Materials Corrosion in High Temperature Supercritical Carbon Dioxide

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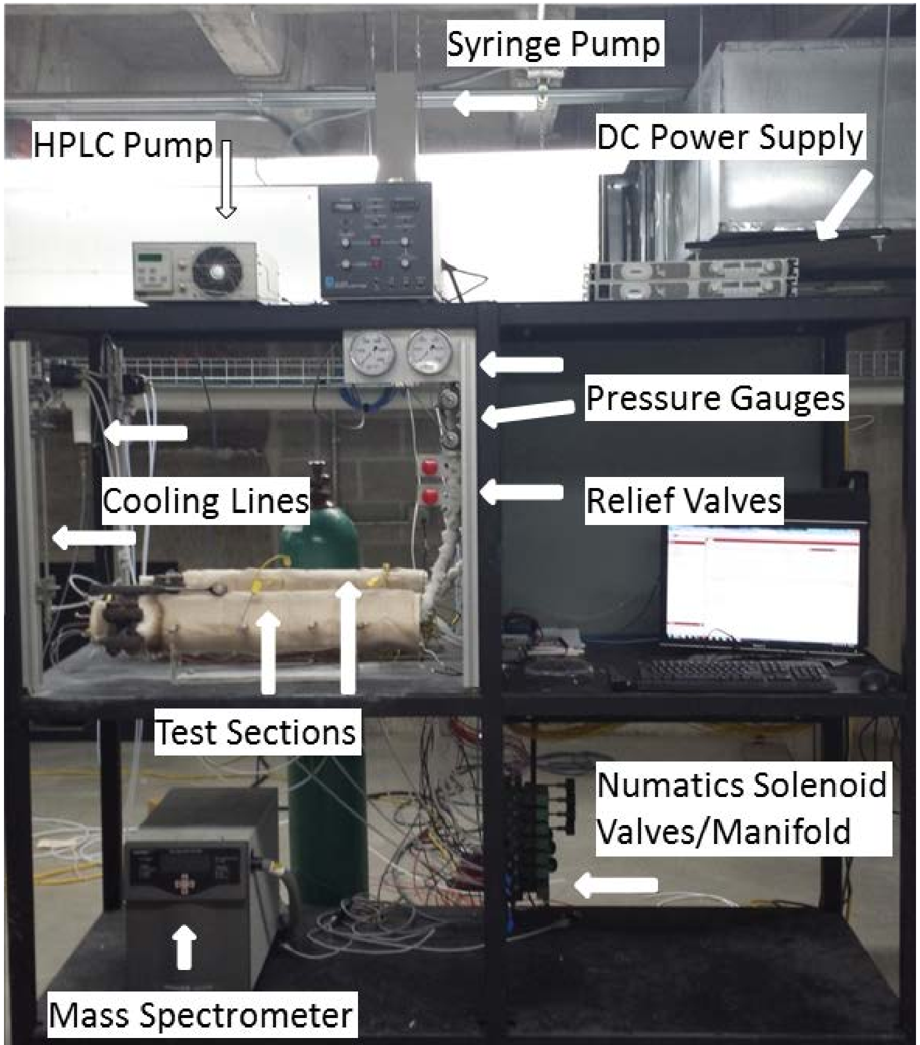
Outline

- Motivation/Background
- Construction of Testing Facility
- Procedure
- Gas Purity
- Sample Compositions
- Weight Gain Analysis
- SEM Images
- Ongoing/Future Work
- Conclusions

Background

- Long-term can corrosion can lead to:
  - Reduction in effective wall thickness
  - Reduction of thermal conductivity
  - Corrosion debris
- Previous work includes:
  - Research vs Industrial grade CO_2 corrosion testing
  - Temperature and time dependence of corrosion
  - Different alloy testing (Iron and Nickel based alloys, high temperature ceramic)
  - Surface treatments (Shot peening, Al/Y coatings)

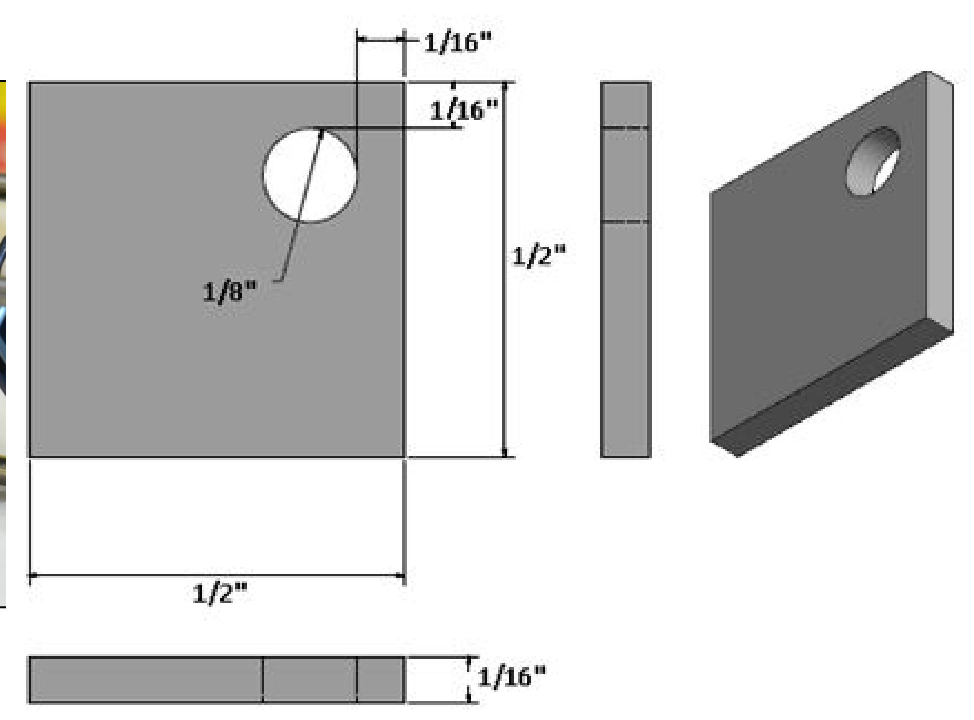
Testing Facility



Current setup of test facility

- Temperature control allows system to operate within ±1.5ºC
- Testing temperatures range from (up to 850ºC)
- Pressure can be held at 3600±2.5psi (temperature dependent)
- System operates at an average flow rate of .11kg/hr, which causes a CO_2 refresh rate every two hours

Sample Holder with Samples



- Made out of Haynes 625 alloy
- Alumina rod suspends samples in continuous stream of CO_2
- Alumina spacers separate samples from each other
- Fits roughly 70 samples total when full

Testing Procedure

- Samples polished to 800 grit, then cleaned with ethanol and DI water
- Autoclave cleaned and dried
- Samples are tested for 200 hour intervals out to 1000 hours
- Weight measurements are accurate to ± 2µg and dimensions have an accuracy of ± 2µm
- Finished samples are analyzed using SEM, EDS, XRD, ect

