Effect of Oxygen Impurity on Corrosion in Supercritical CO_2 Environments

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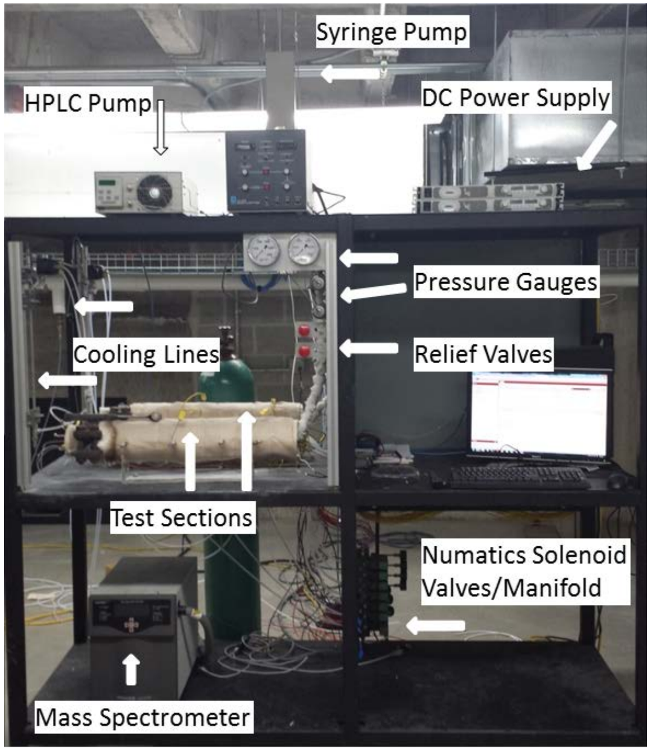
5th International Supercritical CO_2 Power Cycles Symposium,
March 29 - 31, 2016, San Antonio, Texas

Project Goal

1. Characterize the effect of oxygen on the corrosion rate at high temperatures (650/750ºC) on metallic samples
    1. Oxidation
    2. Carburization
2. Determine time scales and magnitude associated with carbon reacting in CO_2 environments
    1. Boudouard reaction ($CO_2 + C \rightarrow 2CO$)
    2. Oxygen reactivity

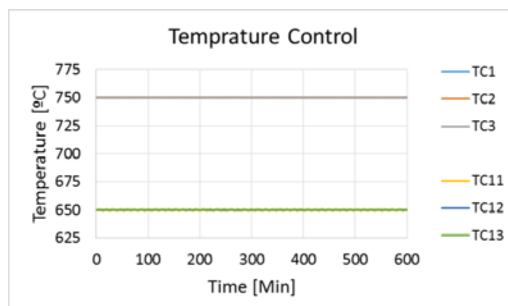
Testing Facilities

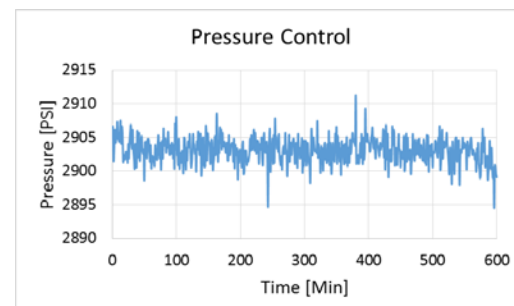


Current setup of test facility

Key features

- Three systems with five total autoclaves
- Temperature control allows system to operate within ±1ºC
- Testing temperature up to 750ºC for IN625 autoclave
- Pressures up to 3000±2 psi for In625 autoclave
- System operates at an average flow rate range of ~0.10 kg/hr
  - CO_2 refresh rate ~ 2 hours





- Mass spectrometer
- Used for impurities
  - Other than O2/CO
  - LLD: 10 ppm
  - Accuracy: ± 5 ppm

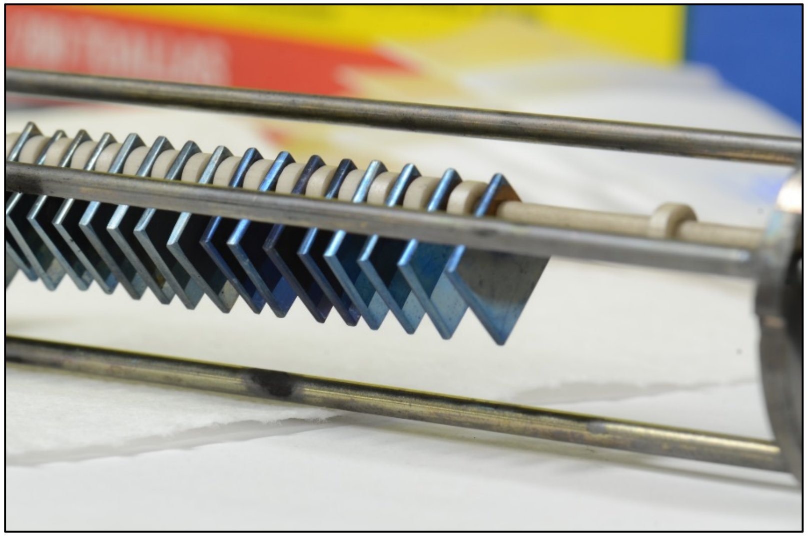
- Oxygen Sensor
- Measures oxygen concentration in CO_2 bulk gas
  - Accuracy: ± 1 ppm

