Corrosion of Nickel-Base Alloys in Supercritical CO_2 Environment

David Adam
Jacob Mahaffey
Arjun Kalra
Dr. Mark Anderson
Dr. Kumar Sridharan

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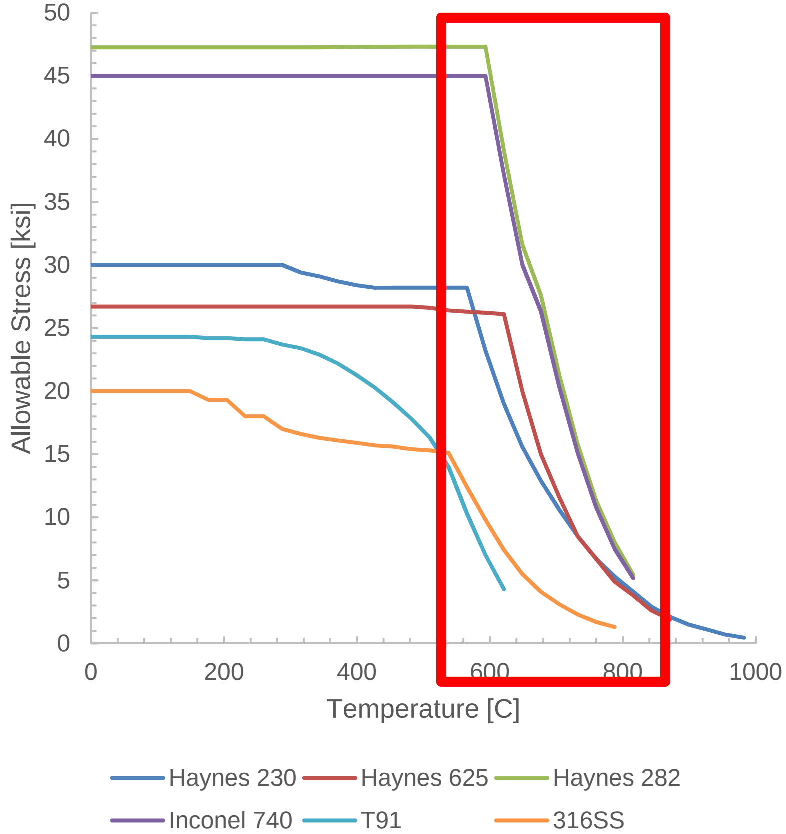
Outline

- Motivation/Background
- Testing Facility and Procedure
- Results
- Discussion
- Conclusions

Motivation/Background

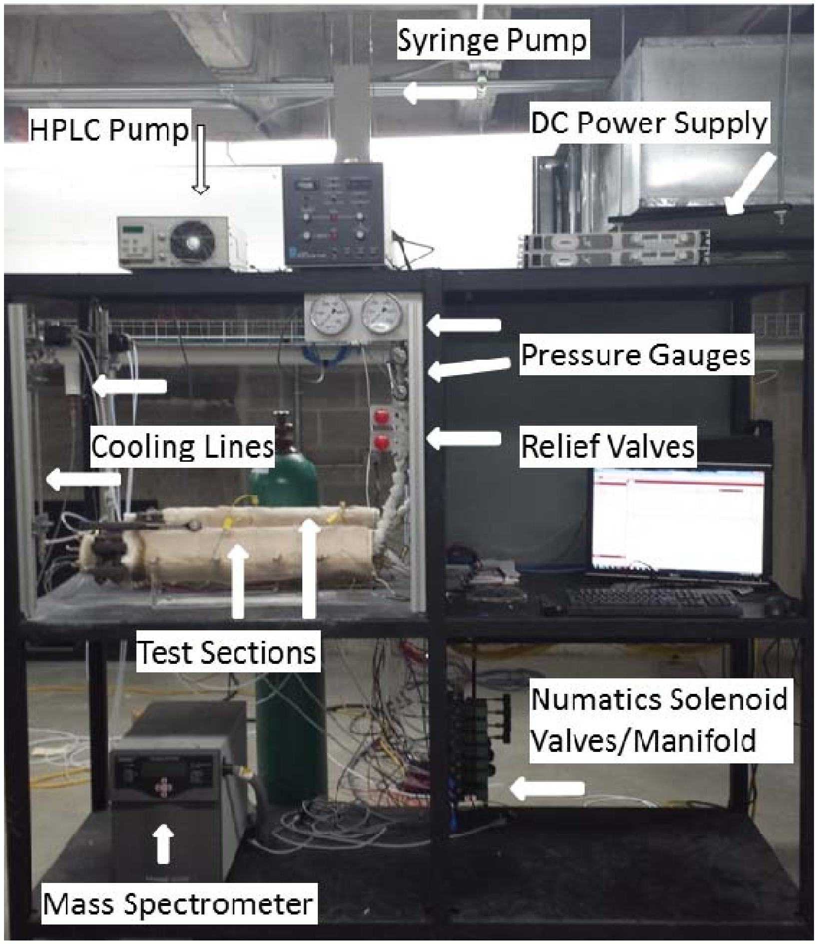
Allowable Stresses for Alloys of Interest



Estimated Data for IN740, Haynes 282 from:
Weitzel, P., Steam Generator for Advanced Ultra Supercritical Power Plants 700C to 760C, Proceedings of the ASME 2011 Power Conference July 12-14, 2011, Denver, Colorado, USA

- High temperature, high pressure conditions of SCO_2 Brayton cycle environments require suitable materials
- Must understand corrosion phenomena to withstand these extreme environments
- Long-term corrosion can lead to:
  - Reduction in effective wall thickness
  - Reduction of thermal conductivity
  - Corrosion debris

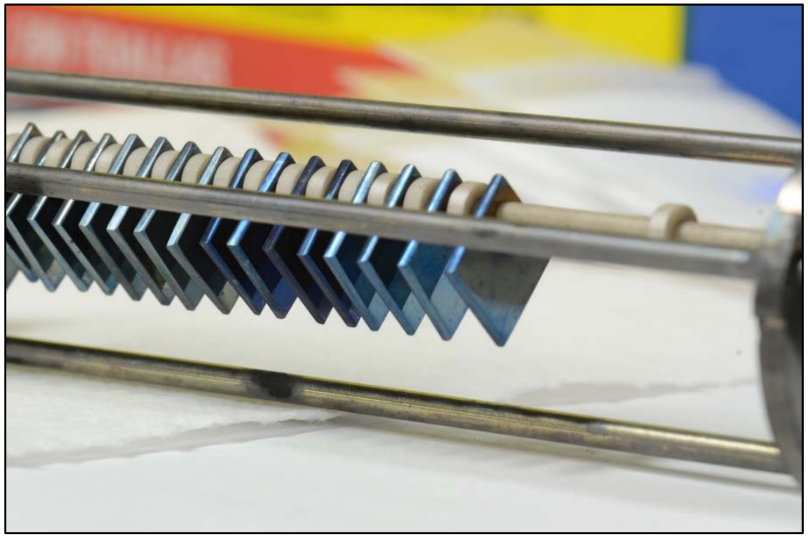
High Temperature, High Pressure SCO_2 Test Facility