Research and Industrial Grade CO_2 Gas Certificates

Research Grade CO2	
Component	Purity Limits
CO2	99.999%
AR+O2+CO	<1 ppm
Total Hydrocarbons	<1 ppm
Moisture	<3 ppm
Nitrogen	<5 ppm

Industrial Grade CO2	
Component	Purity Limits
CO2	99.5%
Oxygen	<50 ppm
Total Hydrocarbons	<50 ppm
Moisture	<32 ppm
Non-Volatile Residue	<10 ppm

Gas samples have been sent out for ISBT analysis

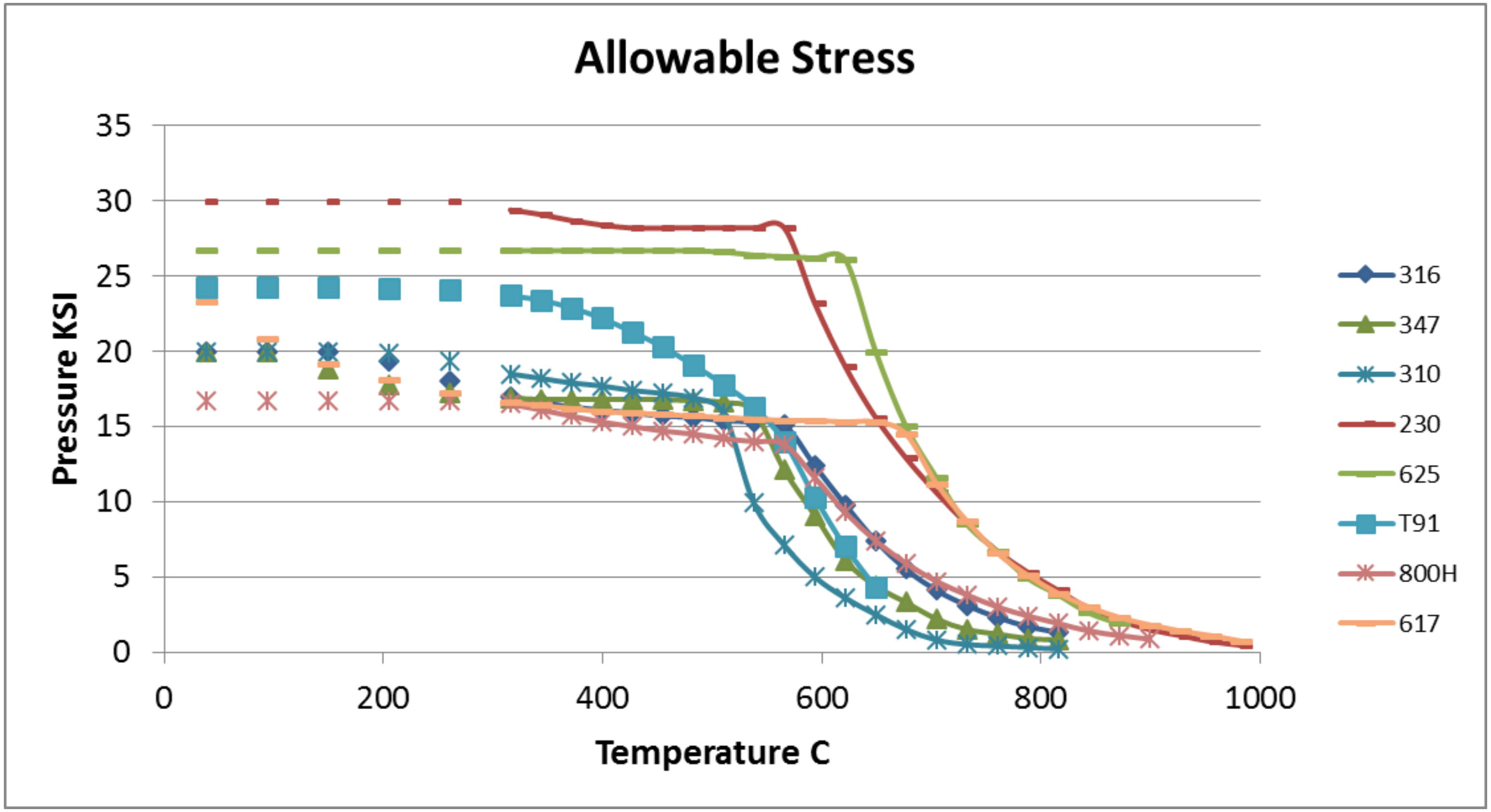
Tested Material Compositions

	Fe	Cr	Ni	Al	Mn	Nb	Cu	Mo	Si	C	W
347	Bal.	17.9	9.53	-	1.7	0.7	0.4	0.4	0.8	0.06	-
AFA-OC6*	Bal.	13.8	25	3.6	2	2.5	0.5	0.2	0.1	0.11	0.2
IN800H	Bal.	19.6	33.2	0.5	0.8	-	0.2	-	0.3	0.06	-

*AFA-OC6: Alumina-Forming Austenitic alloy developed at Oakridge National Lab

Other materials tested include: 230, 625, T92, Fe12Cr, T122, 310, 316, 617, 718, 282, 740, SiC, Ni-22Cr, AFA-OC7, AFA-OC10, PM2000

ASME Pressure Vessel Code Allowable Stress for Some Tested Alloys



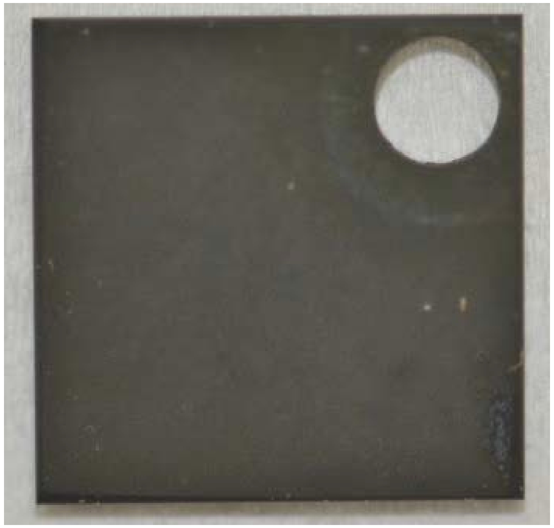
* Chart values based on annealed form of alloys

