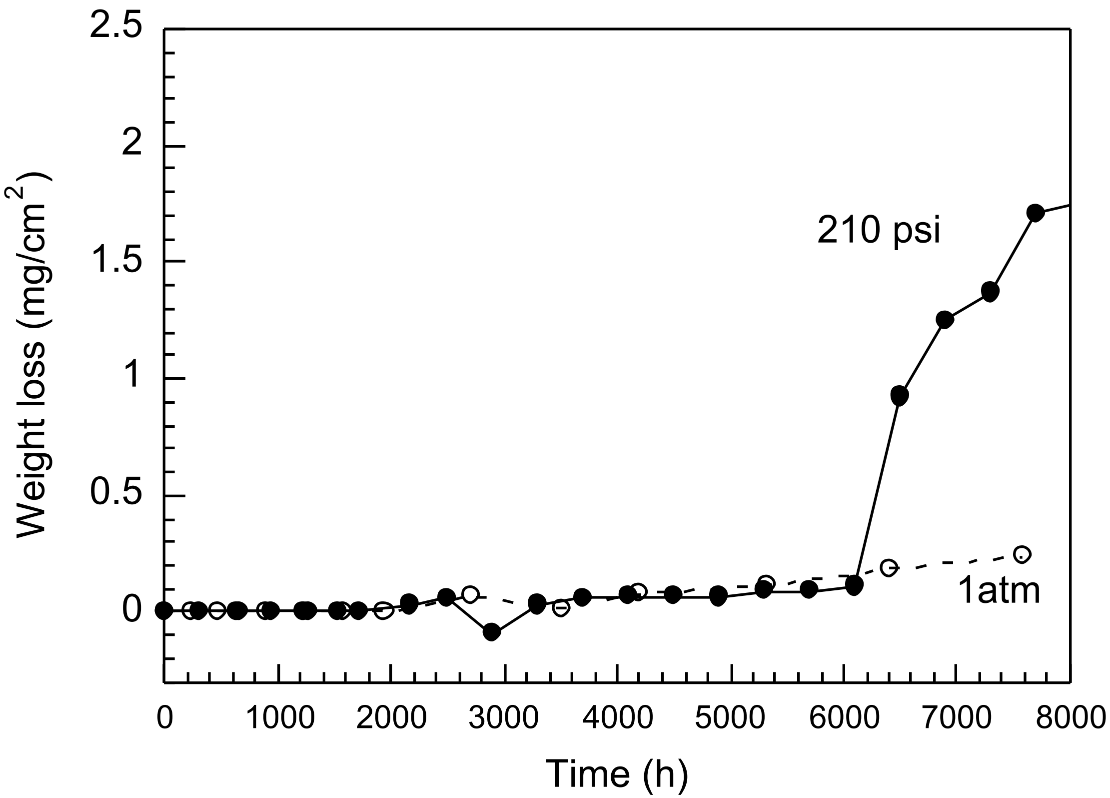
Alloy 690 in Gas 10 (53.4%H_2, 18.4%CO, 5.7%CO_2 and 22.5%H_2O) at 210 psi and Gas 11 (79.5%H_2, 18.2%CO, and 2.3%H_2O) at 1 atm and 593°C.

Weight loss of Alloy 617 in gases with similar carbon activity but at different pressure



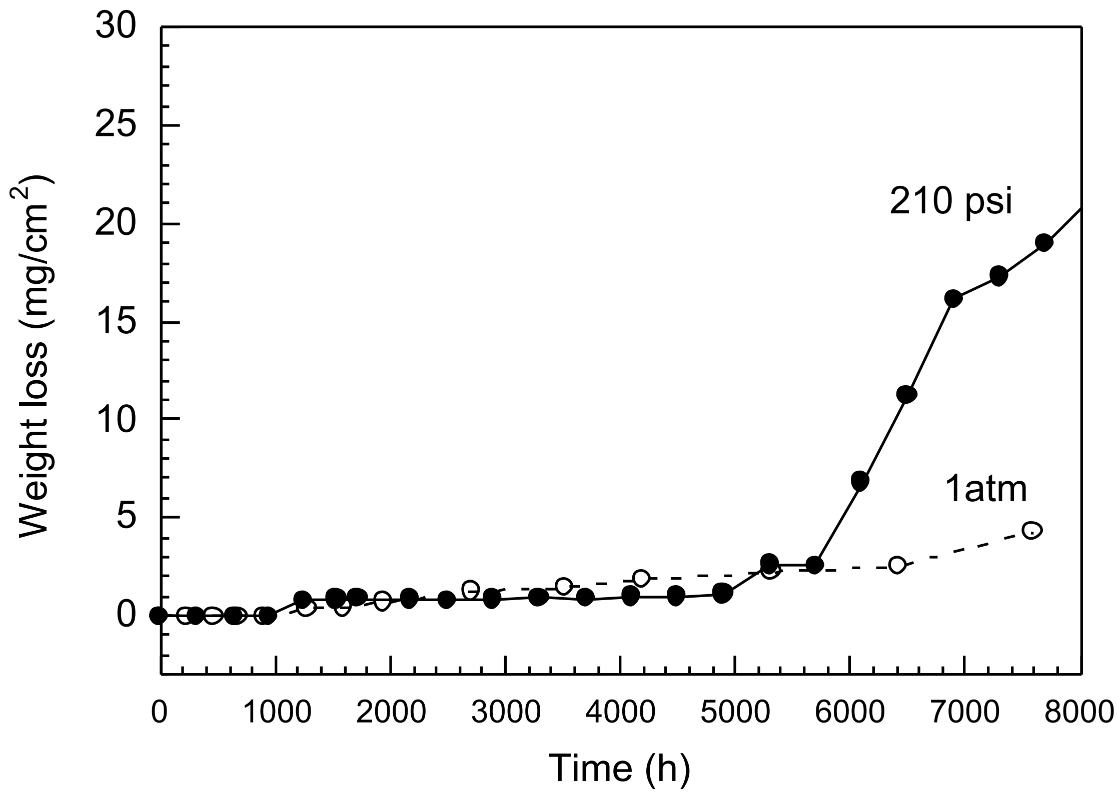
Alloy 617 in Gas 10 (53.4% H_2, 18.4% CO, 5.7% CO_2 and 22.5% H_2O) at 210 psi and Gas 11 (79.5% H_2, 18.2% CO, and 2.3% H_2O) at 1 atm and 593°C.

Weight loss of Alloy 602CA in gases with similar carbon activity but at different pressure



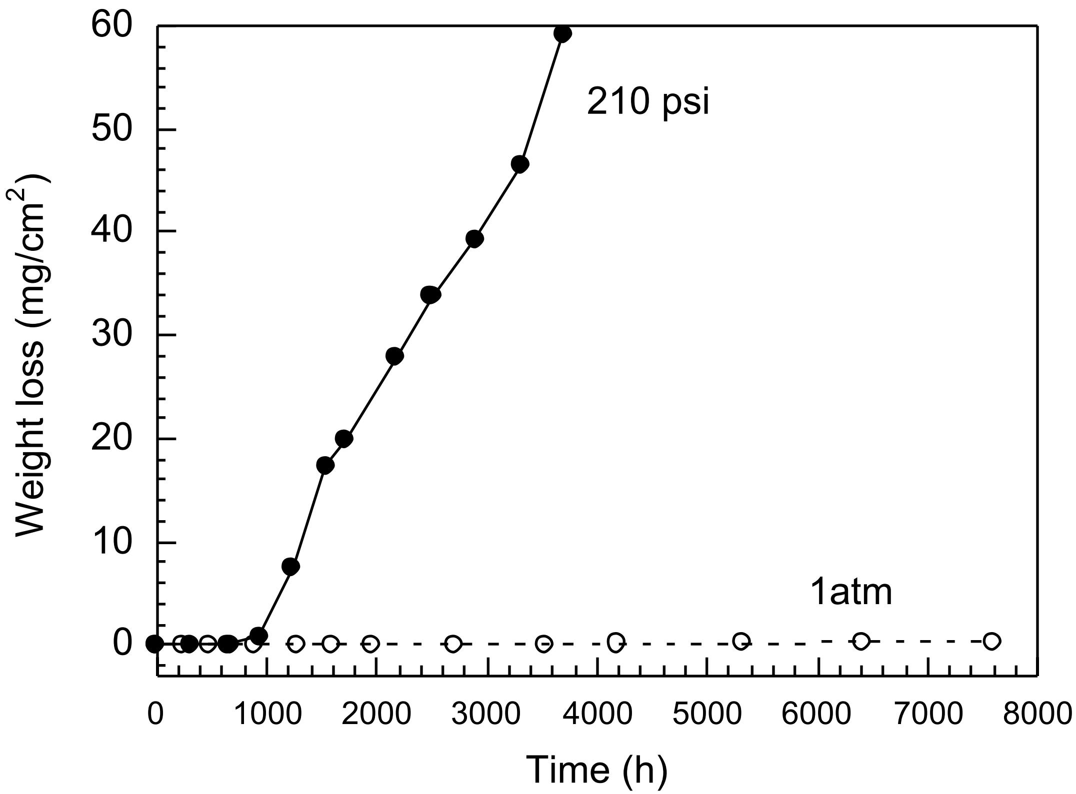
Alloy 602CA in Gas 10 (53.4%H_2, 18.4%CO, 5.7%CO_2 and 22.5%H_2O) at 210 psi and Gas 11 (79.5%H_2, 18.2%CO, and 2.3%H_2O) at 1 atm and 593°C.