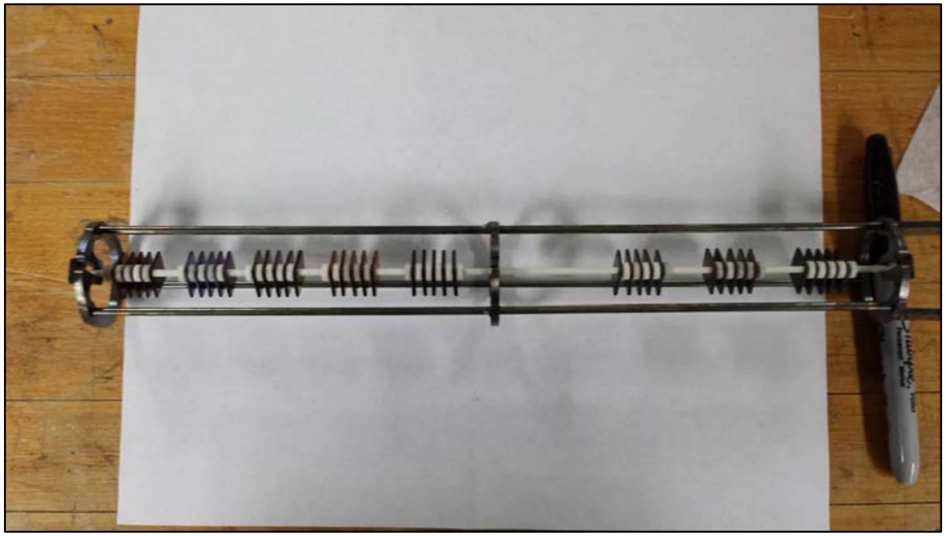
- Gas Chromatograph
- low levels of CO in CO_2 bulk gas
  - LLD: 50 ppb
  - Accuracy: ± 2.5 ppb

Testing Procedure

- Haynes 230, Haynes 625 and NBG-18 Graphite samples were obtained.
- Untested samples polished to 800 grit, then cleaned with ethanol and DI water.
- Samples were tested at 20 MPa and 650ºC, 750ºC at 200 hour intervals up to 1000 hours in research grade (99.999%), and 100ppm O_2 doped CO_2 environments.
- Weight measurements are accurate to ± 2µg and dimensions have an accuracy of ± 2µm.
- Samples analyzed using SEM, EDS, XRD, etc.

Sample Composition/Prep

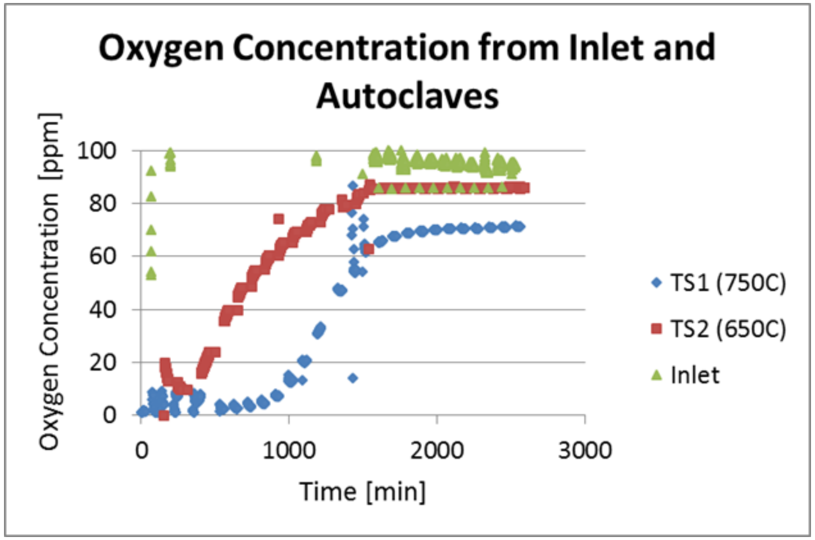


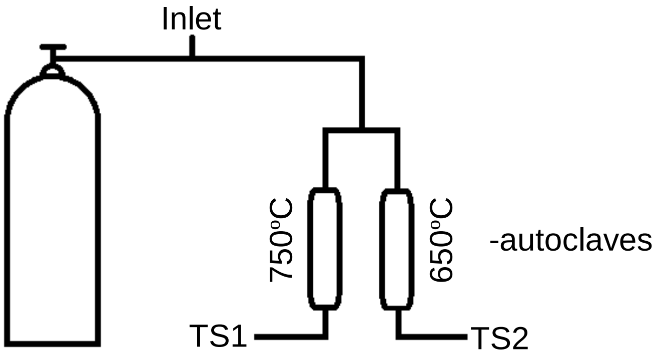


	C	Mn	Fe	Si	Cu	Ni	Cr	Al	Ti	Co	Mo	Nb	W	S	Ta	P	B	La
H230 (Haynes)	0.1	0.52	1.02	0.31	0.04	Bal~59.94	22.08	0.37	0.01	0.21	1.23		14.17	0.002			0.002	0.012
H625 (Haynes)	0.02	0.26	5	0.25		Bal~59.63	21.89	0.22	0.29	0.28	8.59	3.51		0.002	0.05	0.006		

- Sample holder made out of Haynes 625 alloy
- Samples are 0.5”x0.5”x0.0625” square coupons
- Alumina rod suspends samples in continuous stream of CO_2
- Alumina spacers separate samples
- Fits up to 70 samples