Bare Sample vs Tested Samples After 200 Hours

IN800H

347SS

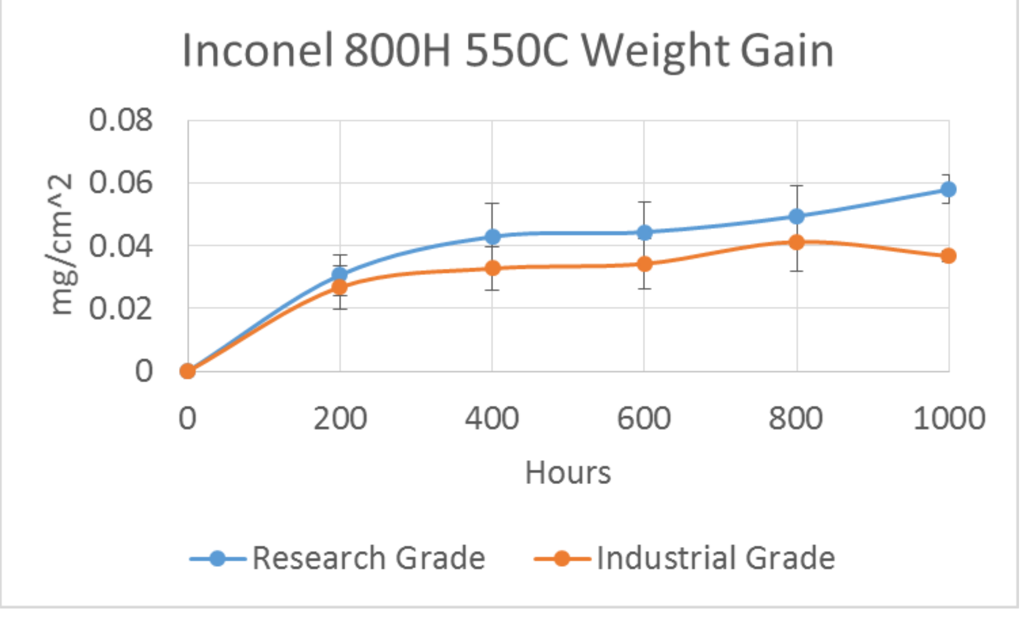
IN800H

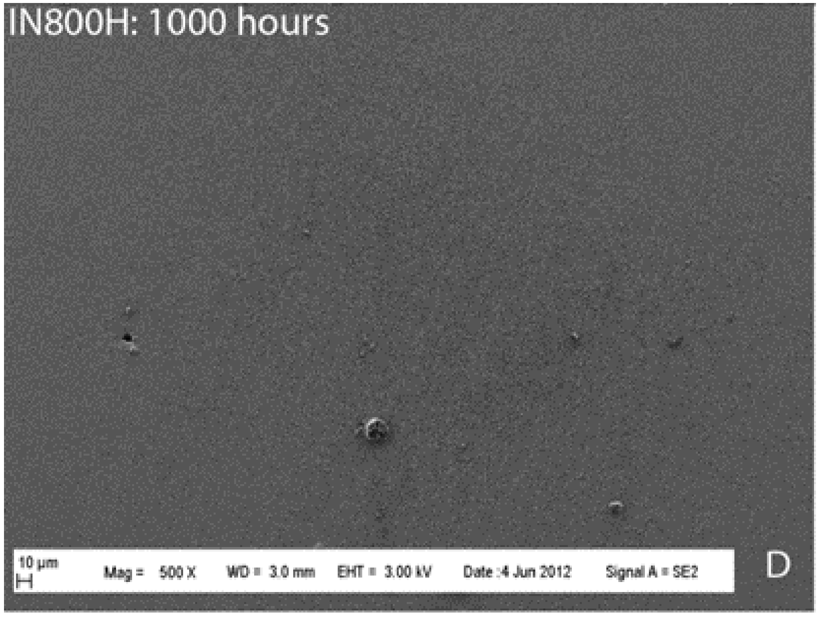


Before testing

After 200 hours of testing

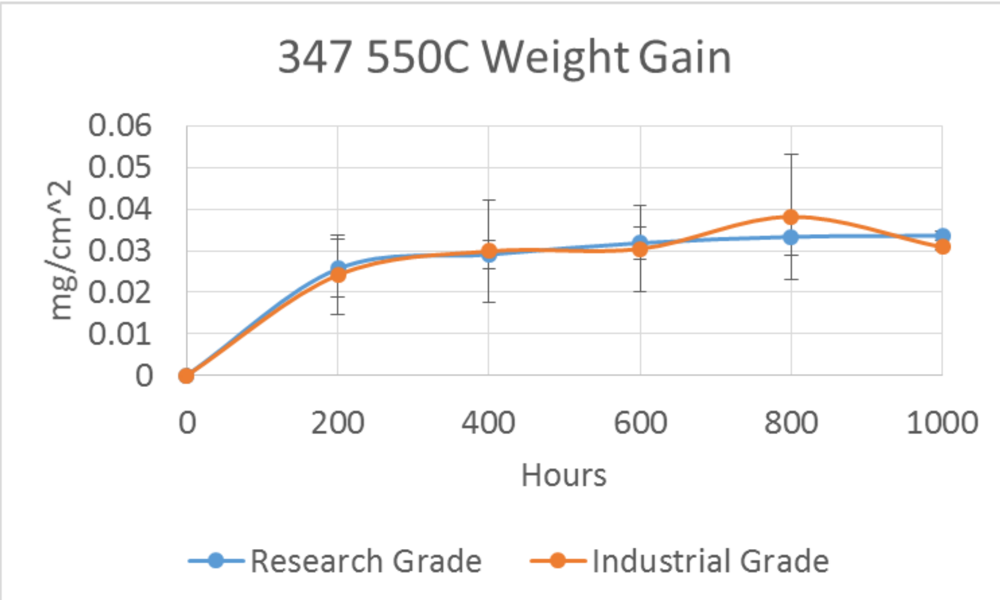
Inconel 800H

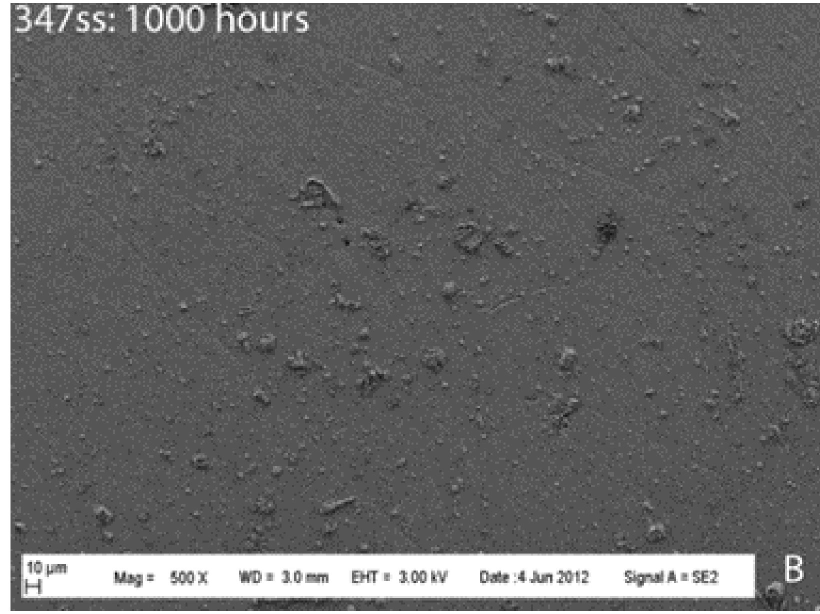