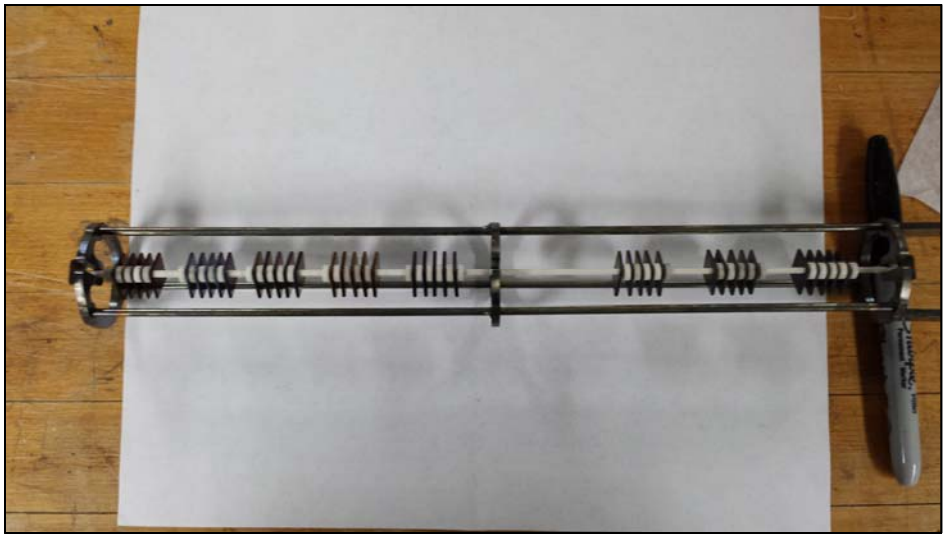


Current setup of test facility

- Testing temperature up to 750ºC
- Temperature control allows system to operate within ±1ºC
- Pressures up to 3600±2 psi (temperature dependent)
- System operates at an average flow rate of .11kg/hr
  - CO_2 refresh rate every two hours

Sample Holder with Samples





- 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

Testing Procedure

- Untested samples polished to 800 grit, then cleaned with ethanol and DI water
- Weight measurements are accurate to ± 2µg and dimensions have an accuracy of ± 2µm
- Samples are tested at 20 MPa and 450ºC-750ºC at 200 hour intervals up to 1000 hours
- Samples analyzed using SEM, EDS, XRD, etc.

Composition of Alloys by Weight %

	C	Mn	Fe	Si	Cu	Ni	Cr	Al	Ti	Co	Mo	Nb	W
IN740 (Special Metals)	0.023	0.245	0.1491	0.17	0.015	50.04	24.57	1.33	1.33	20.09	0.35	1.46	0.022
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
H625 (Haynes)	0.02	0.26	5	0.25		Bal~59.63	21.89	0.22	0.29	0.28	8.59	3.51	
H282* (Haynes)	0.06	0.3	1.5	0.15		57	20	1.5	2.1	10	8.5		
Ni-20Cr*						80	20						

* - nominal composition

Trace Elements:

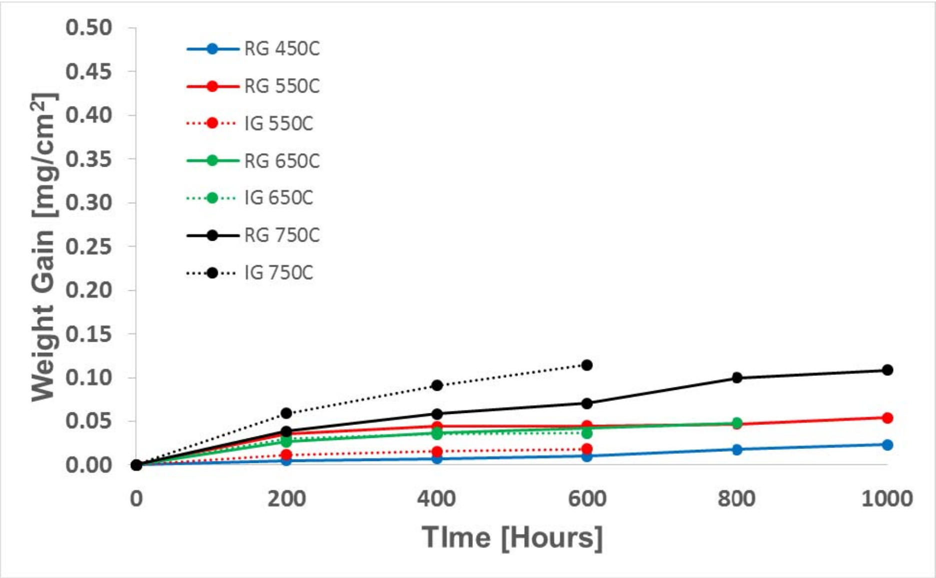
Alloy	S	Ta	P	B	N	V	Zr	La
IN740	0.003	0.004	0.0023	0.0013	0.0038	0.012	0.021	
H230	0.002			0.002				0.012
H625	0.002	0.05	0.006					

Research and Industrial Grade CO2 Gas Certificates

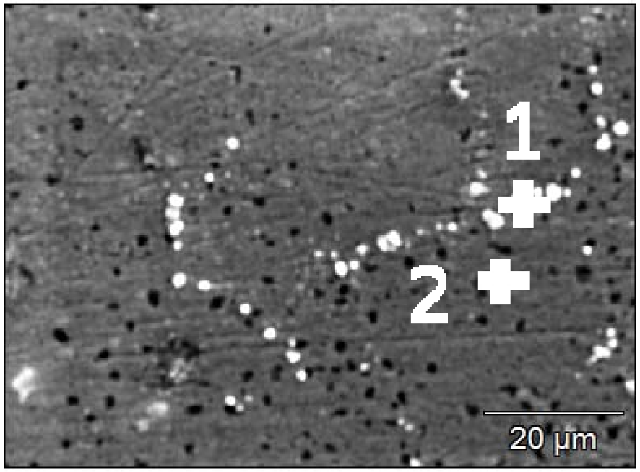
	Research Grade CO_2	Industrial Grade CO_2
Component	**Purity Limits**	**Purity Limits**
CO_2	99.999%	99.5%
$Ar+O_2+CO$	<1 ppm	<50 ppm
Total Hydrocarbons	<1 ppm	<50 ppm
Moisture	<3 ppm	<32 ppm
Nitrogen	<5 ppm	

Gas analysis has been conducted by third party

Haynes 230 Weight Change Data



Highest weight gain for each temperature		
	IG	RG
550°C		√
650°C		√
750°C	√	

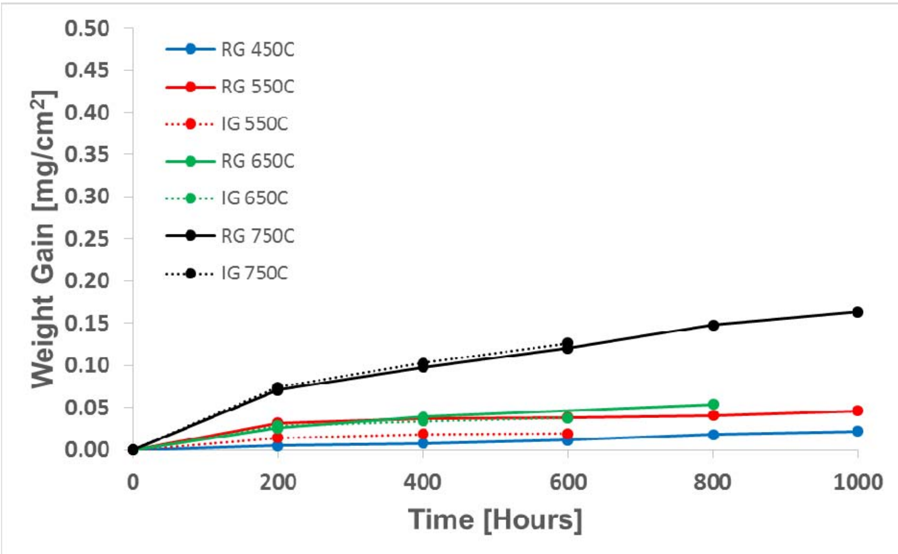


	Pt. 1	Pt. 2
Cr	64.42	48.94
Mn	**20.91**	**2.88**
Fe		1.03
Ni	9.52	41.38
Mo	4.12	1.26
W	0.5	4.33