Weight loss of Alloy 214 in gases with similar carbon activity but at different pressure



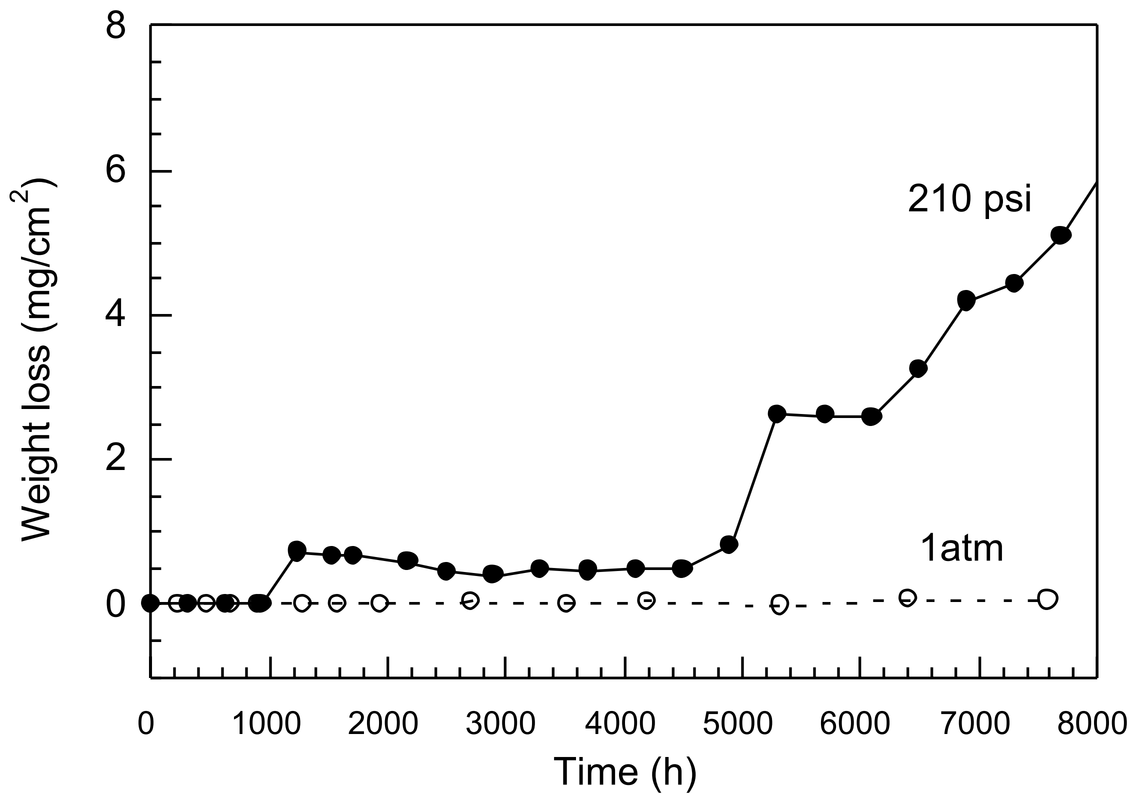
Alloy 214 in Gas 10 (53.4%H_2, 18.4%CO, 5.7%CO_2 and 22.5%H_2O) at 210 psi and Gas 11 (79.5%H_2, 18.2%CO, and 2.3%H_2O) at 1 atm and 593°C.

Weight loss of Alloy 45TM in gases with similar carbon activity but at different pressure



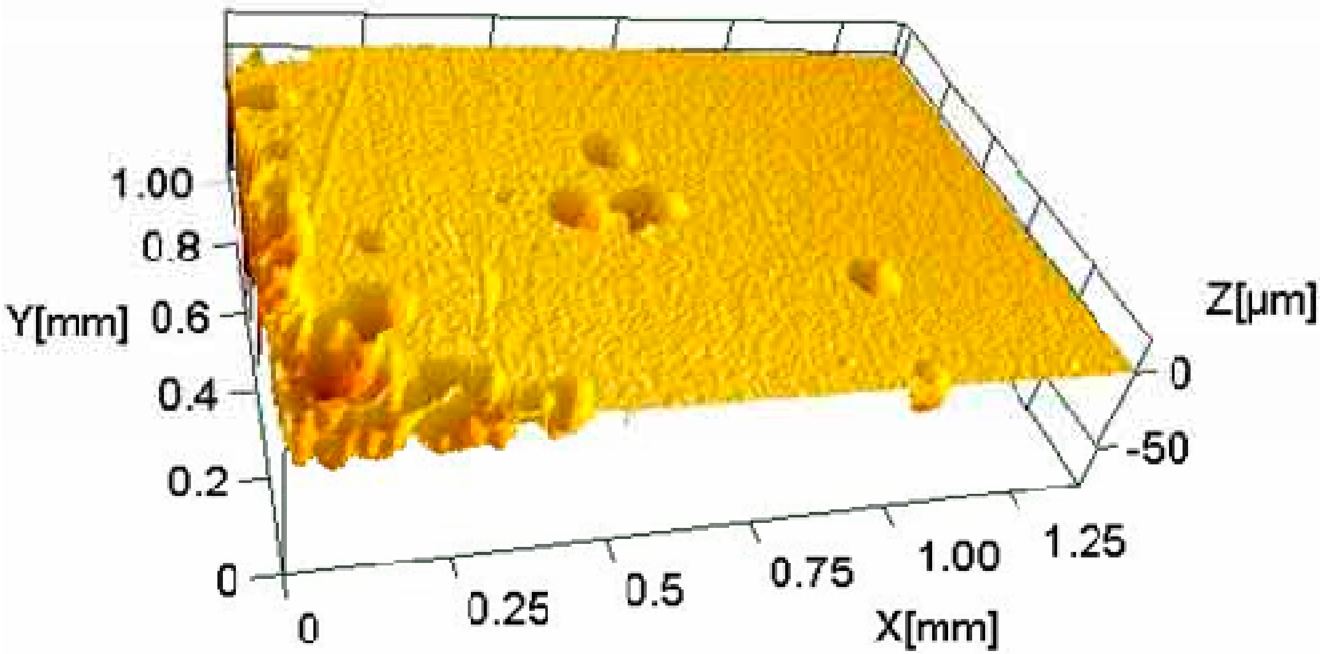
Alloy 45TM in Gas 10 (53.4%H_2, 18.4%CO, 5.7%CO_2 and 22.5%H_2O) at 210 psi and Gas 11 (79.5%H_2, 18.2%CO, and 2.3%H_2O) at 1 atm and 593°C.

Weight loss of Alloy HR160 in gases with similar carbon activity but at different pressure