	T-Value	T-Crit (95%)	Conclusion
800H IG	6.211	4.303	TRUE
800H RG			

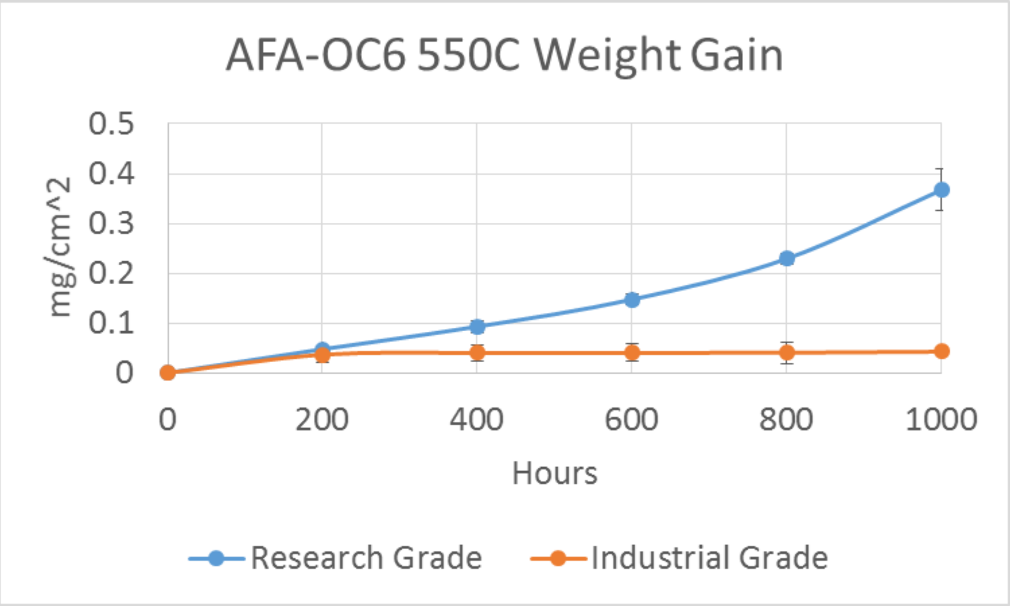
347 Stainless Steel

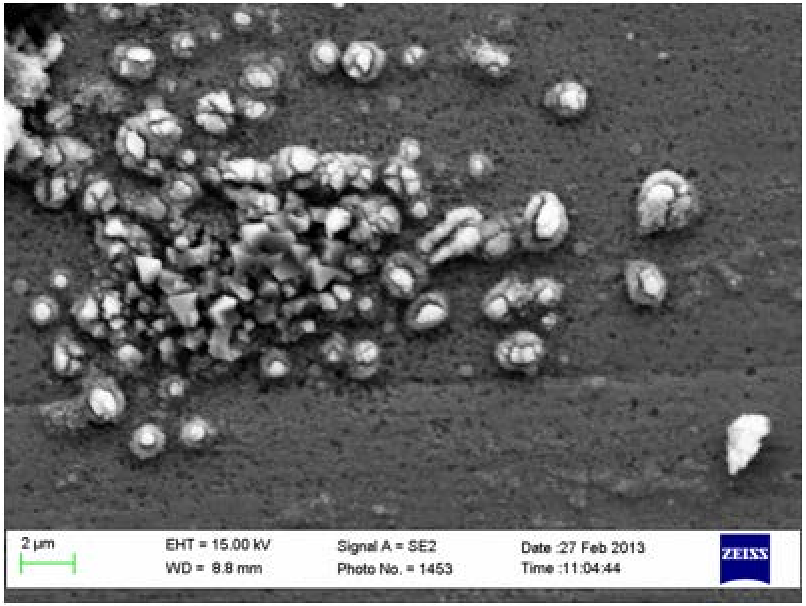




	T-Value	T-Crit (95%)	Conclusion
347 IG	2.985	4.303	FALSE
347 RG			

Alumina-Forming Austenitic (AFA-OC6)