100ppm Oxygen Testing



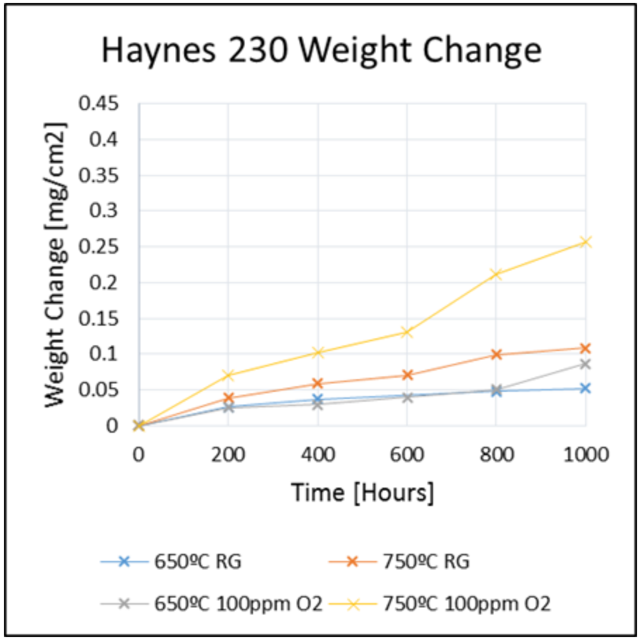


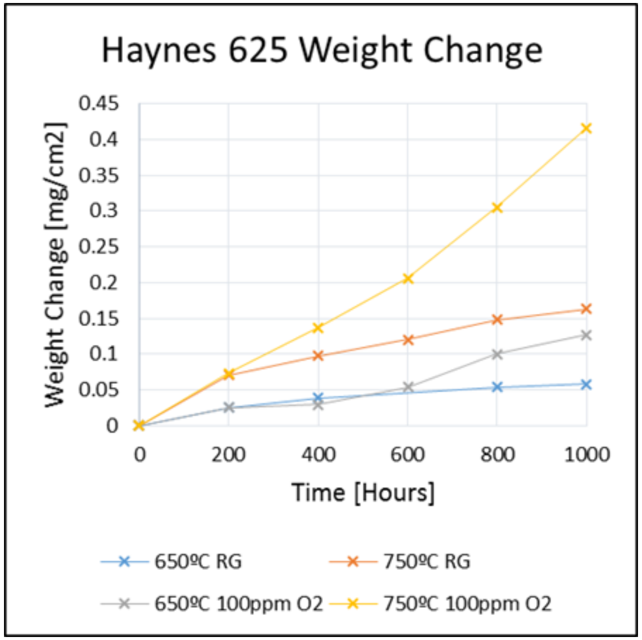
– **Plot of oxygen concentration vs time for first 200 hours of 100ppm oxygen doped test.**

- Oxygen levels were recorded in CO_2 gas before entering the testing autoclave (inlet), as well as at the exit of the autoclave for 650 and 750°C tests. (Plotted for 100ppm test above)
- 100ppm testing showed lower oxygen levels during the initial stages of the first 200 hours of testing, then reached equilibrium at around 1400 min for 650°C exposure, and 1700 min for 750°C exposure.

RG CO_2	CO_2	$Ar+O_2+CO$	Total Hydrocarbons	Moisture	Nitrogen
Purity Limit	99.999%	<1 ppm	<1 ppm	<3 ppm	<5 ppm

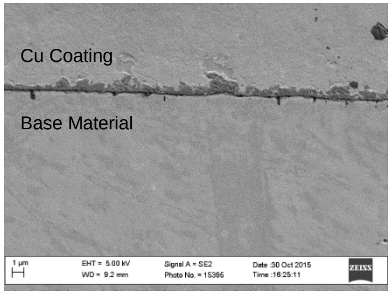
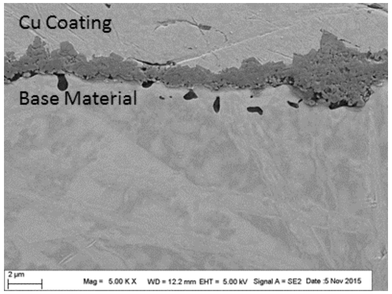
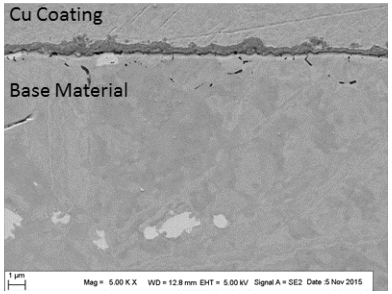
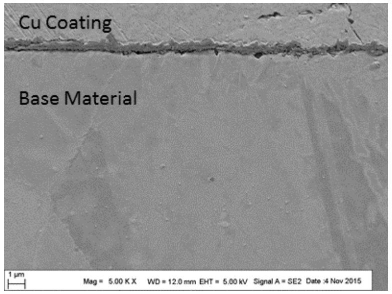
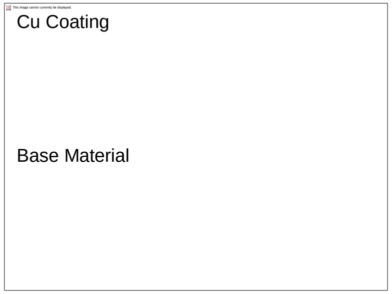
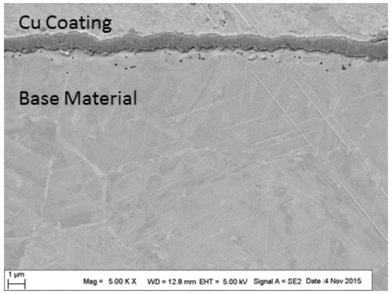
Weight Change Analysis





- Samples exposed to RG CO_2 showed protective oxide development.
- Weight change increased with temperature (650ºC to 750ºC).
- H230 generally showed better oxidation protection than H625.
- Samples exposed to oxygen impurities showed significantly larger weight change.
  - Weight change data, and SEM imaging show evidence of spallation, thicker oxides, and Fe, Cr, Al, and Mo rich oxides.