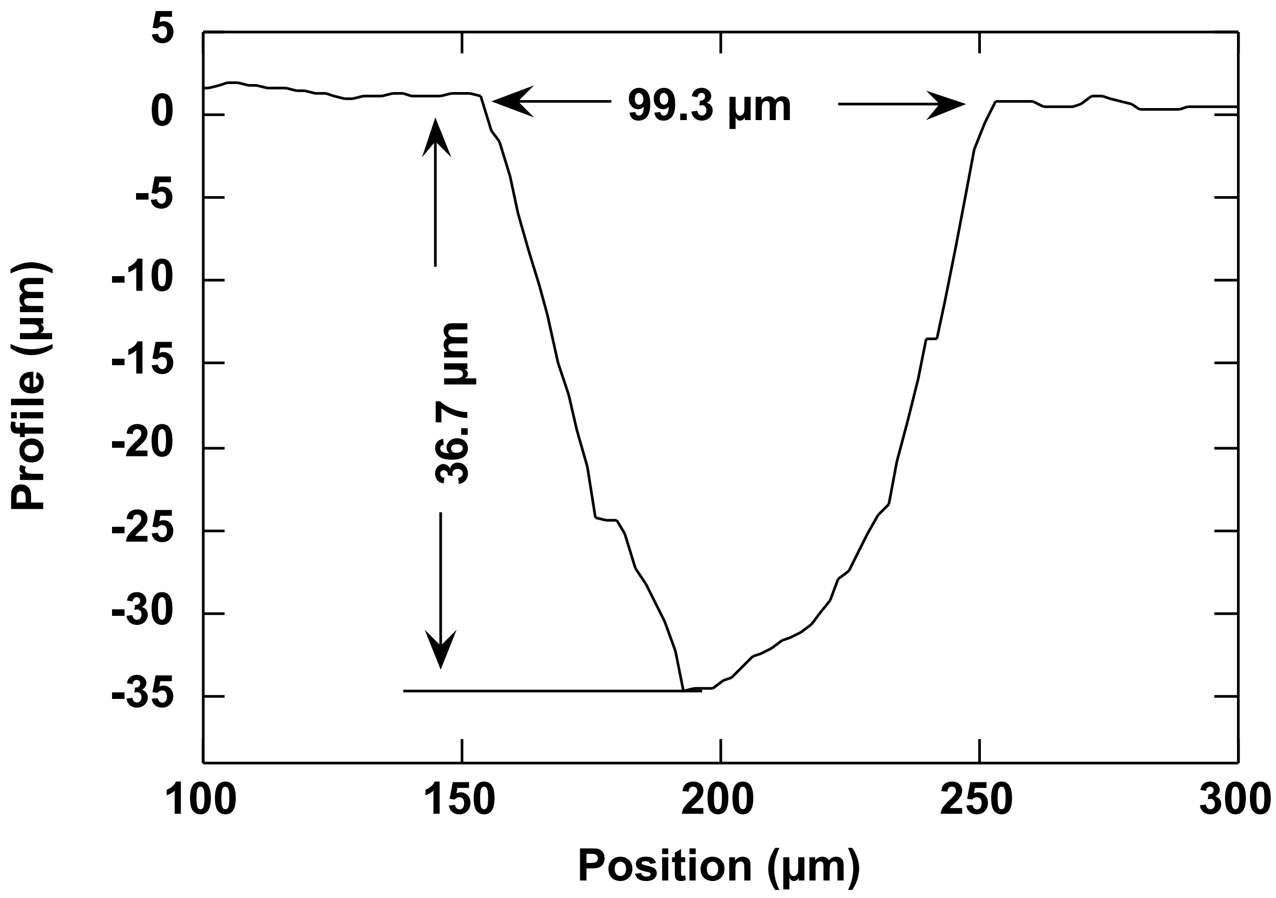


Alloy HR160 in Gas 10 (53.4%H_2, 18.4%CO, 5.7%CO_2 and 22.5%H_2O) at 210 psi and Gas 11 (79.5%H_2, 18.2%CO, and 2.3%H_2O) at 1 atm and 593°C.

Profile map of Alloy 693 exposed to Gas 10 at 593°C, 210 psi for 9700 h



Pit depth of Alloy 693 exposed to Gas 10 at 210 psi and 593°C for 9700 h



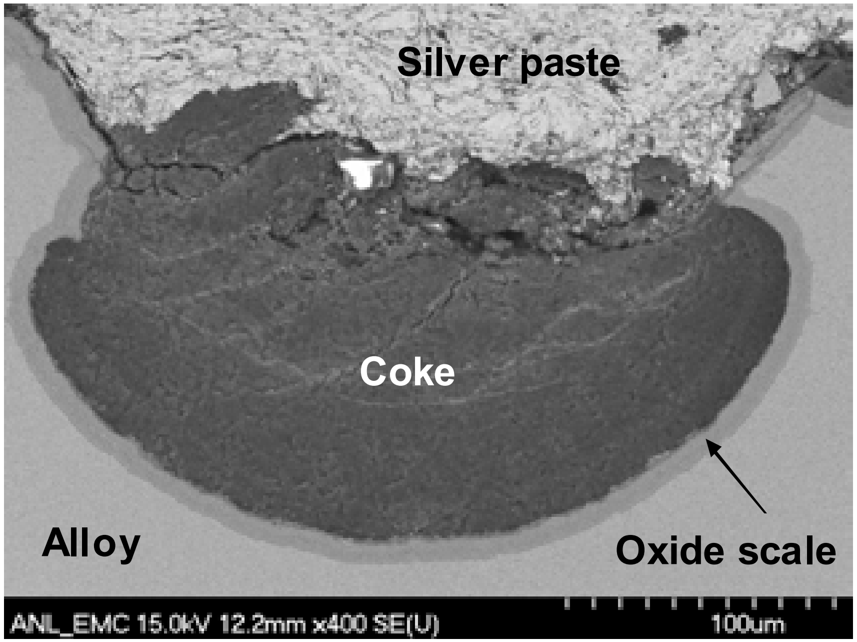
Metal dusting corrosion of Alloy 800 from a hydrogen reformer of Air Products and Chemicals

Gas composition: 43.8 H_2-7.2CO-5.7CO_2-39.2H_2O-4.1CH_4

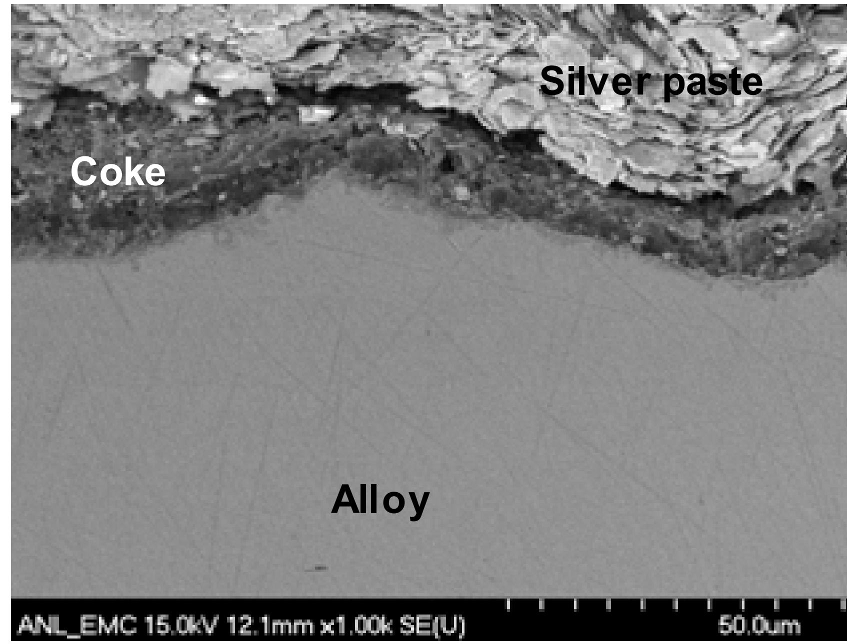
Exposure Temperature: 1100°F-1200°F

Exposure Time: >10 years

SEM micrograph of Alloy 800 from a hydrogen reformer of Air Products and Chemicals