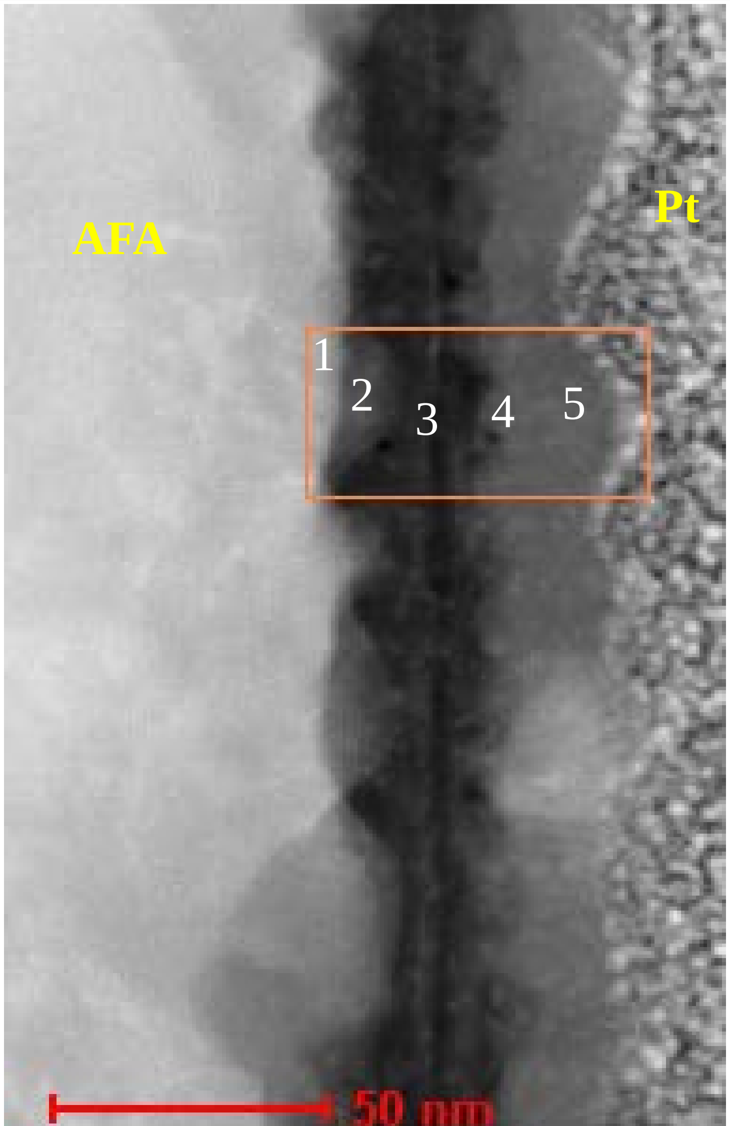


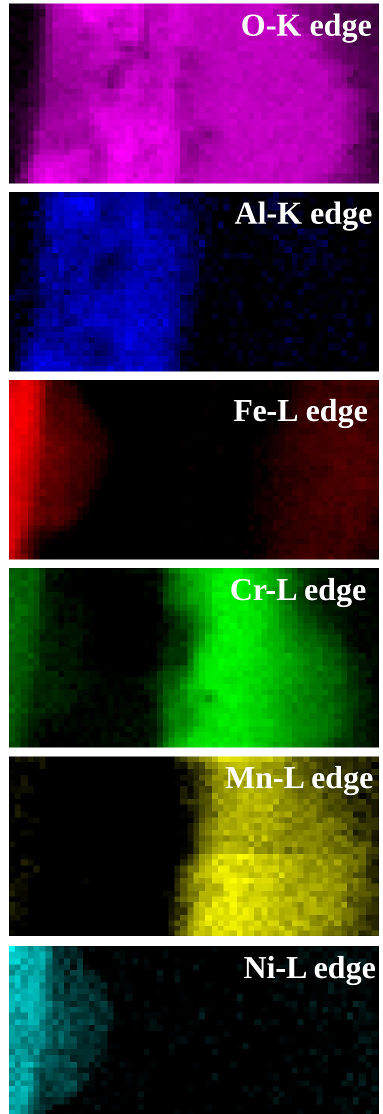


	T-Value	T-Crit (95%)	Conclusion
AFA-OC6 IG	10.821	4.303	TRUE
AFA-OC6 RG			

STEM Cross Section of AFA-OC6

AFA-OC6 @ 550°C, 200 hrs, pure CO_2



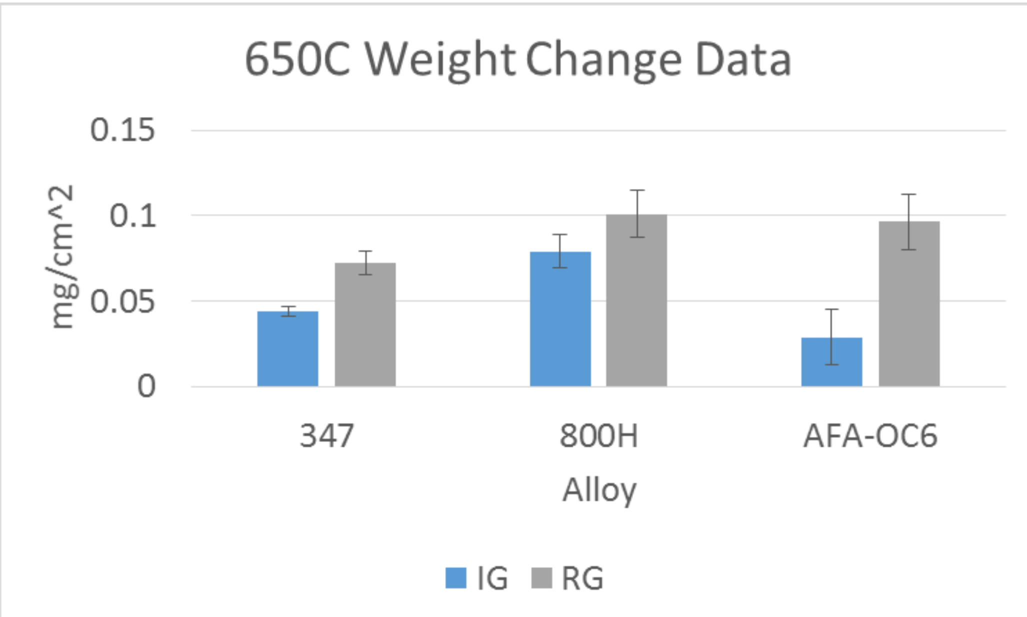


Al + Fe + Cr + Mn + Ni = 100 at.%

Position	Al	Fe	Cr	Mn	Ni
1	12.0	51.9	14.9	1.2	20.0
2	78.2	13.6	4.0	0.0	4.1
3	98.6	0.4	1.0	0.0	0.0
4	8.1	3.5	68.2	20.2	0.0
5	24.8	33.1	23.6	18.5	0.0

1. AFA matrix
2. Al_2O_3 + (Fe, Cr, Ni) containing oxides
3. Al_2O_3
4. Al, Fe –containing $(Cr, Mn)_3O_4$
5. (Fe, Al, Cr, Mn)-containing oxides

Weight Gain Data for 200 hours at 650C



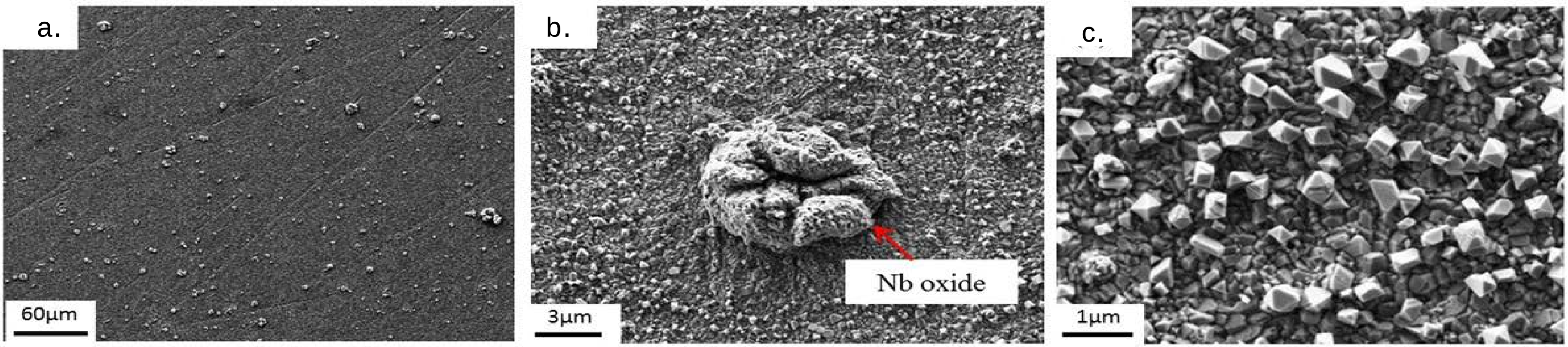
a) Weight change data shows statistically significant difference between RG and IG CO_2 for 347ss, Inconel 800H, and AFA-OC6

b) Weight Gain data increases significantly for 650C tests compared to the 550C testing for the first 200 hours