Atomic Percent

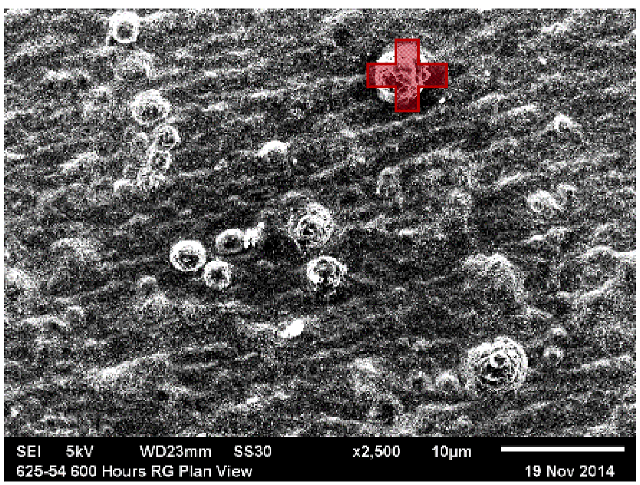
- Overall highest weight gain: 750°C IG
- Uniform chromia with Mn/Mo oxide clusters present

Haynes 625 Weight Change Data



Highest weight gain for each temperature		
	IG	RG
550°C		✓
650°C	Similar	Similar
750°C	Similar	Similar

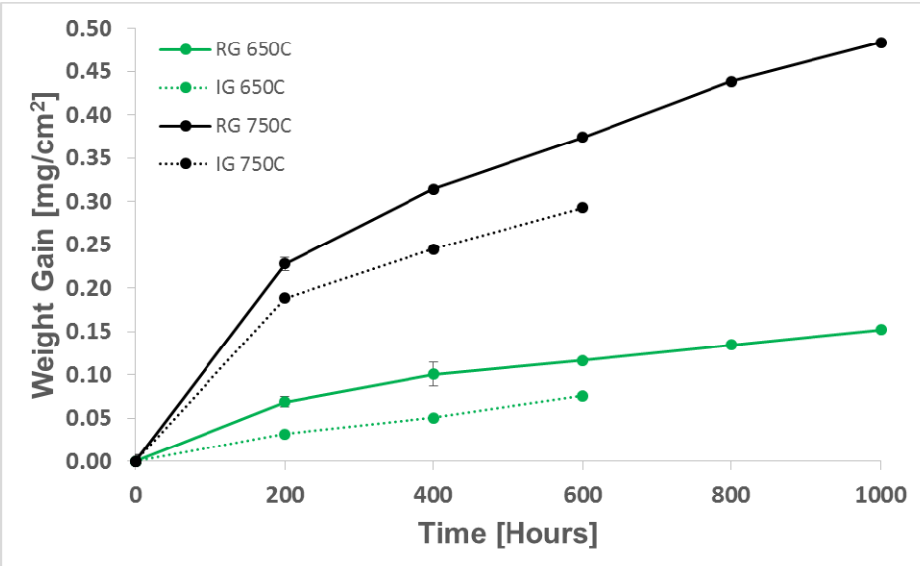
- Overall highest weight gain: 750°C RG
- Very little difference between 650°C RG, and 650°C IG
- Very little difference between 750°C RG, and 750°C IG
- Uniform chromia with Ti/Mn oxide clusters present



	Point
Ti	**24.95**
Cr	63.24
Mn	**4.06**
Ni	5.99
Nb	0.32
Mo	0.98

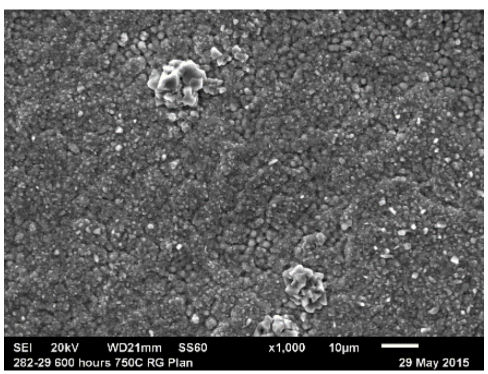
Atomic Percent

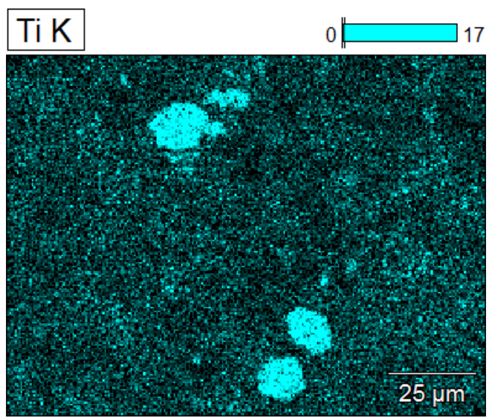
Haynes 282 Weight Change Data



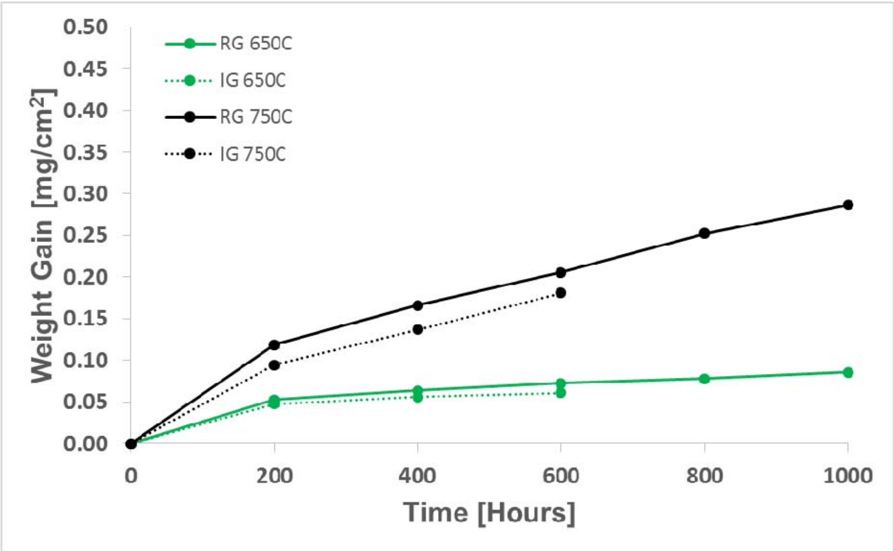
Highest weight gain for each temperature		
	IG	RG
650°C		✓
750°C		✓

- Overall highest weight gain: 750°C RG
- Uniform chromia with Ti oxide clusters present
- Highest weight gain of all alloys at 750°C