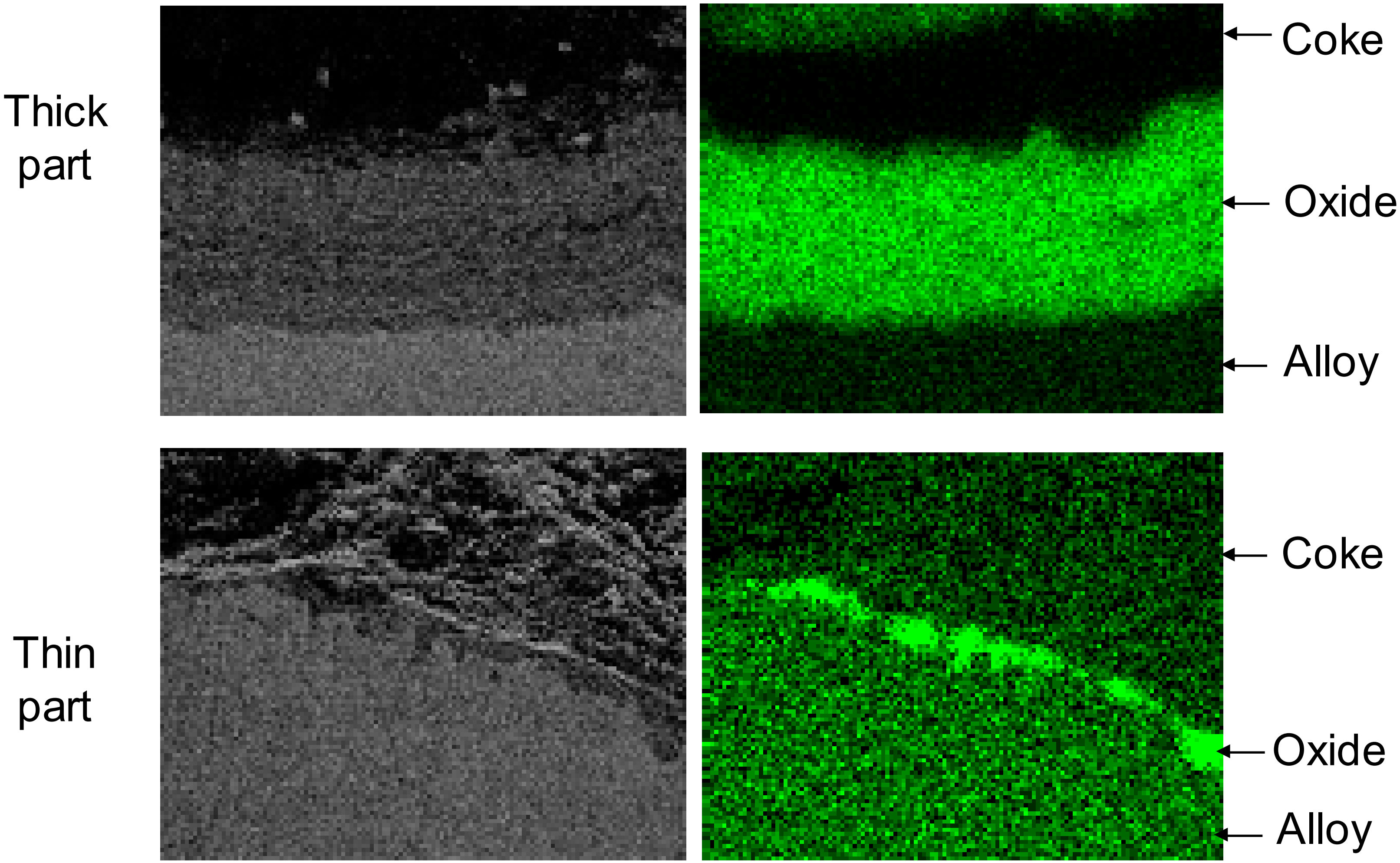


Thick part of Alloy 800 tube

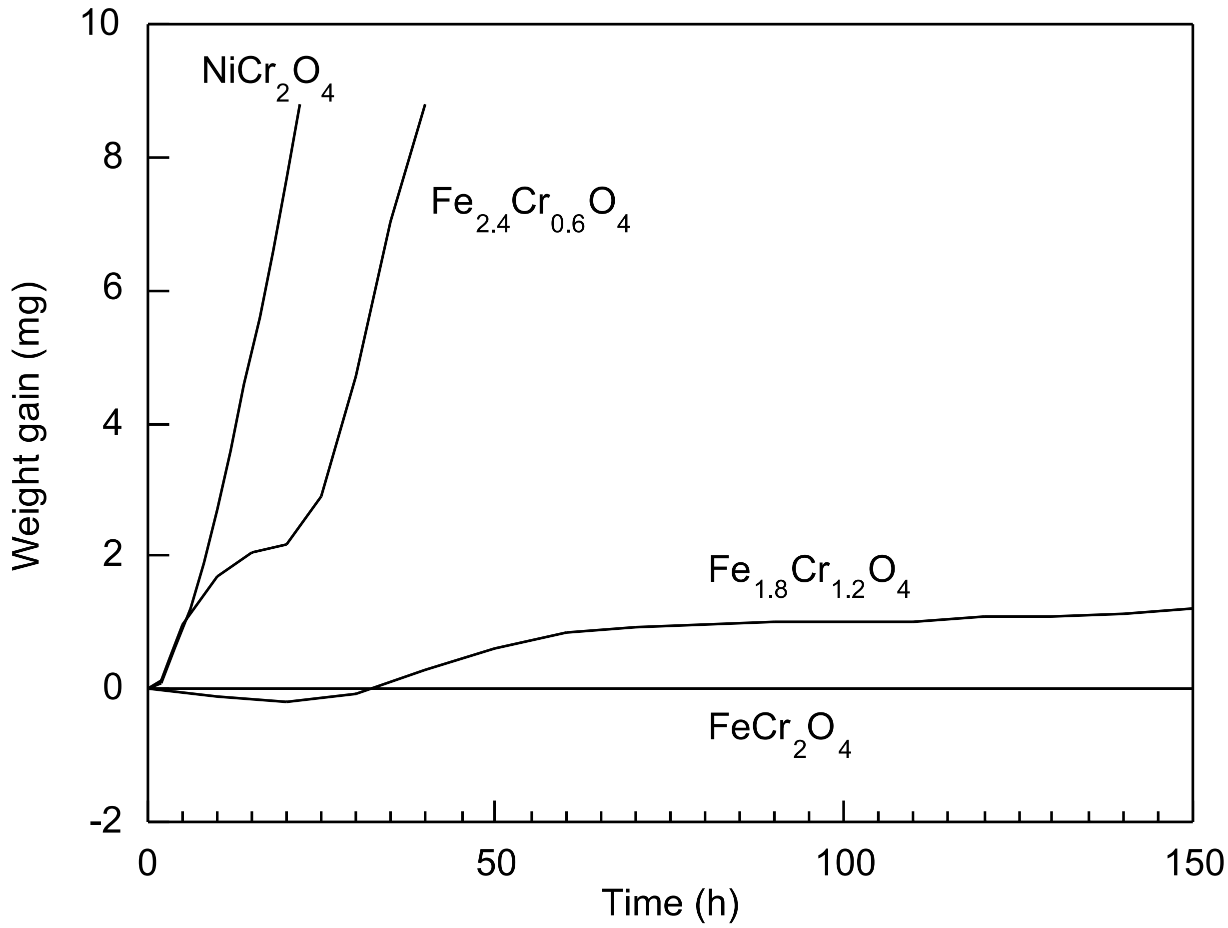


Thin part of Alloy 800 tube

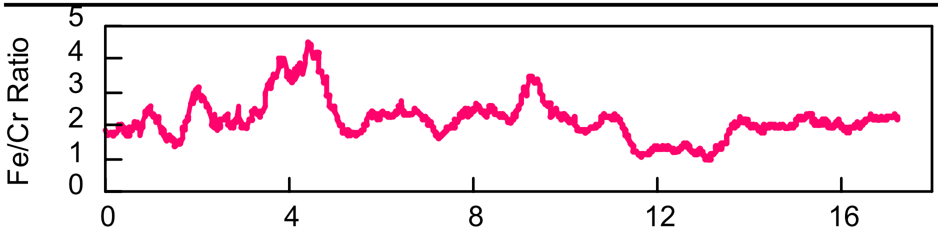
EDX mapping on cross section of Alloy 800 tube