SEM Cross-Sectional Images 1000hrs (5000x)

	650ºC, 100ppm	750ºC, 100ppm	750ºC, RG
H230			
H625			

- Adding 100 ppm of oxygen caused significant increase in oxide thickness (observed above) for both 650 and 750ºC.
- H230 shows thinner oxide development for all conditions:
  - High carbide (Tungsten) concentration along grain boundaries could limit Cr diffusion to surface.

Extrapolated Thickness

Weight change thickness points from averaged oxide density

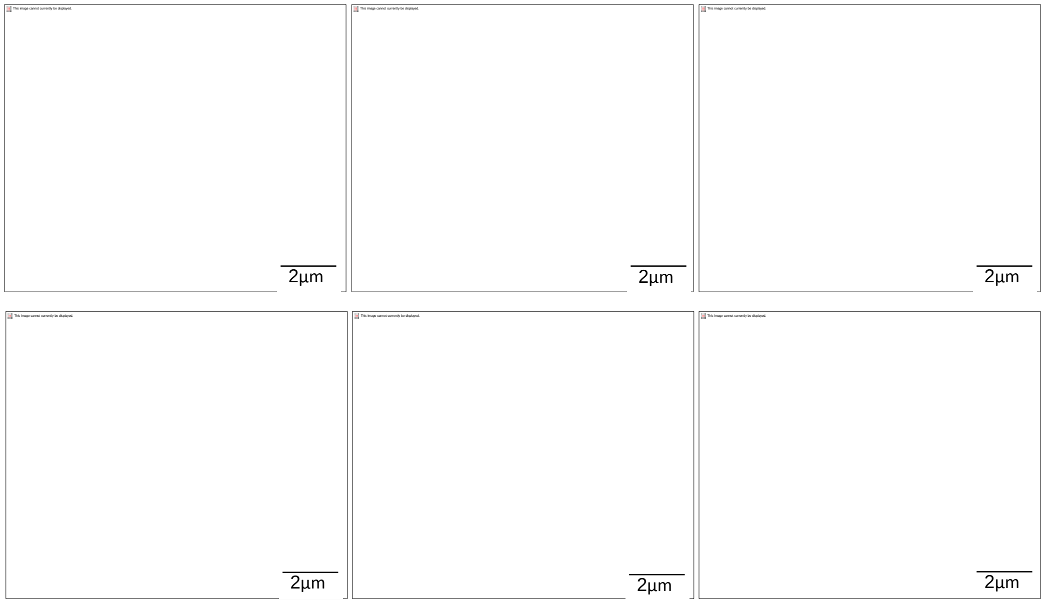
SEM thickness is observed thickness from SEM imaging

- Based on power fit equation:

$$W = a * t^b$$

- Used time dependent data out to 1000 hours
- Used ratio of thickness to weight change from SEM to determine approximate thickness of oxide after 1 year

H230 EDS Mapping (100ppm O_2, 1000 hrs)



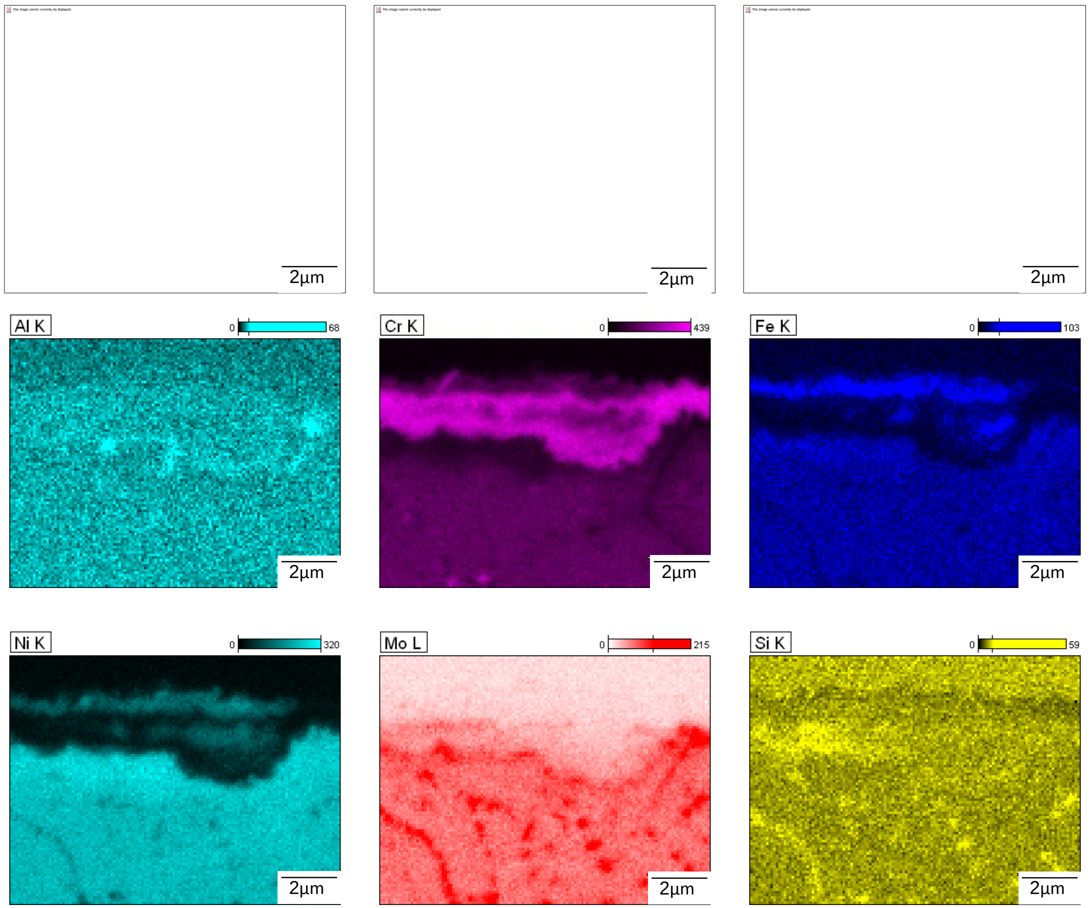
EDS cross sectional mapping of alloy Haynes 230 after 1000 hours of exposure to CO_2 doped with 100 ppm O_2 at 750ºC