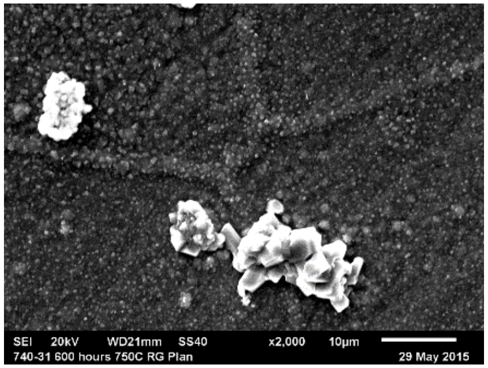


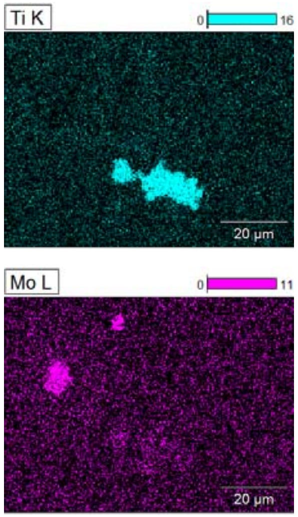
Inconel 740 Weight Change Data



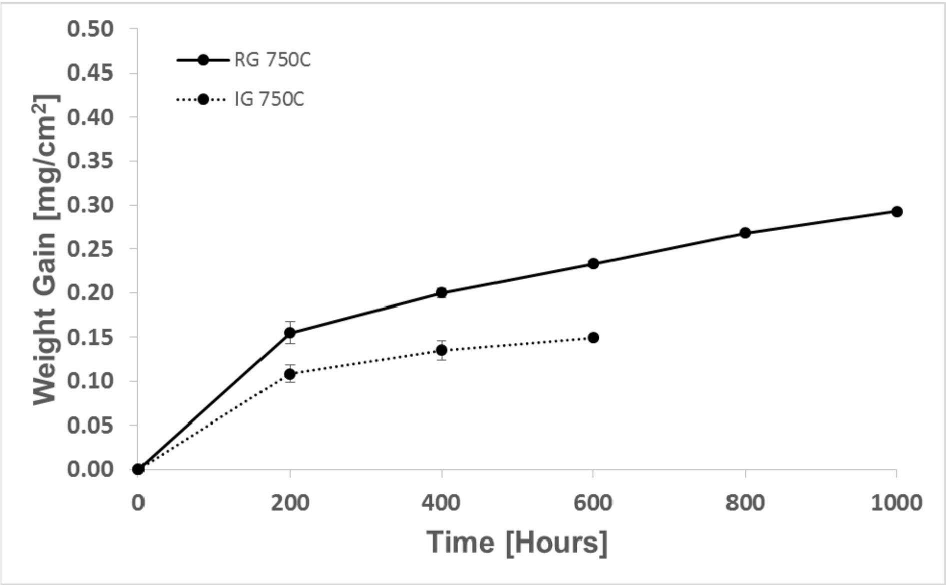
Highest weight gain for each temperature		
	IG	RG
650°C		✓
750°C		✓

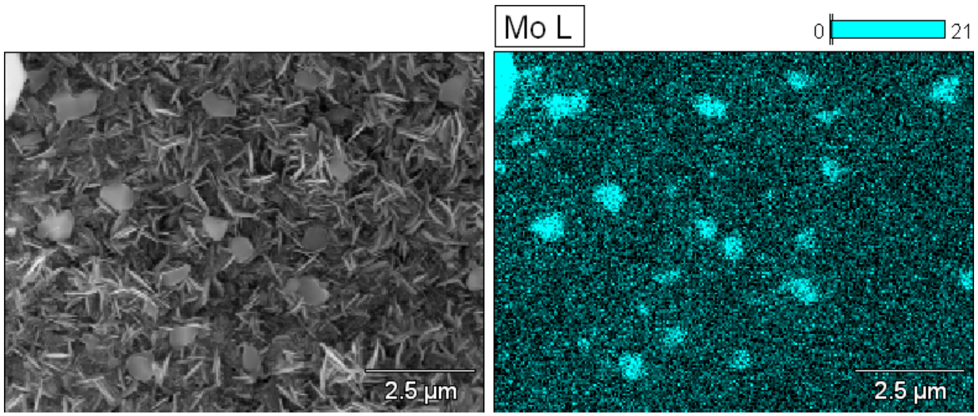
- Overall highest weight gain: 750°C RG
- Uniform chromia with Ti/Mo oxide clusters present
- Increased corrosion along grain boundaries





Ni-20Cr Binary Alloy Weight Change Data



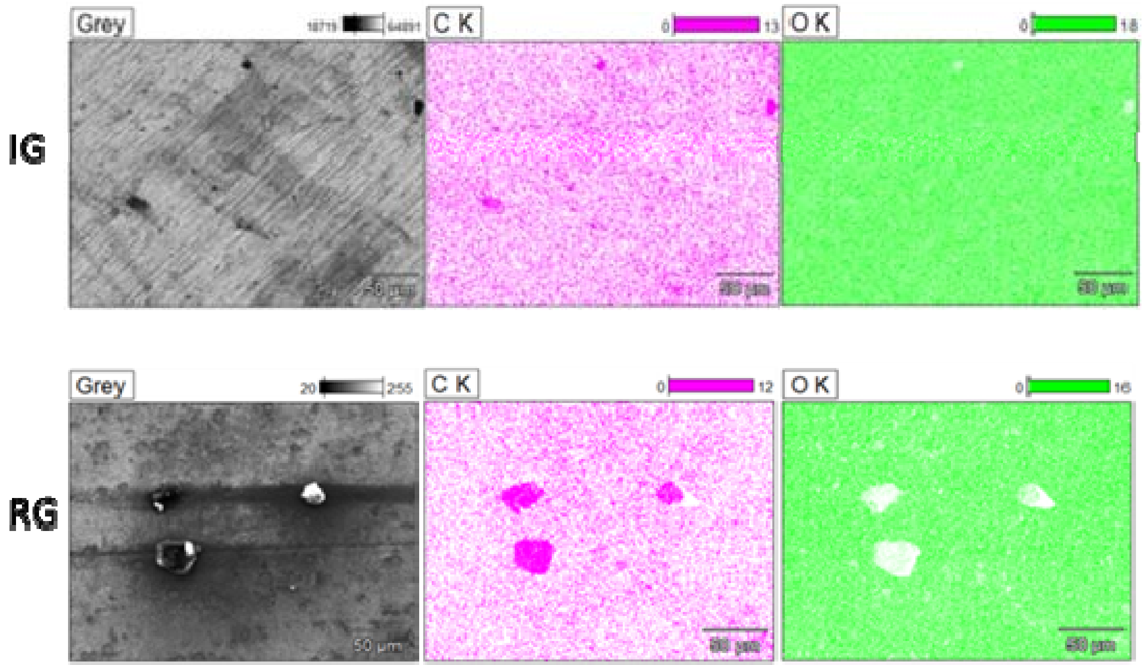


Highest weight gain for each temperature		
	IG	RG
750°C		✓

- Highest weight gain: 750°C RG
- Uniform chromia with Mo oxide clusters present
- Mo oxide clusters believed to be from volatilized Mo oxide from other samples or from Haynes 625 autoclave†

† - Smolik, G.R., Petti, D.A., Schuetz, S.T., (2000). "Oxidation, Volatilization, and Redistribution of Molybdenum from TZM Alloy in Air." Idaho National Engineering and Environmental Laboratory, INEEL/EXT-99-01353