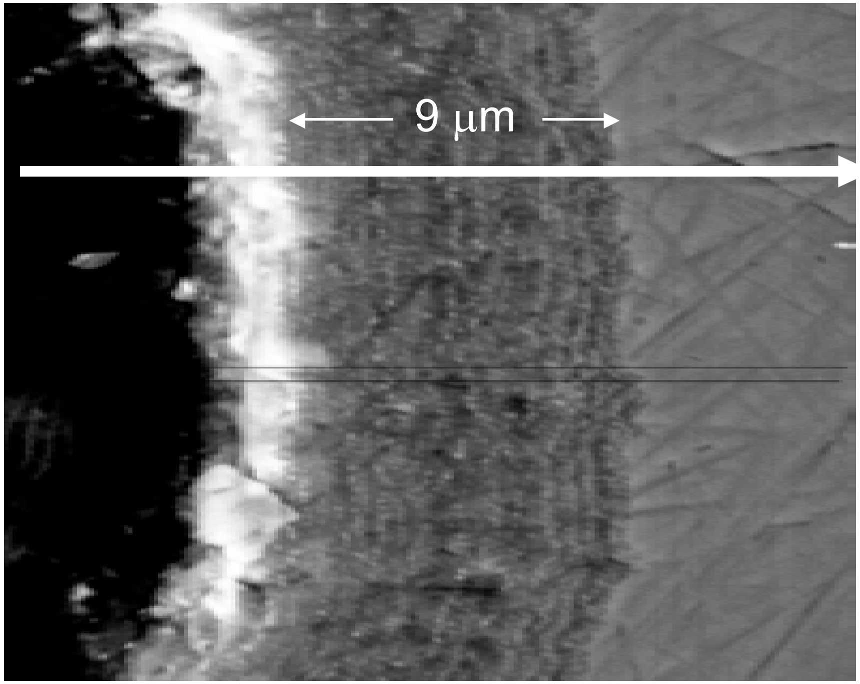


Weight change for different spinels in metal dusting environment



Fe/Cr ratio in the spinel developed on Alloy 800

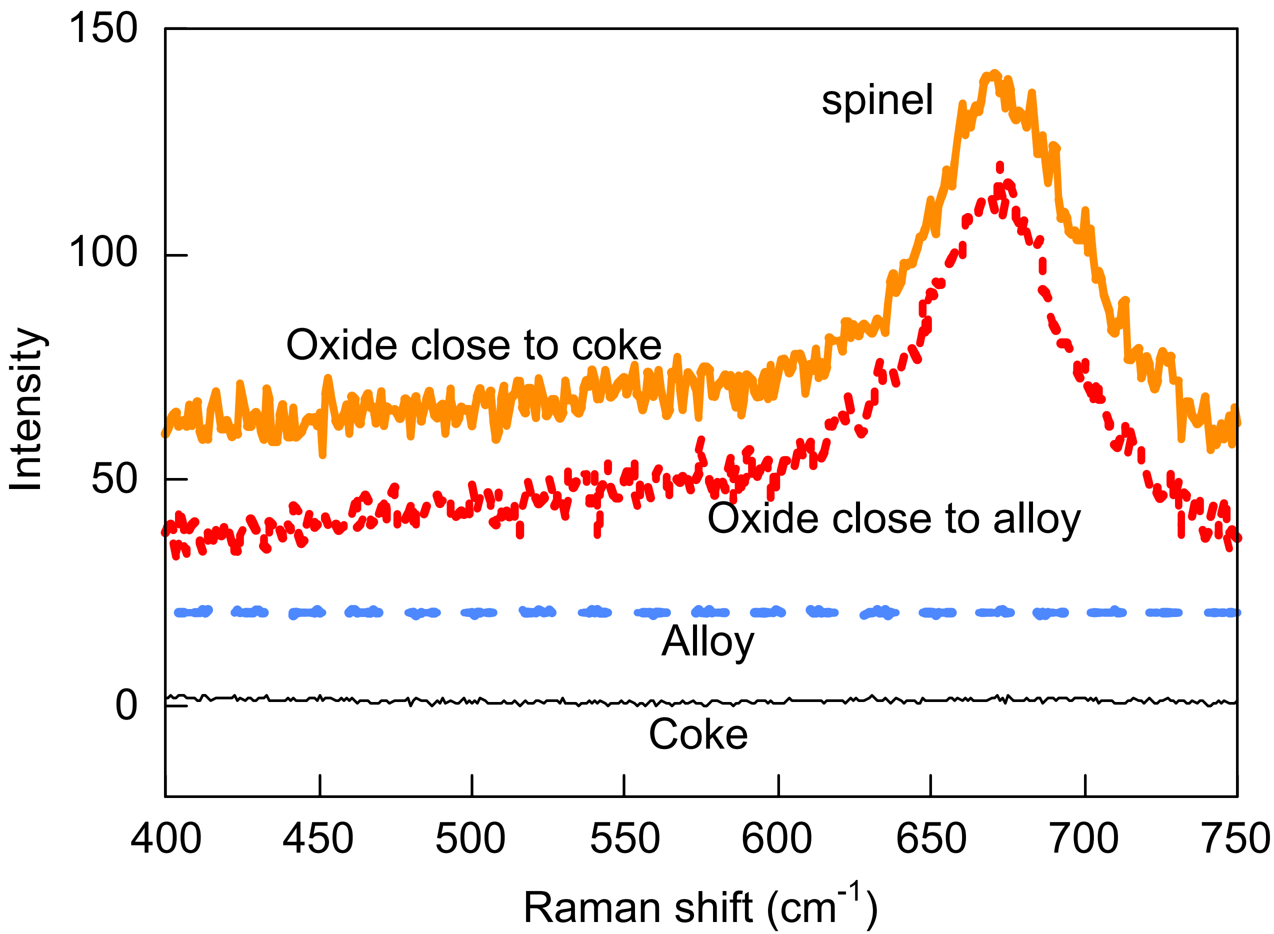




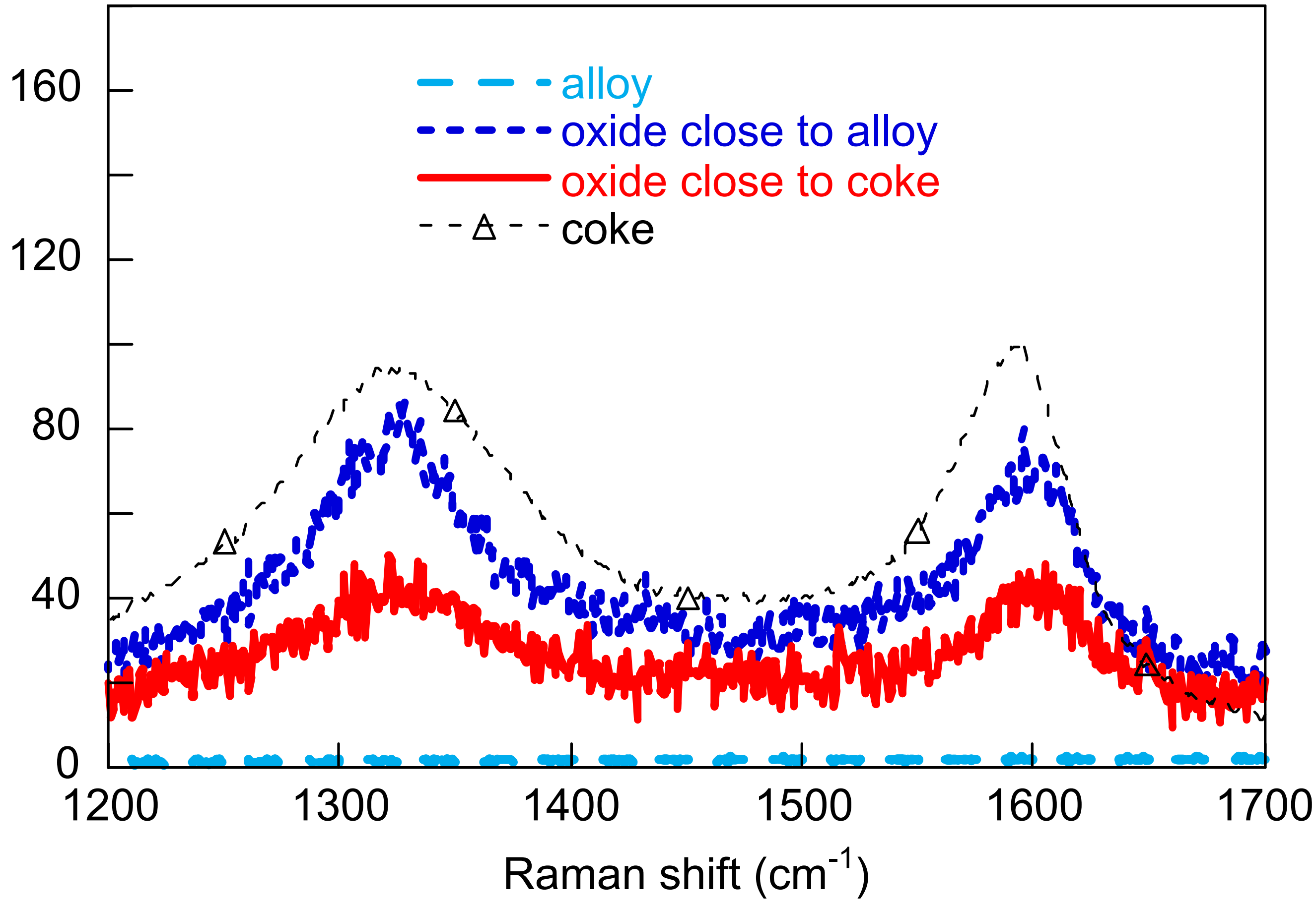
Fe/Cr = 2.18 $FeCr_2O_4$ $Fe_{1+x}Cr_{2-x}O_4$

Spot Pos.	Composition (At%)			
	Cr	Mn	Fe	Ni
At Oxide	19.41	1.07	52.35	27.17
At Alloy	21.54	0.71	46.88	30.87