Both the Boudouard reaction, and presence of oxygen suggest that testing at 750ºC doped with 100ppm O_2 is the most oxidizing environment that samples were exposed to.

- This would indicate that little or no carbon should be observed in the oxide.

- The presence of carbon in the EDS mapping above suggests that adding oxygen does not completely stop the deposition of carbon during the oxidation process.
- Increase in chromium along grain boundary suggests presence of chromium carbide.
- Void formation and chromium depletion zone observed in EDS scan.
- Formation of Iron oxide and increase Al concentration observed in EDS mapping.

H625 EDS Mapping (100ppm O_2, 1000 hrs)

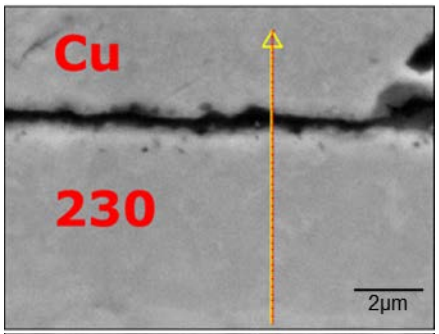


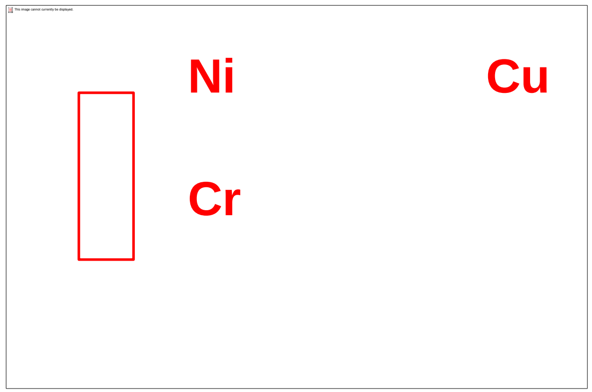
EDS cross sectional mapping of alloy Haynes 625 after 1000 hours of exposure to CO_2 doped with 100 ppm O_2 at 750ºC

- Carbon observed throughout the oxide
- Concentration of Fe, Ni, Al increases in oxide
- Increase in Mo along grain boundaries
  - Depletion of Ni, Cr, Fe
- Very thick oxide compared to RG conditions

EDS Line Scans of H230 Exposed to RG vs 100ppm Doped CO_2 (1000 hours) 750ºC

RG CO_2

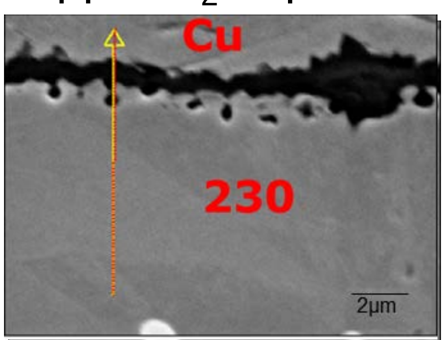


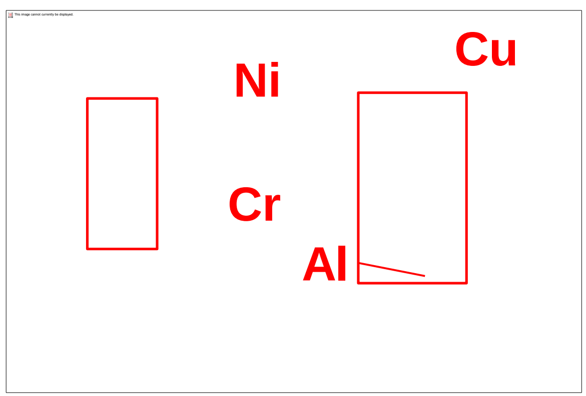


Sample exposed to RG CO_2 showed no observable chromium depletion zone.

Chromium depletion zone for oxygen doped exposure in red box on right.