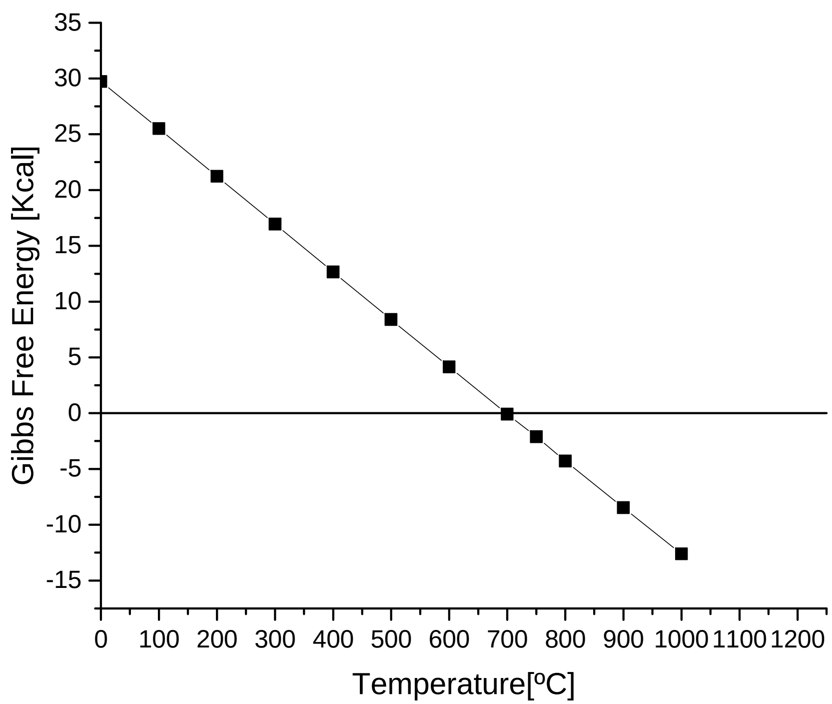
Surface SEM of H230 in IG/RG CO_2 after 400 hours at 650C



- Large carbon clusters observed on the surface of the sample tested in RG-CO_2
- Clusters reduced significantly for IG sample
- Caused by compositional differences in gas (O_2, N_2, H_2O, Hydrocarbons)
- Phenomena believed to be attributable to Boudouard reaction

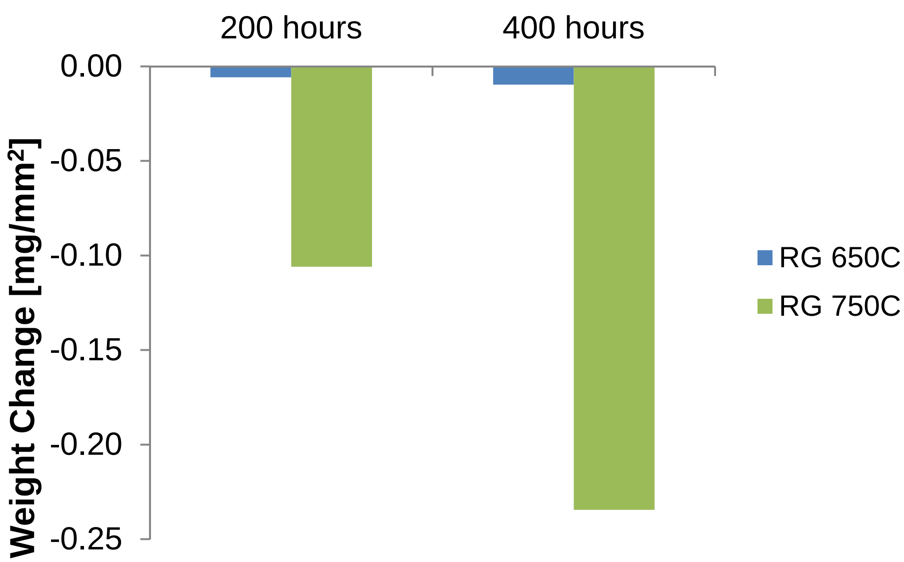
Gibbs Free Energy Diagram for Carbon Removal in Carbon Dioxide

$$CO_2 + C \rightleftharpoons 2CO$$



- HSC Chemistry used for thermodynamic modeling of Boudouard Reaction
- $CO_2 + C \rightarrow 2CO$ becomes thermodynamically favorable at 700ºC
- Reaction believed to be present in 750ºC testing, removing free carbon and thus impacting weight gain as seen in H230 and H625

Graphite Testing



- 750ºC graphite samples lost 15 times more weight than samples exposed to 650ºC CO_2
- 750ºC samples have 6 times the surface roughness than those exposed to 650ºC
- Carbon is removed from graphite at a much faster rate at temperatures above 700ºC

Surface Roughness Measurements [µm]			
	Untested Graphite	200 hrs at 650ºC	200 hrs at 750ºC
Average	0.357	0.648	4.01
St-Dev	0.0808	0.222	1.02
Relative Roughness		1.82	11.2

Untested

200 hours at 750ºC

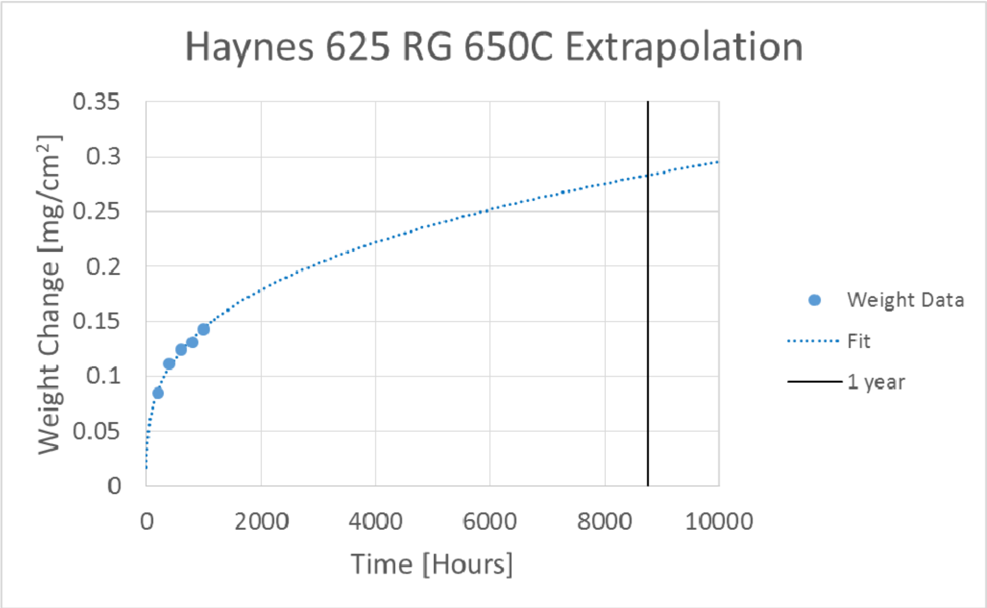
400 hours at 750ºC

Extrapolated Weight Gain

- Weight gain data fit using power law to give yearly extrapolated weight gain

$$W = a \cdot t^n$$

  - W = weight change [mg/cm^2]
  - a = pre-exponential factor
  - t = time [hours]
  - n = growth parameter



Extrapolated Oxide Thickness

- Method to evaluate oxide thickness of alloys investigated
- Calculation of effective oxide density:

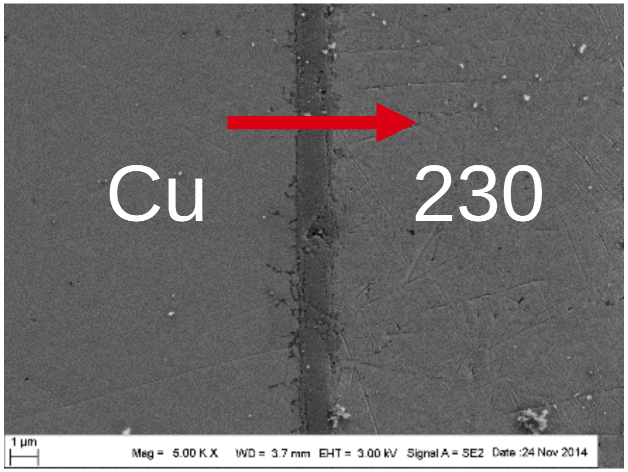
$$\text{Effective Oxide Density} = \frac{\text{Experimental Weight Change}}{\text{Experimental Oxide Thickness}}$$

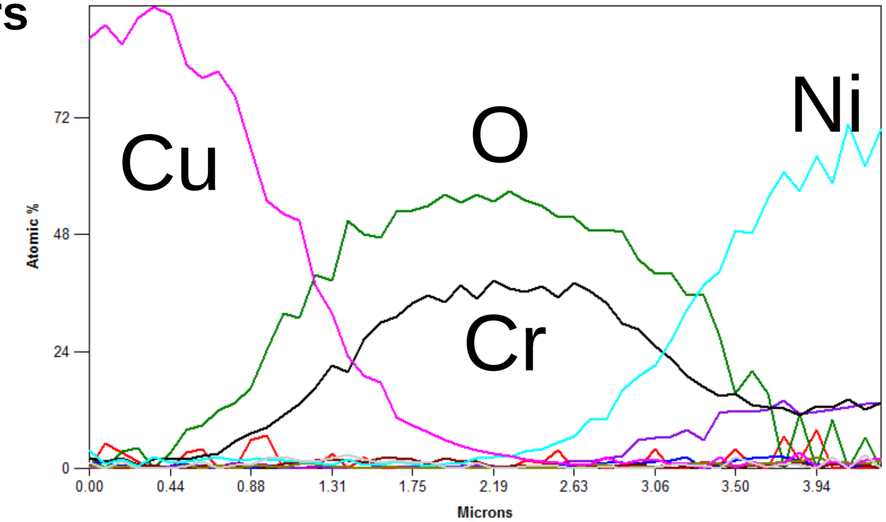
- Use effective oxide density to calculate extrapolated oxide thickness

$$\text{Extrapolated Thickness} = \frac{\text{Extrapolated Weight Gain}}{\text{Effective Oxide Density}}$$

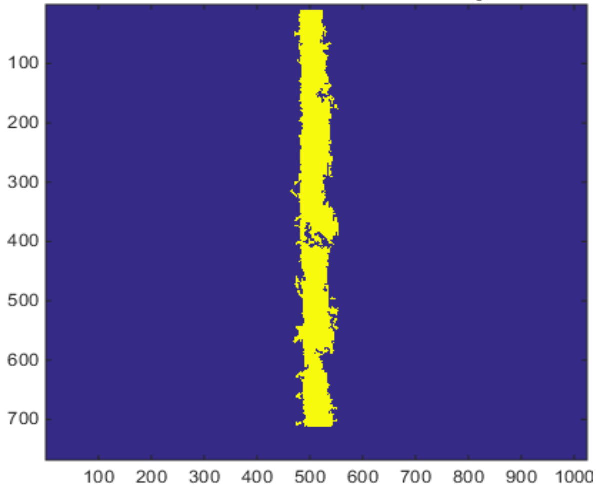
Effective Oxide Density Calculation

Haynes 230, 650ºC RG SC-CO_2, 600 hours





Processed Image



Example:

From Processed Image: 0.799 ± 0.123 µm

Weight Gain of H230: 1.23 µg/cm^2

Effective Density of H230: 1.54 g/cm^3

Averaging across all 230 and 625 alloys,

Effective Density: 1.79 ± .25 g/cm^3

Effective Oxide Thickness for Example: 0.573 µm/year

Effective Oxide Density Discussion

- Chromia assumed to be only numerically significant contributor to oxide weight and thickness
- Calculated effective oxide density much less than that of chromia (1.79 g/cm^3 effective vs 5.22 g/cm^3 theoretical)
  - Attributable to oxide porosity and cracking
- All alloys satisfied less than 30 [µm/year] at all conditions except IN740 at 750ºC IG
  - Data for IN740 at only 750ºC IG available through 600 hours, could be power fit artifact
- Further investigations include alloy specific oxide thicknesses

Conclusions

Alloy	Oxide	Surface Features	Weight gain [mg/cm²] 1000 hours 750ºC RG	Yearly extrapolated thickness [microns] 750ºC RG	Presence of Carbon
H230	Chromia	Mn/Mo oxide clusters	0.1087*	10.3 at 450ºC RG	RG 650ºC
H625		Ti/Mn oxide clusters	0.1635*	4.99 at 750ºC IG	RG 650ºC
H282		Ti oxide clusters	0.4837*	10.6 at 750ºC RG	RG 650ºC
IN740		Ti/Mo oxide clusters	0.2863*	89.0 in at 750ºC IG	‡
Ni-20Cr		Mo oxide clusters	0.2929*	15.5 in at 750ºC RG	‡

- * - No spallation observed on any sample surfaces
- ‡ - presence of carbon not tested for in IN740 and Ni-20Cr

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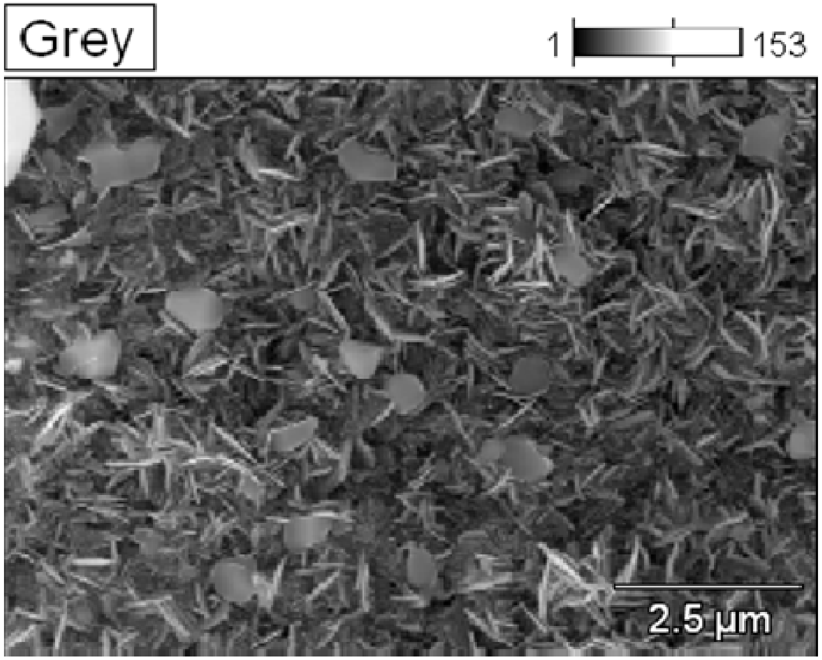
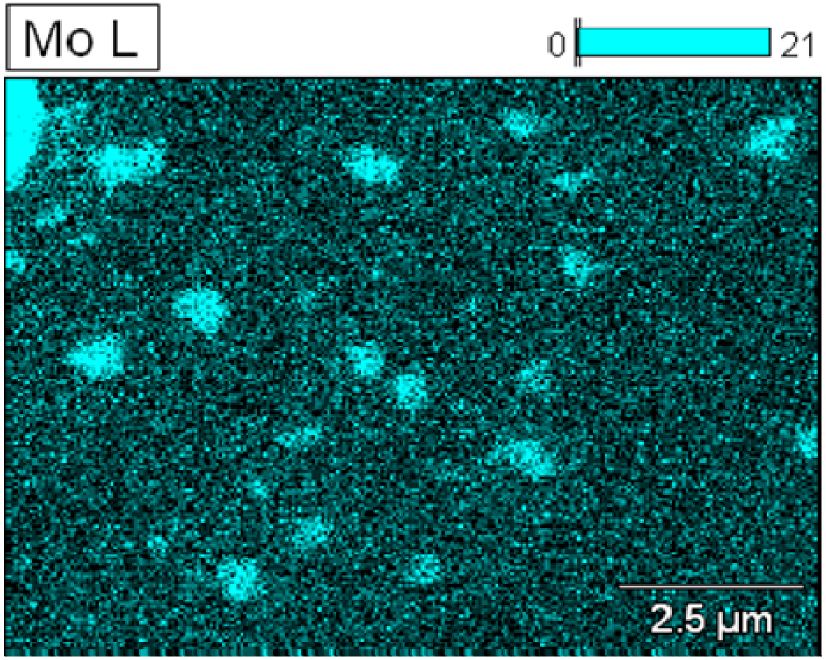
Backup Slides