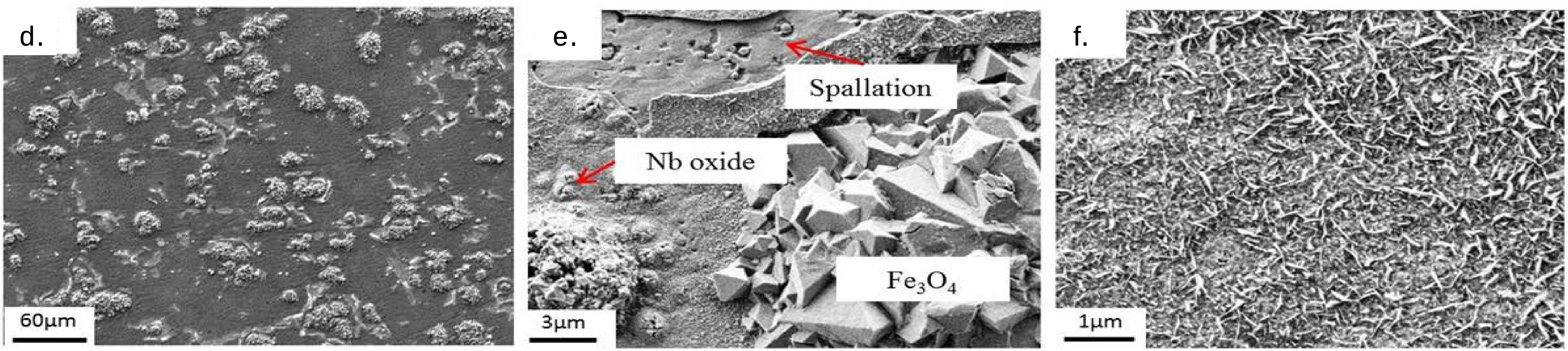
	347			800H			AFA-OC6		
Test	T-Value	T-Crit	Conclusion	T-Value	T-Crit	Conclusion	T-Value	T-Crit	Conclusion
IG-RG	9.32	2.15	TRUE	3.37	2.15	TRUE	7.99	2.15	TRUE
***n>5 for all tests**									

SEM Images Comparing RG to IG CO2 Testing

Industrial



Research



Distribution and morphology of oxides on the surface of 347 after tested in (a)(b)(c)Research , (d)(e)(f)Industrial S-CO2 Industrial SC-CO_2 at 650°C for 200hrs

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Ongoing Work

- Current testing is being completed for the following materials at each given temperatures:

Temp	Materials										
450	Haynes 230	Hanes 625				347	310	316			
550	Haynes 230	Hanes 625				347	310	316		617	718
650	Haynes 230	Hanes 625	800H	282	740	347	310	SiC		617	718
750	Haynes 230	Hanes 625	800H	282	740	347	310	SiC	Ni-22Cr	617	718

- Future testing also includes:
  - Elevated temperatures up to 850C
  - Effects of impurities on corrosion (H2O, O2, hydrocarbons)
  - Varying pressures
  - Elevated flow rates (erosion)

Conclusions

- Research grade CO_2 showed a statistically higher difference in the corrosion of Inconel 800H and AFA-OC6 compared to industrial grade CO_2 at 550C
- At 650ºC higher weight gain was observed in research grade CO_2 for all three alloys
  - SEM imaging supports this conclusion
- Further testing, and significant analysis will need to be completed to determine oxide growth
  - TEM, Cross Sections, EDS, XRD

Acknowlegements

Acknowledgements

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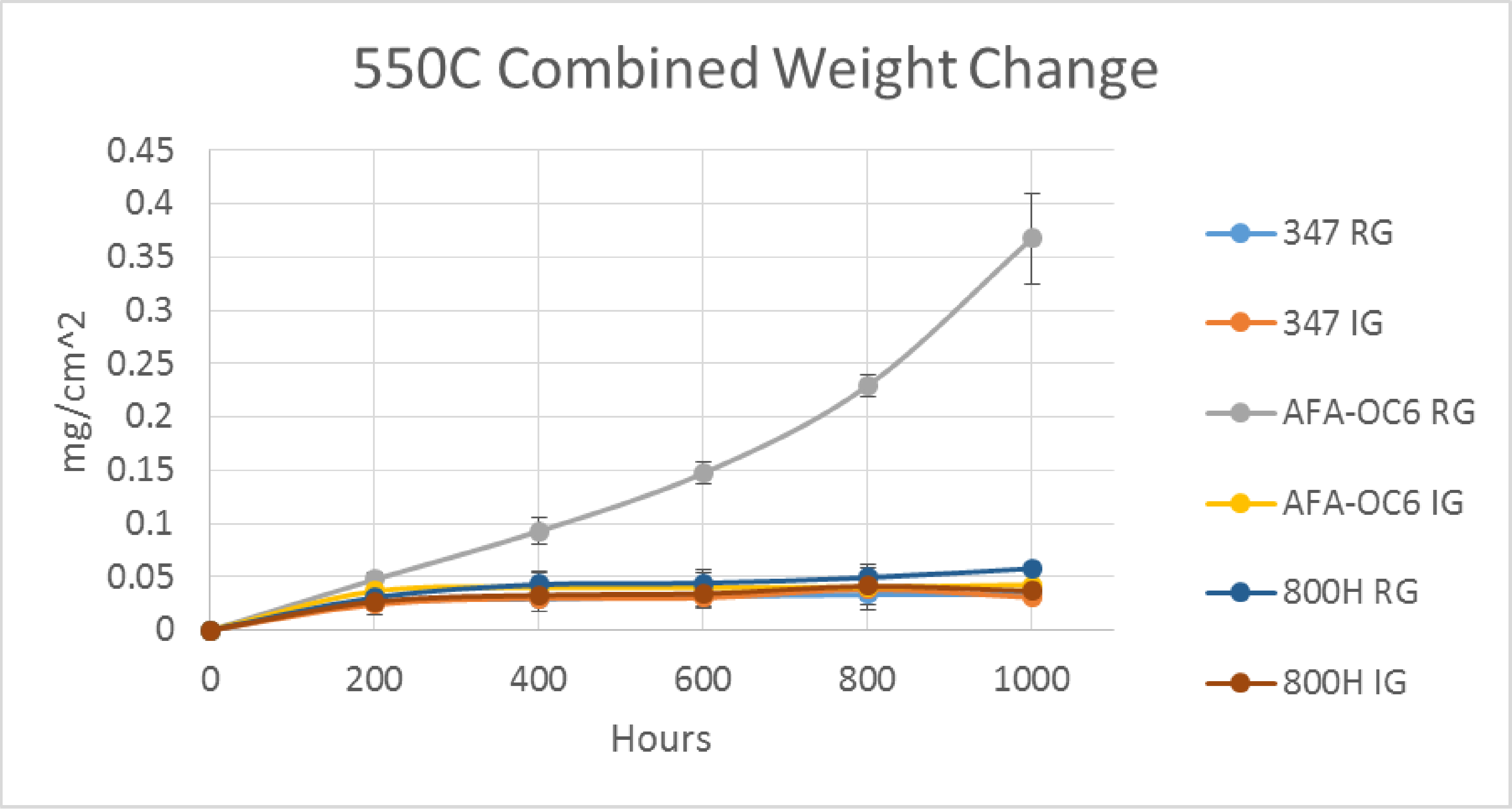
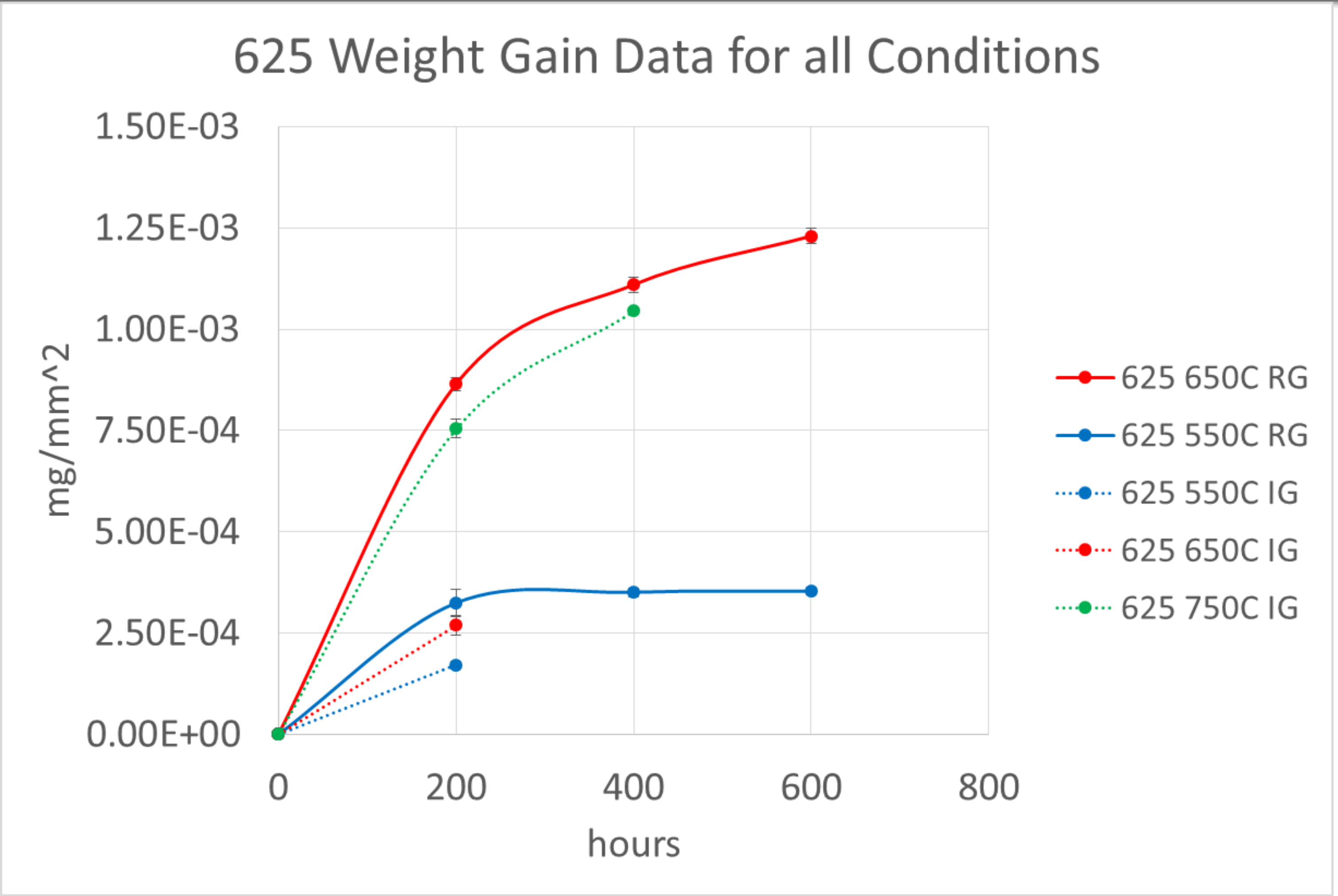
550C 1000 Hour Weight Gain