100ppm O_2 doped CO_2



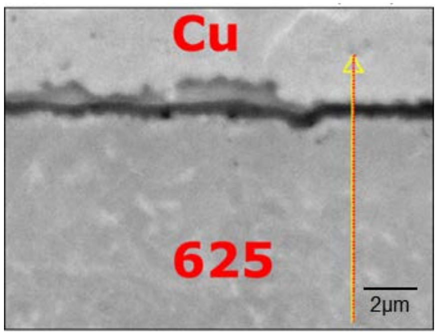


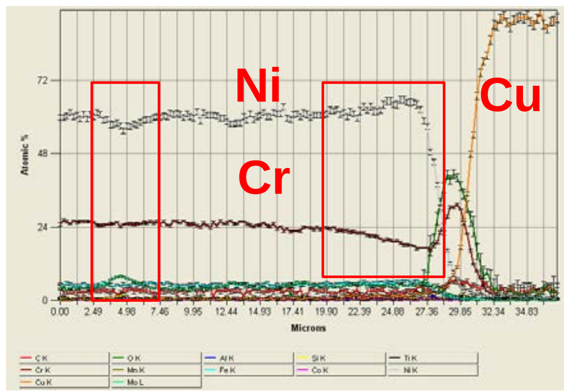
Chromium carbides found in both samples (indicated by red boxes on left side of both line scans).

Spike in Al concentration could be either Ni_3Al, or Al_2O_3.
bonding structure unknown

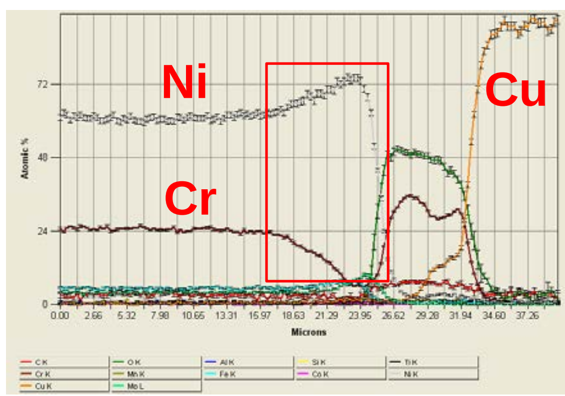
EDS Line Scans of H625 Exposed to RG vs 100ppm Doped CO_2 (1000 hours) 750ºC

RG CO_2





100ppm O_2 doped CO_2



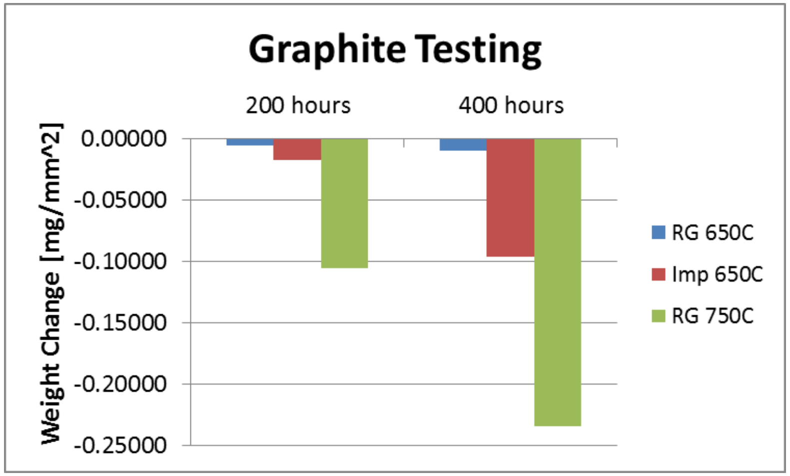
Sample exposed to RG CO_2 had much smaller chromium depletion zone.

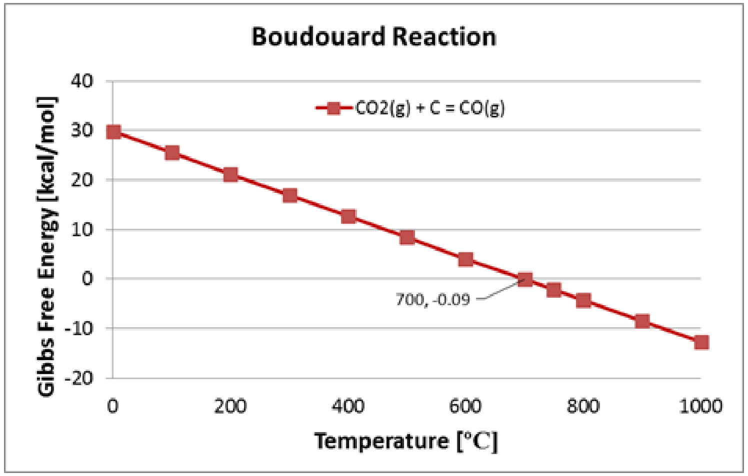
Chromium concentration near zero at oxide-metal interface for doped case

- Chromium diffusion is limiting the formation of oxide on the surface

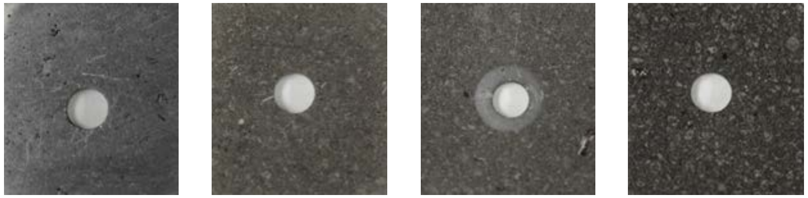
Molybdenum carbides found in both samples (indicated by red box on left side of top line scan, and slide 11 for doped case).