Presence of Molybdenum on Ni-20Cr Alloys Exposed to CO2 at 750ºC





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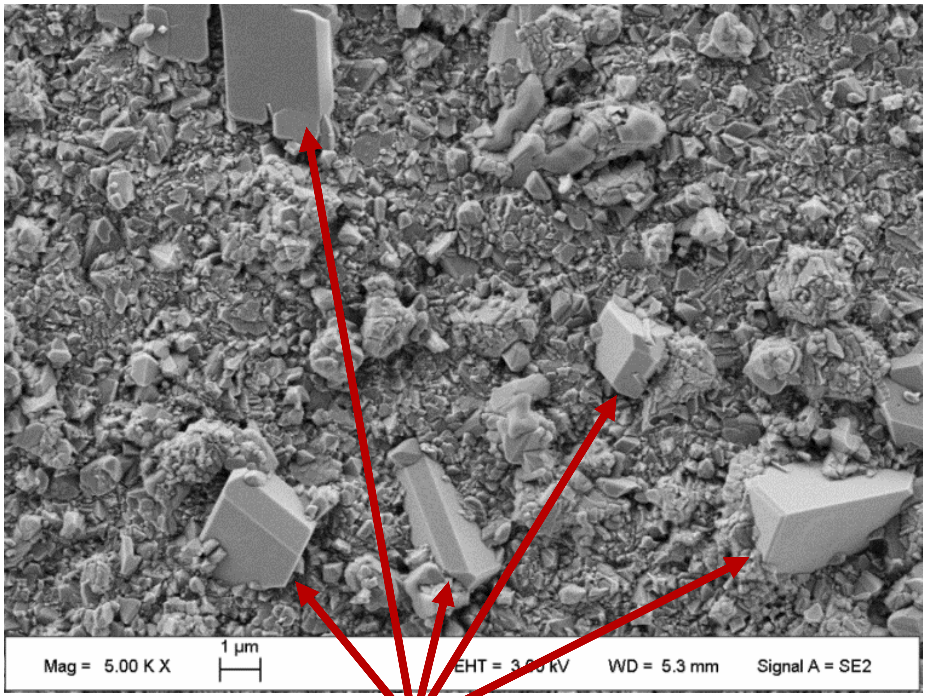
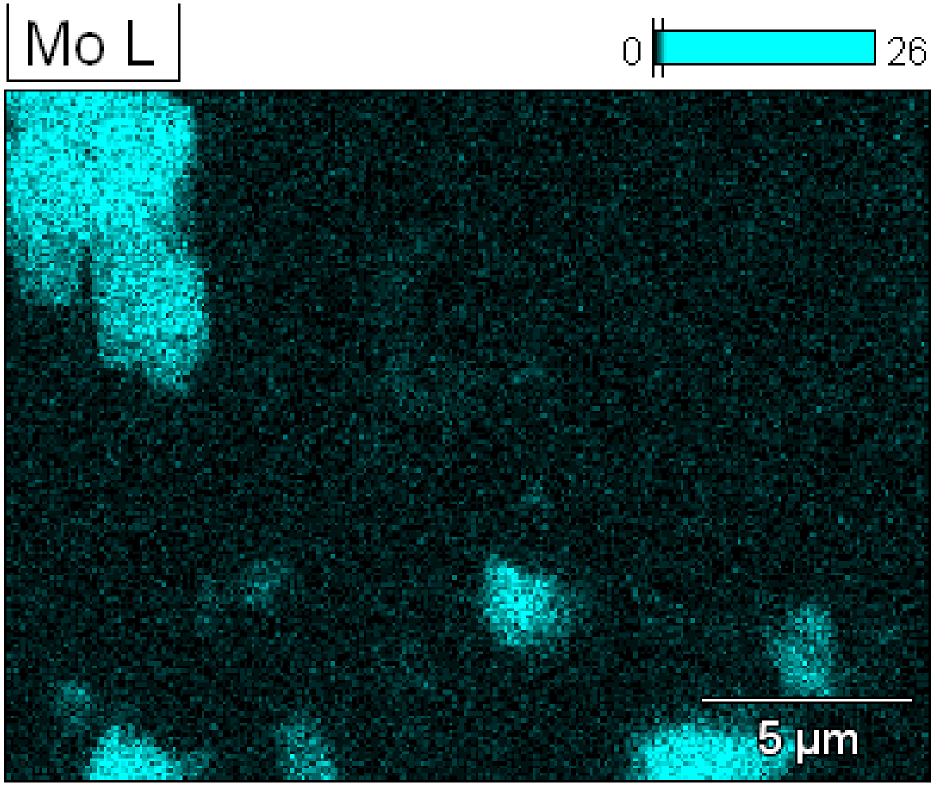
310SS (750ºC/1000hr) Moly Evidence





Molybdenum
Oxide

Trends observed through weight gains

450°C

	H230	H625
Notes	Similar weight change, less than 0.02 mg/cm^2 difference	

550°C

	H230	H625
Higher weight gain environment	RG-CO_2	RG-CO_2

650°C

	H230	H625	H282	IN740
Higher weight gain environment	RG-CO_2	RG-CO_2	RG-CO_2	RG-CO_2

750°C

	H230	H625	H282	IN740	Ni-20Cr
Higher weight gain environment	IG-CO_2	Similar	RG-CO_2	RG-CO_2	RG-CO_2

H230 vs H625

	H230	H625
Notes	Exhibited similar/lesser weight gain at 750°C than 650°C	

Research and Industrial Grade CO2 Gas Certificates

Airgas Certificates

	Research Grade CO_2	Industrial Grade CO_2
Component	**Purity Limits**	**Purity Limits**
CO_2	99.999%	99.5%
$AR+O_2+CO$	<1 ppm	<50 ppm
Total Hydrocarbons	<1 ppm	<50 ppm
Moisture	<3 ppm	<32 ppm
Nitrogen	<5 ppm	