550C 1000 Hour Weight Gain Zoomed

H625 RG vs IG Preliminary Data



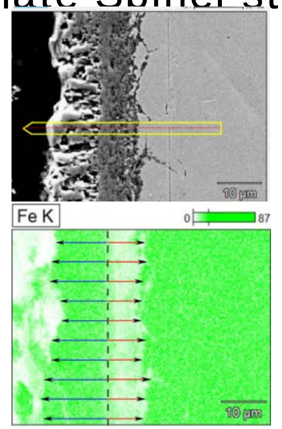
Small standard deviation of samples, statistically significant difference between IG and RG

Modeling Effort Based on Measurements

- Duplex oxide is formed in 316 exposed in $SCCO_2$ at 650C
  - Outer magnetite (Fe_3O_4)
  - Inner Fe-Cr spinel ($Fe_{3-x}Cr_xO_4$)

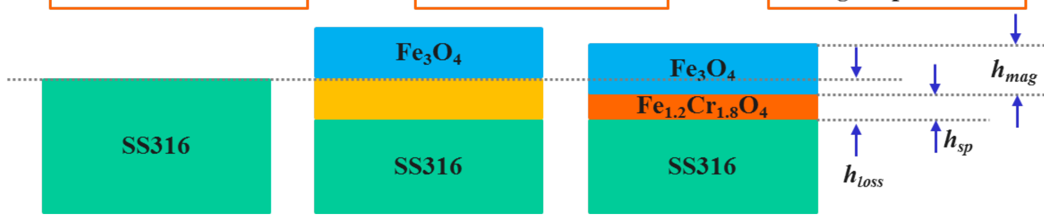
C	Fe	Cr	Ni	Mn	Mo	Si	Cu	Co
0.03	68.2	17.1	10.1	1.56	2.01	0.29	0.45	0.31

- Correlate Spinel stoichiometry with the composition of Fe and Cr



Fe/Cr concentration in substrate metal → Spinel stoichiometry ⇄ Ratio of h_{mag}/h_{sp}

SS316 | $Fe_{1.2}Cr_{1.8}O_4$ | $h_{mag}/h_{sp} \sim 1.75$

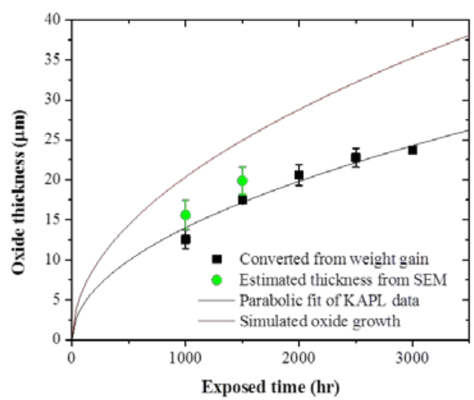


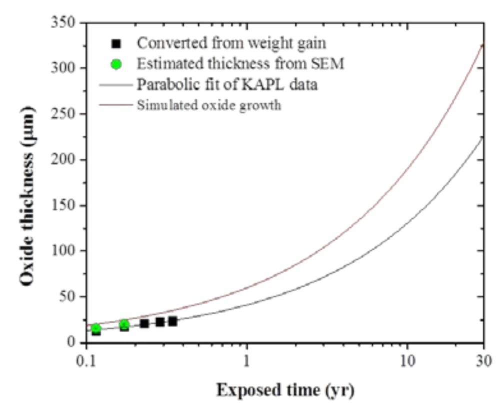
- Estimation of oxide growth from the D_{Fe} [1]