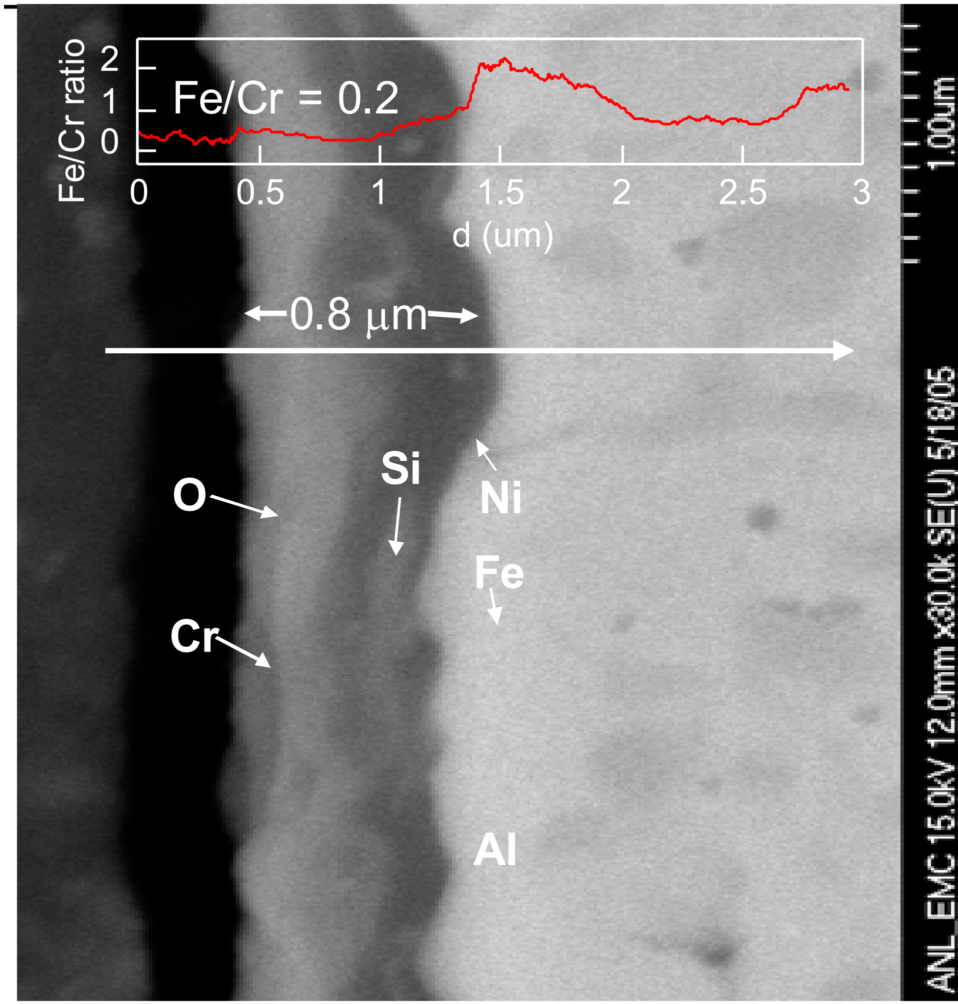
Major phase of oxide scale on Alloy 800 is spinel



Raman spectra indicates that carbon can penetrate through the oxide scale on Alloy 800



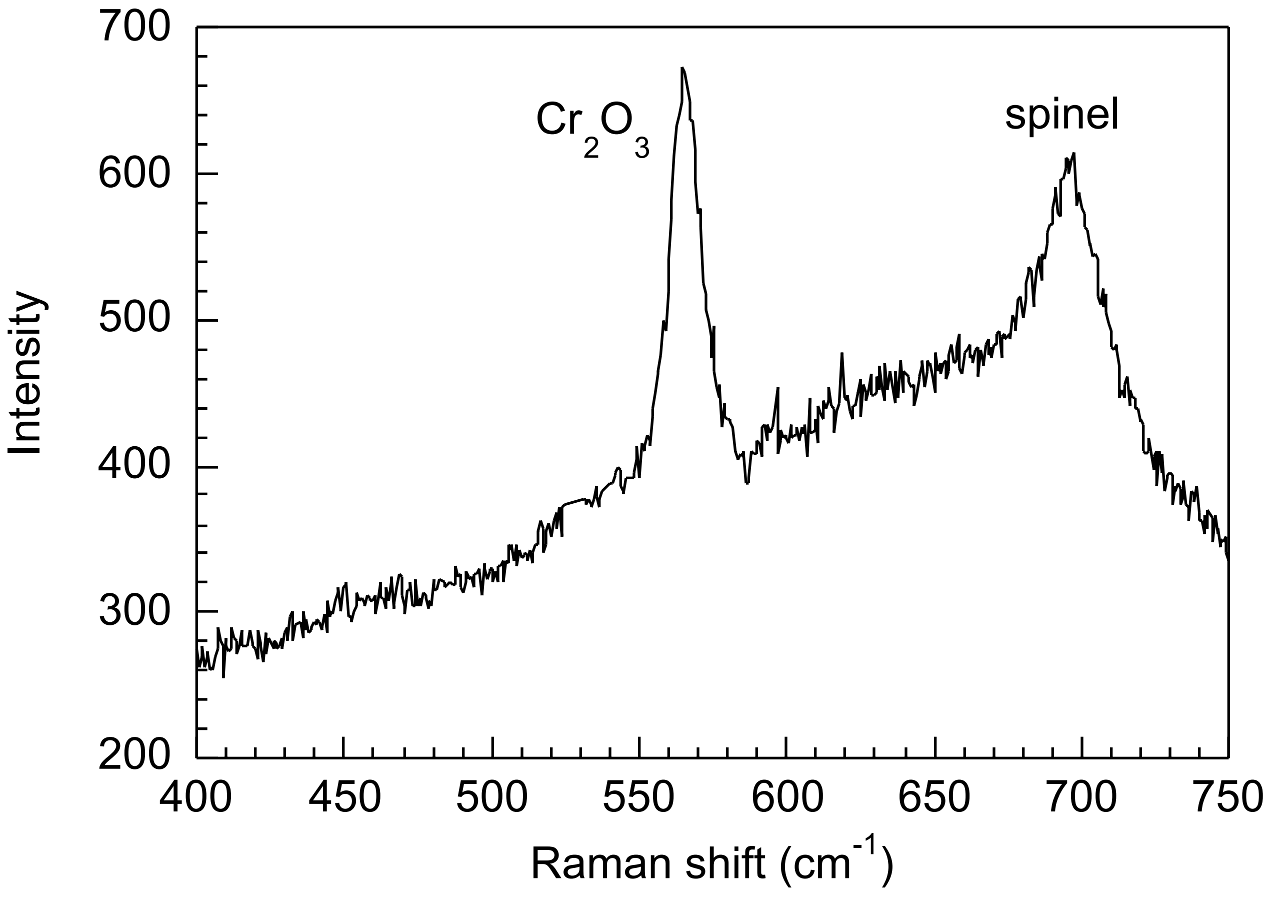
Composition of the oxide scale on Ni-base alloys is low in Fe than observed in the scale on Alloy 800



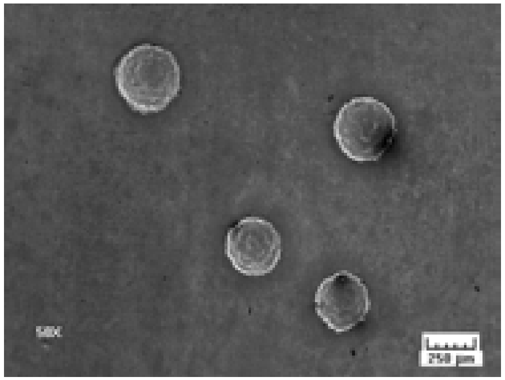
Composition (at%)

	At Oxide	At Alloy
Cr	53.81	31.32
Mn	5.45	0.12
Fe	11.56	21.34
Ni	4.92	41.88
Si	23.21	5.08
Al	1.05	0.26

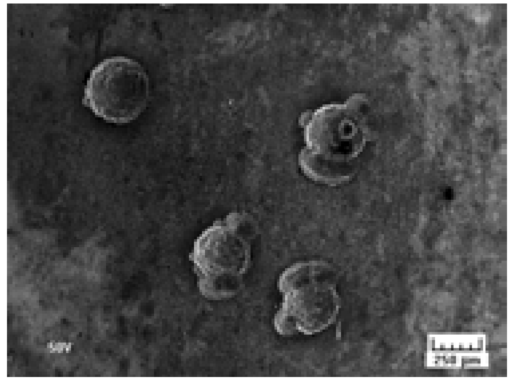
Both chromium oxide and spinel phase were observed in oxide scale on Alloy 45TM



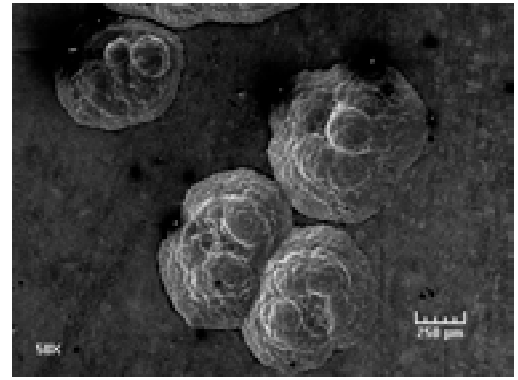
Pit Growth Rates in Alloy 617 at 593°C and 210 psi