Graphite Testing





Untested	400 hours at 650ºC RG	400 hours at 650ºC O2 IMP	400 hours at 750ºC RG



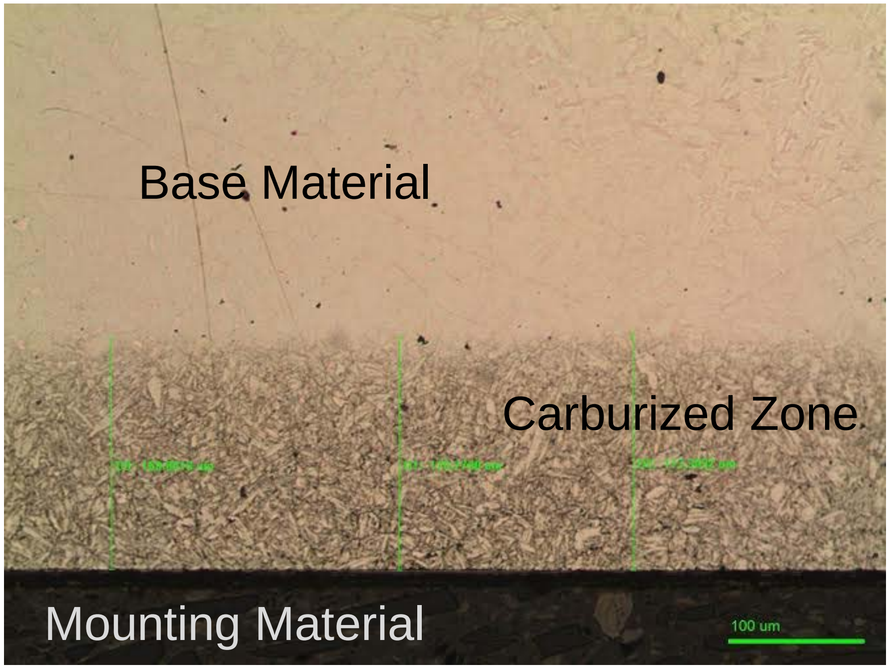
Images of Graphite samples displaying different surface roughness based on testing conditions.

The Boudouard Reaction (top right) becomes thermodynamically favorable (negative ΔG) at 700ºC.

Weight change measurements (top left) show that the reaction rate of the Boudouard Reaction occurs on a time scale that is significant in testing conditions.

Carburization of Ferritic Steel (T92)

Etched T92 sample exposed to research grade CO_2 for 600 hours at 450ºC

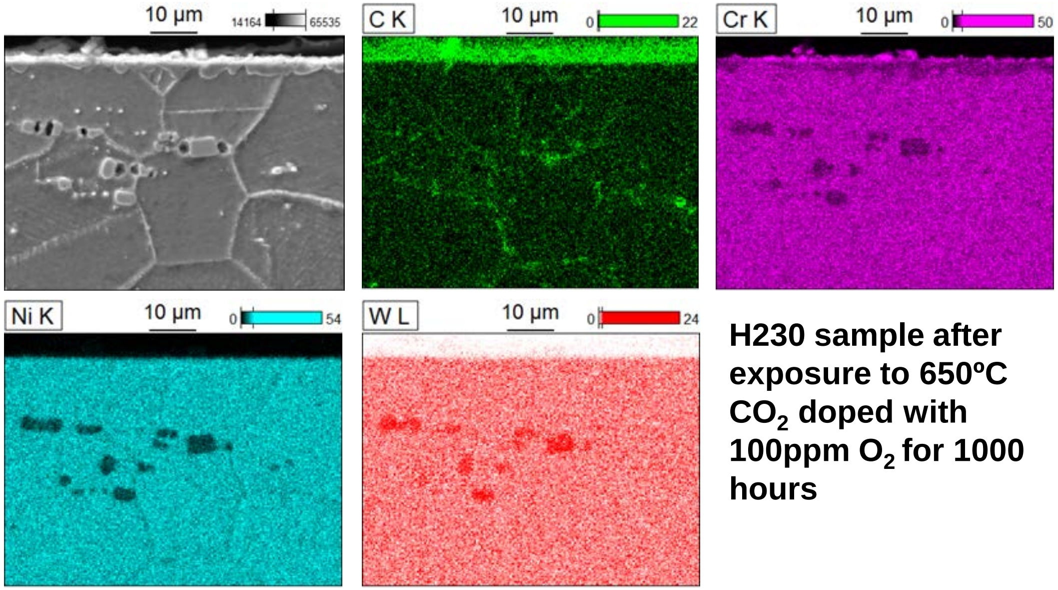


- Three oxide layers: hematite, magnetite, Fe/Cr spinel
- Carburization roughly 180 µm beneath oxide
- Spinel layer grows from voids left from Fe diffusion
- Micro-environments underneath oxide produce high CO/C activity[1]

	C	Mn	Fe	Si	Cu	Ni	Cr	Al	Ti	V	Mo	Nb	W	S	Al	P	B	N
T92	.12	.45	Bal	.1	-	.21	8.94	.016	-	.2	.5	.08	1.91	.003	.016	.016	.001	.047

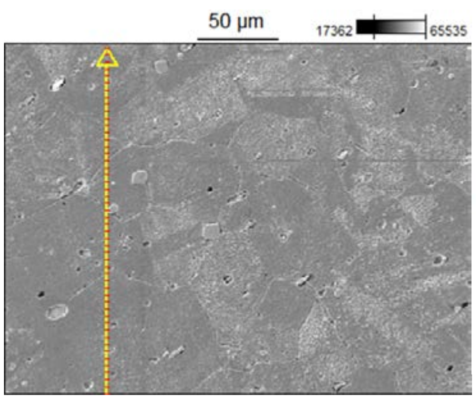
[1]Rouillard, F., and T. Furukawa. "Corrosion of 9-12Cr Ferritic–martensitic Steels in High-temperature CO2." Corrosion Science 105 (2016): 120-32.