Isotech Labs Analysis

Research Grade CO_2

Component	Chemical mol. %
Carbon Monoxide	nd
Helium	nd
Hydrogen	nd
Argon	nd
Oxygen	nd
Nitrogen	nd
Carbon Dioxide	100.00
Methane	nd
Ethane	nd
Ethylene	nd
Propane	nd
Propylene	nd
Iso-butane	nd
N-butane	nd
Iso-pentane	nd
N-pentane	nd
Hexanes +	nd

Industrial Grade CO_2

Component	Chemical mol. %
Carbon Monoxide	nd
Helium	nd
Hydrogen	nd
Argon	nd
Oxygen	nd
Nitrogen	nd
Carbon Dioxide	100.00
Methane	nd
Ethane	nd
Ethylene	nd
Propane	nd
Propylene	nd
Iso-butane	nd
N-butane	nd
Iso-pentane	nd
N-pentane	nd
Hexanes +	nd

*Limit of detection: 100 ppm

Trends observed through weight gains

450°C

- H230 and H625 exhibited similar weight gains in RG-CO_2 on the order of 0.02 mg/mm2 after 1000 hours of exposure

550°C

- H230 and H625 exhibited higher weight gains in RG-CO_2 compared to IG-CO_2

650°C

- H230, H625, H282, IN740 exhibited higher weight gains in RG-CO_2 compared to IG-CO_2

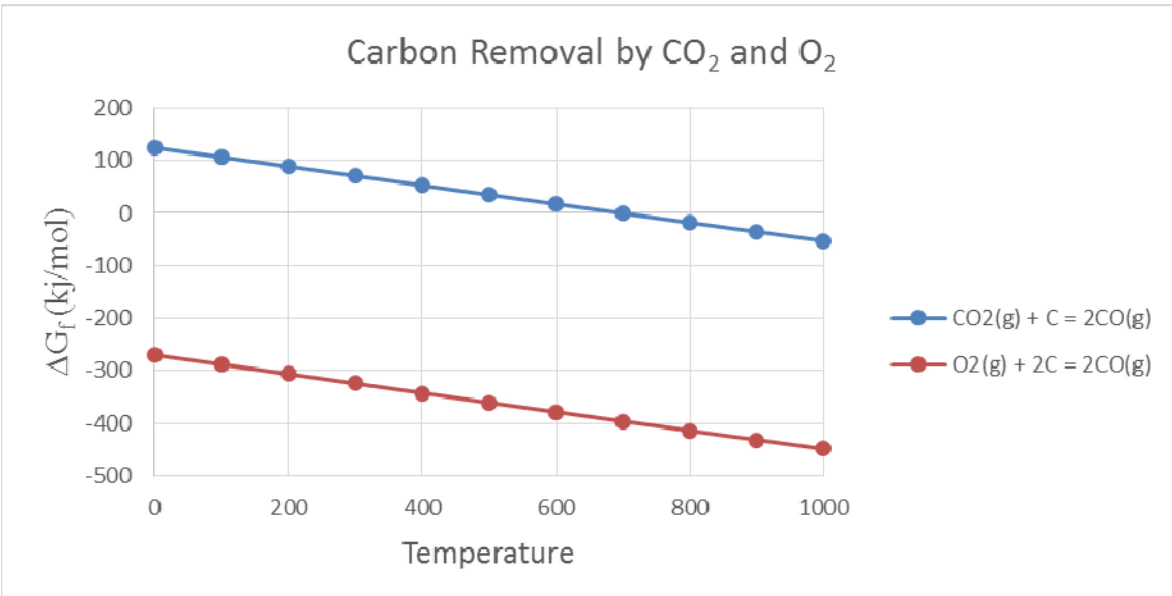
750°C

- H282, IN740, Ni-20-Cr exhibited higher weight gains in RG-CO_2 compared to IG-CO_2
- H625 exhibited similar weights gains between RG-CO_2 and IG-CO_2
- H230 exhibited lower weight gains in RG-CO_2 compared to IG-CO_2

H230 vs H625

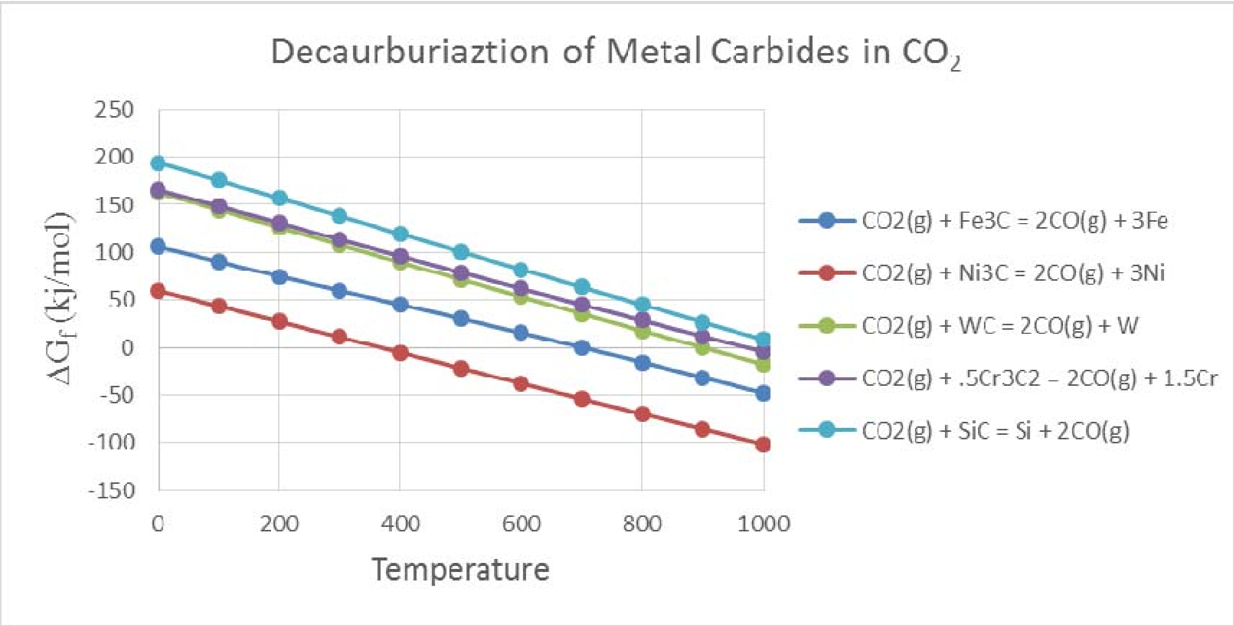
- H230 and H625 exhibited similar or lower weight gains at 750°C compared to 650°C for RG-CO_2

Gibbs Free Energy Diagrams for Carbon Removal in Carbon Dioxide and Oxygen



- HSC Chemistry thermodynamics modeling of the Boudouard Reaction
- Both CO_2 and O_2 can react with carbon
  - O_2 + C is a much more favorable reaction
  - CO_2 + C becomes thermodynamically favorable at 700ºC

Gibbs Free Energy Diagrams for Carbon Removal in CO2 and Metal Carbides



- Free carbon has been observed to form carbides along grain boundaries
- CO_2 can react with carbides to remove carbon
- Consistent with weight loss in SiC samples