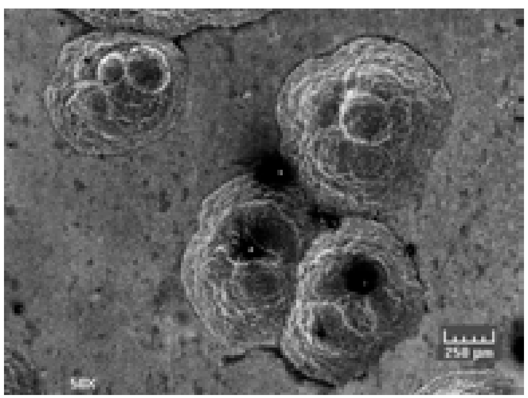
2,900 h



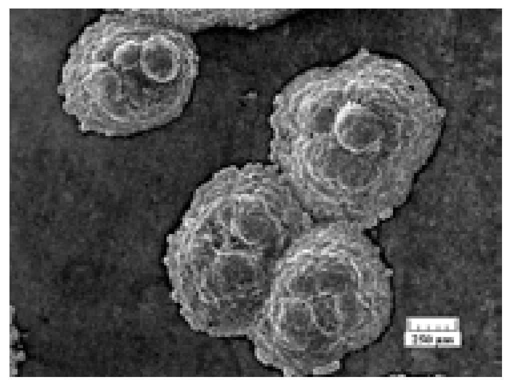
4,100 h



6,900 h

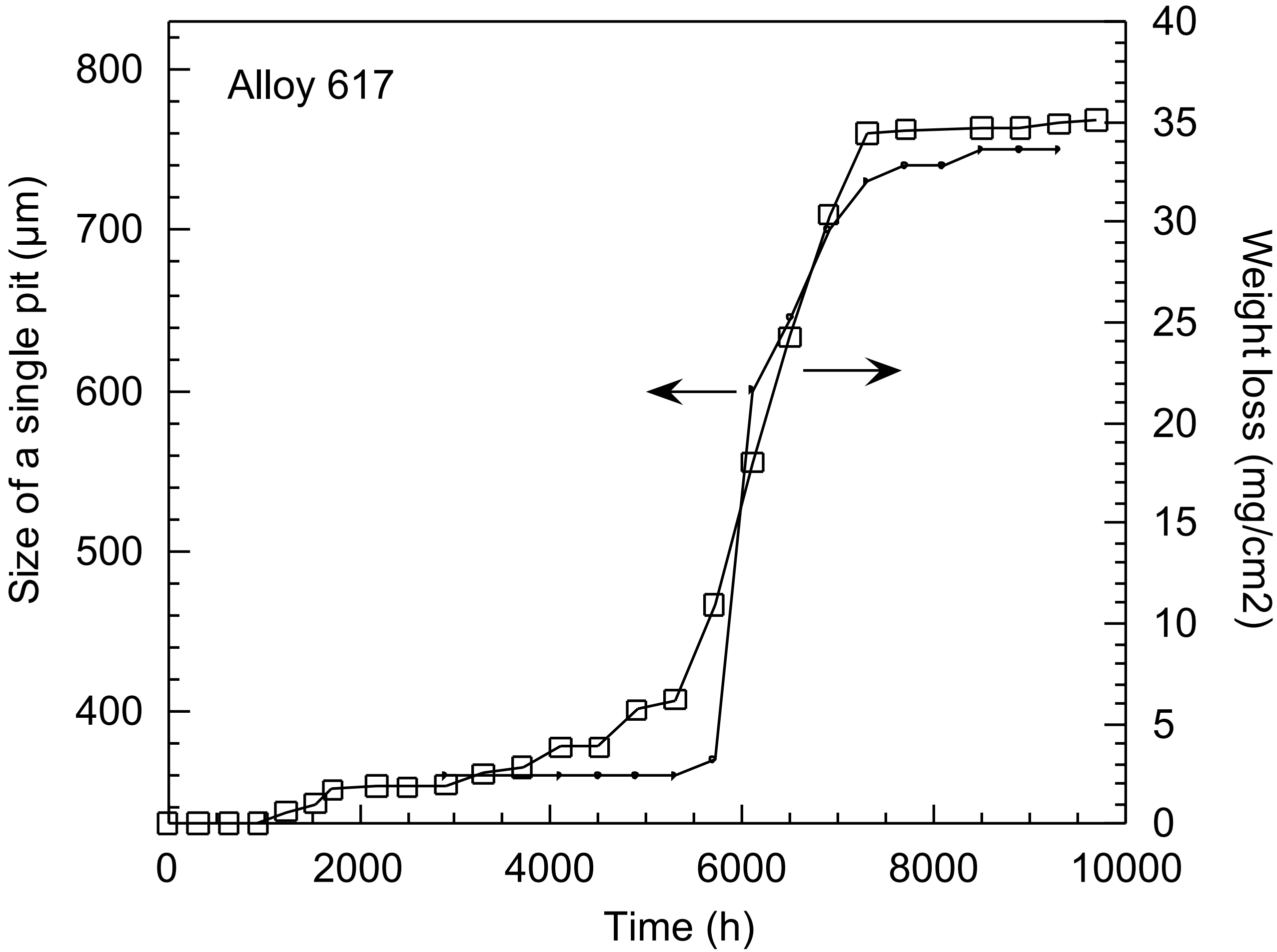


8,100 h

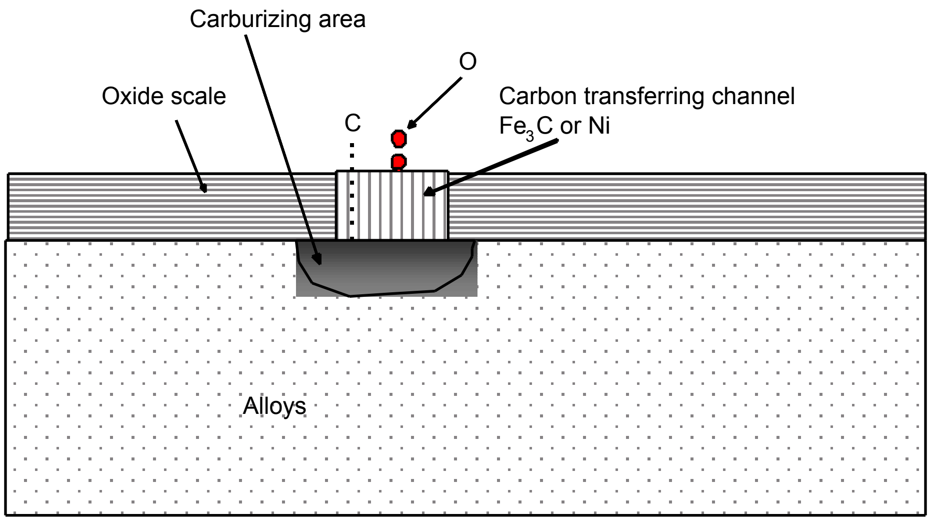


9,300 h

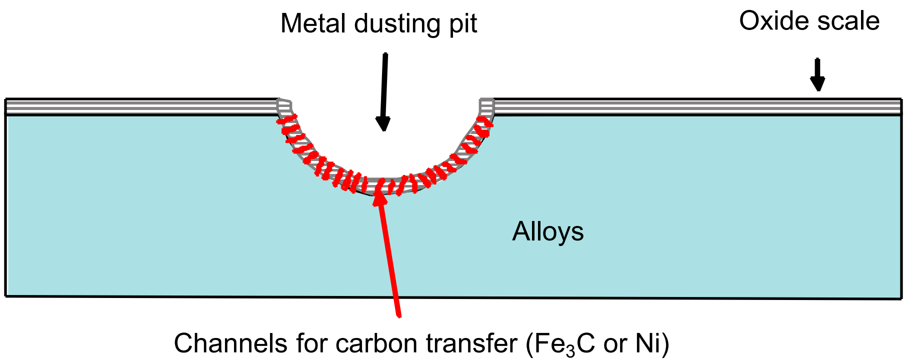
Run 59HP - Pit Depth and Weight Loss Correlation



Mechanism of the Growth of Metal Dusting Pits

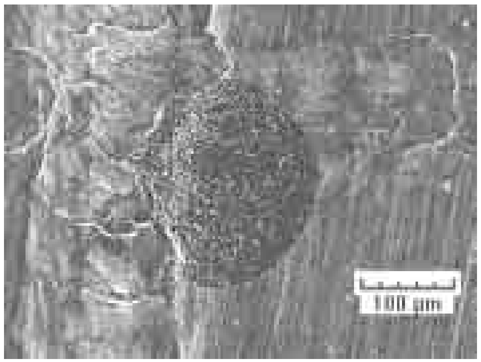


Initiation of pits

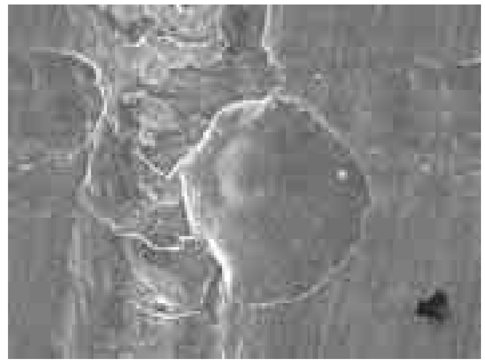


Propagation of pits

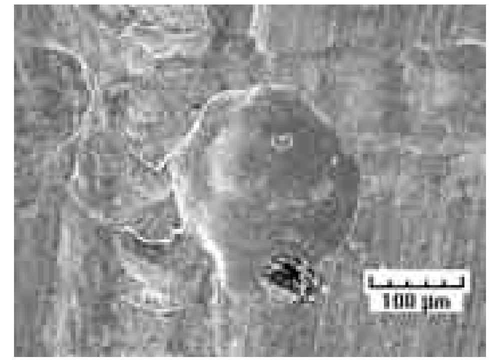
Mitigation of metal dusting pit growth by an intermediate oxidation



After 5-day exposure to carburizing atmosphere at 593°C.