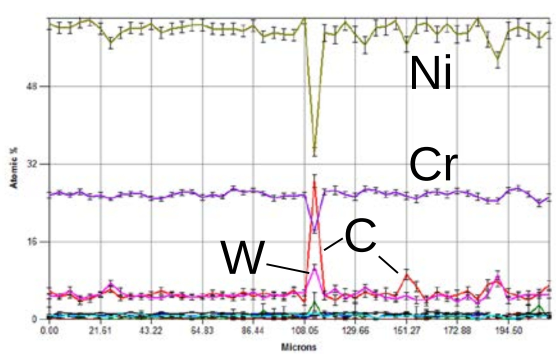
Carbide Formation along Grain Boundaries



H230 sample after exposure to 650ºC CO_2 doped with 100ppm O_2 for 1000 hours

-Untested H230 sample





Since carbon is observed in EDS after the oxidation process, samples were etched to make carbides visible.

- Tungsten carbides observed in EDS (on the left) have been observed on untested H230 samples.
- Visible grain boundaries indicate carbide formation.

An untested sample (bottom left) also showed carbides along the grain boundaries.

*Carburization is not greatly effected by CO_2 exposure, but rather a result of alloy creation (.1% C in base material).

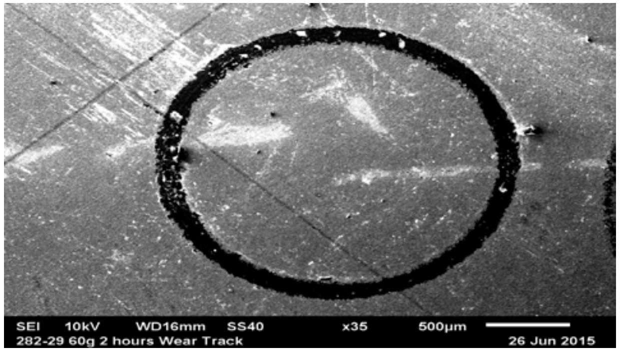
Conclusions

1. Corrosion testing at University of Wisconsin has been completed for ferritic, austenitic and nickel based superalloys. The focus of this study was on Haynes 230 and Haynes 625 exposed to research grade CO_2 and 100ppm O_2 doped CO_2.
2. Samples exposed to research grade CO2 produced protective uniform chromium rich oxides.
3. Samples exposed to 100ppm oxygen doped CO2 showed significantly higher oxidation rates, as well as production of Fe and Ni rich oxides.
4. Aluminum was observed beneath the oxide layer, and believed to be either Ni_3Al or Al_2O_3. More work needs to be completed to determine bonding structure.
5. Fast diffusion rates in the oxygen doped cases resulted in chromium depletion, and void formation beneath the oxide described by the Kirkendall Effect.
6. Carbides were found in both tested and untested samples in all conditions. Further testing needs to be completed to determine the magnitude of carburization. Less significant than iron-chromium rich alloys.

Future Work

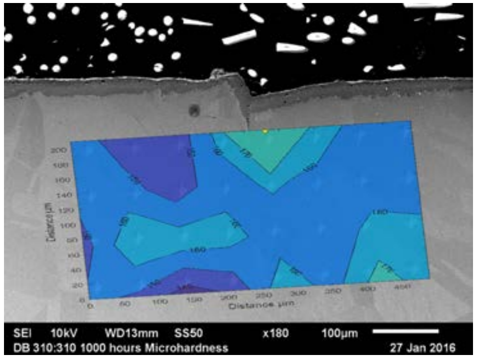
- Completed 1000 hours of testing for 10ppm oxygen doped CO2.
- Use XPS analysis to determine composition as a function of depth throughout thinner oxides.
- Use TEM EELS analysis to determine composition through oxide and base material.
- SCC, tensile testing, wear track analysis, diffusion bonding, CO impurities testing

Haynes 282



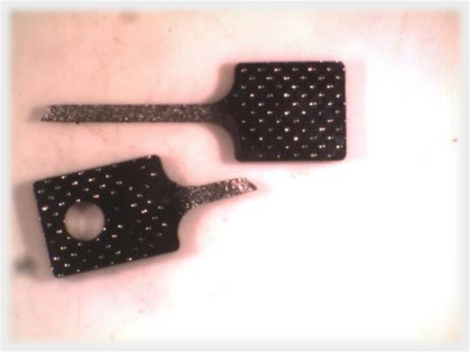
750C RG CO2 600 hr

DB 310:310



1000 hours 650C RG

Haynes 282



Untested: Baseline

Acknowledgments

This work is supported by NREL Subcontract No. AXL-3-23308-01, under DOE Prime Contract No. DE-AC36-08GO28308 to Alliance for Sustainable Energy, LLC, Management and Operating Contractor for the National Renewable Energy Laboratory and Cooperative Agreement DE-NE0000677 from the U.S. Department of Energy, Idaho Operations.

The authors gratefully acknowledge the support of Department of Energy Nuclear Energy University Program (NEUP) Grant No. DE-NE0000677 for this work.