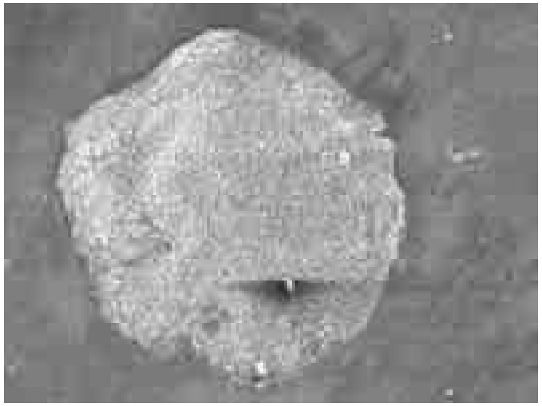
After an intermediate oxidation in H_2-2%H_2O gas mixture at 593°C for 2 days and subsequent 2-day exposure to the carburizing atmosphere at 593°C.

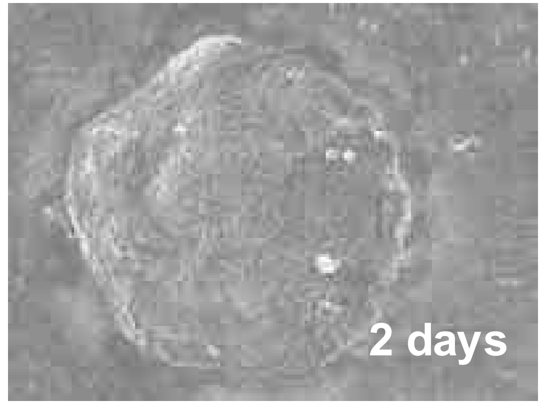


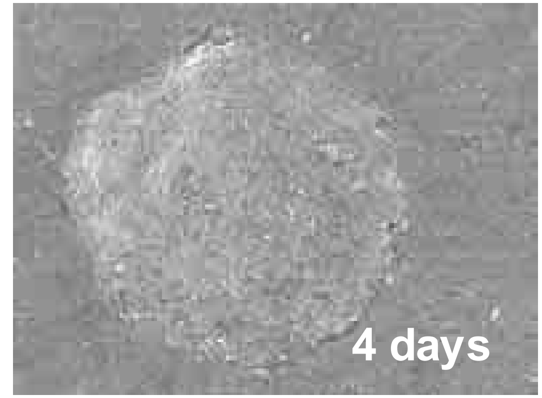
After 4 days of exposure to the carburizing gas mixture at 593°C.

Incubation time of Alloy 800 is ≈ 4days.

Effect of intermediate oxidation at 760°C for 6 hours

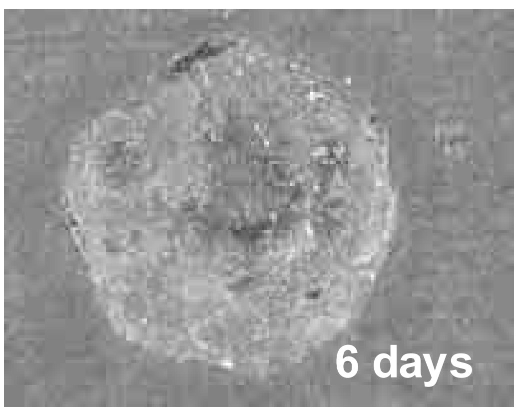


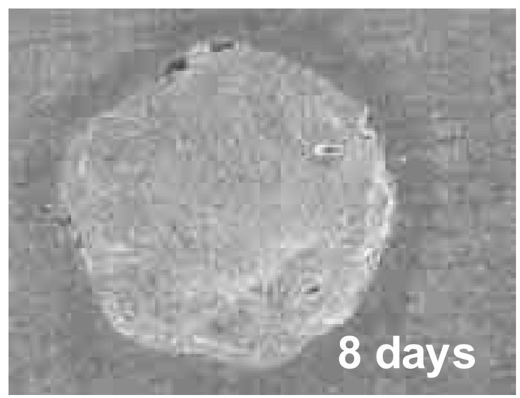




After oxidation in H_2-2%H_2O gas mixture at 760ºC for 6 hours

Subsequent 2-day exposure to the carburizing atmosphere at 593ºC.





Oxidation conditions to mitigate metal dusting corrosion

Alloy 800 samples with metal dusting pits were exposed in various atmospheres with steam and temperatures, and then exposed to a carburizing gas again. The pit growth was monitored by SEM.

Oxidizing atmosphere	T(°C)	Time (h)	Pit grow or not after exposed to Gas 5 again for 2 days	Pit grow or not after exposed to Gas 5 again for 4 days	Pit grow or not after exposed to Gas 5 again for 6 days	Pit grow or not after exposed to Gas 5 again for 10 days
2%H2O+98%H2	593	48	no	yes	yes	yes
2%H2O+98%H2	593	24	yes	yes	yes	yes
2%H2O+98%H2	593	6	yes	yes	yes	yes
95% H2O+5%H2	593	24	yes	yes	yes	yes
95% H2O+5%H2	593	6	yes	yes	yes	yes
100%H2O	593	24	yes	yes	yes	yes
100%H2O	593	6	yes	yes	yes	yes
2%H2O+98%H2	760	24	no	no	no	no
2%H2O+98%H2	760	6	no	no	no	no
95%H2O+5%H2	760	24	no	no	no	no
95%H2O+5%H2	760	6	no	no	no	no
100%H2O	760	24	no	no	no	grew again
100%H2O	760	6	no	grew again	grew again	grew again

Weldment Specimens

- **Weldment specimens have been procured from several alloy manufacturers for evaluation in the current project.**
- **Alloys selected for weldments:**

Fe-base:	**347ss**	**-**	**ANL**
	APMT	**-**	**Sandvik**
	310ss	**-**	**ANL**
	890	**-**	**Special Metals**
	353MA	**-**	**ATI**
Ni-base:	**601**	**-**	**Special Metals**
	690	**-**	**"**
	693	**-**	**"**
	230	**-**	**Haynes International**
	HR-160	**-**	**"**
	602CA	**-**	**Krupp VDM**

Project Summary

- There are two major issues of importance in metal dusting. First is formation of carbon and subsequent deposition of carbon
- on metallic materials. Second is the initiation of metal dusting degradation of the alloy

- Raman spectra show the existence of spinel, Cr_2O_3, and disordered chromium oxide in the scale grown on Fe-Cr alloys. All three phases act as protective layers to prevent alloys from metal dusting corrosion

- The spinel phase is not as stable as Cr_2O_3. It could be reduced, and metal dusting corrosion would initiate from the reduced defects

- If the spinel content (with high Fe/Cr ratio) in the oxide scale is high, the alloy may be more easily attacked by carbon, leading to metal dusting

Project Summary (continued)

- We have made a substantial progress in our project on metal dusting. We have conducted a test with candidate Ni-base alloys at high pressure in an environment simulating that of an H_2 reformer. Test was conducted at 593°C (1100°F) and 210 psia (14.3 atm) for about 10,000 h
- Specifically, we have examined the Ni-base alloy specimens from the standpoint of incubation and pit development (growth, size, density, and distribution). Some typical data are presented in this talk and additional information was presented at the steering committee and MTI meetings and in ASM and NACE conferences and in journal publications
- Additional tests are in progress under more severe reformer conditions (carbon activity of 100) and under heat-treat conditions (almost no H_2O)

Project Summary (continued)

- **Testing of weldment specimens (procured from several alloy manufacturers) is in progress at 593°C and 1 atm**

- **We have also developed new alloys with improved metal dusting resistance and a patent application is submitted. The alloys have accumulated 3,000 h of exposure with no pitting.**