Parabolic Const.	Expt.	Calc.
$k_p \times 10^{-13}$ (cm²/s)	5.46±0.24	11.52

$$h_{mag}^2 = \frac{2}{2.4} A \left[\frac{D_{Fe}^{sp,\,Topfer}}{D_{Fe}^{mag,\,Topfer}}(V) \frac{Dv}{8} \ln\left(\frac{1+2K_v a_{O_2}^{sp/mag^{2/3}}}{1+2K_v a_{O_2}^{T91/sp^{2/3}}} \right) - 4 \frac{D_{Fe}^{sp,\,Topfer}}{D_{Fe}^{mag,\,Topfer}}(I) D_I K_I \left(a_{O_2}^{sp/mag^{-2/3}} - a_{O_2}^{T91/sp^{-2/3}} \right) \right] t$$

$$h_{mag}^2 = \left[\frac{Dv}{12} \ln\left(\frac{1+2K_v a_{O_2}^{mag/Pb-Bi^{2/3}}}{1+2K_v a_{O_2}^{sp/mag^{2/3}}} \right) - \frac{8}{3} D_I K_I \left(a_{O_2}^{mag/Pb-Bi^{-2/3}} - a_{O_2}^{sp/mag^{-2/3}} \right) \right] t$$



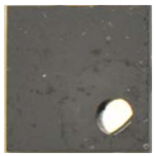


[1] L. Martinelli et al., Corrosion Science, 50 (2008) 2537-2548.

Effect of Surface Treatment (HCM12A, 550^{o}C, 20 MPa)

HCM12A

Uncoated (200 hrs)

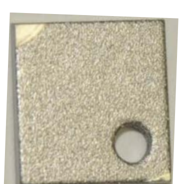


Al Coated (200 hrs)

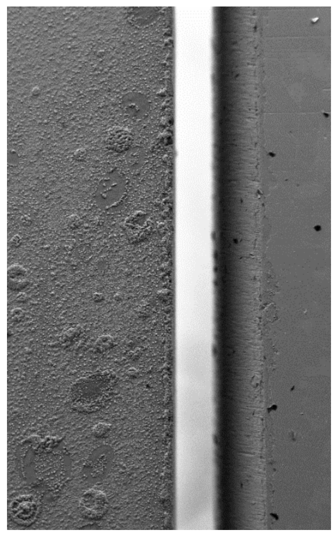
Y Coated (200 hrs)

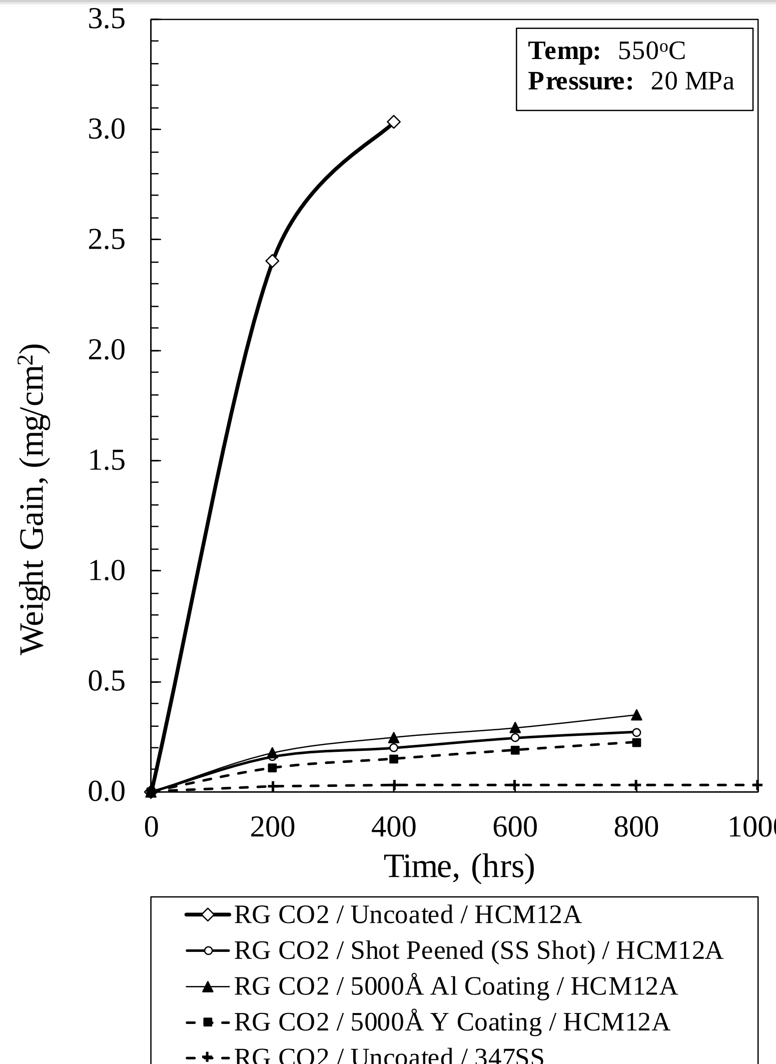
Shot Peen (200 hrs)

Shot Peen (0 hrs)

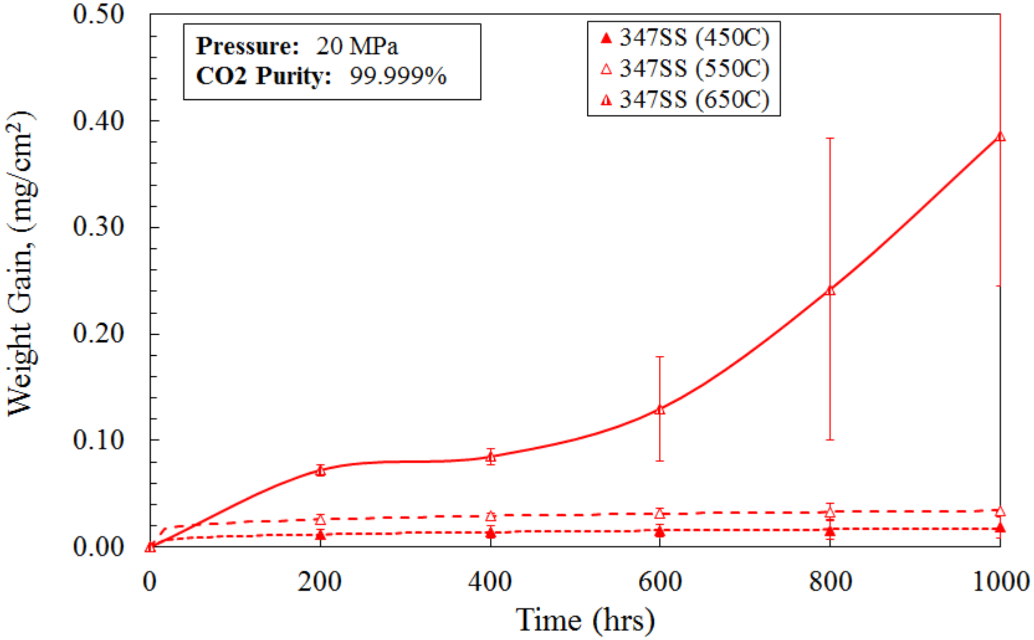


Al Coat Y Coat





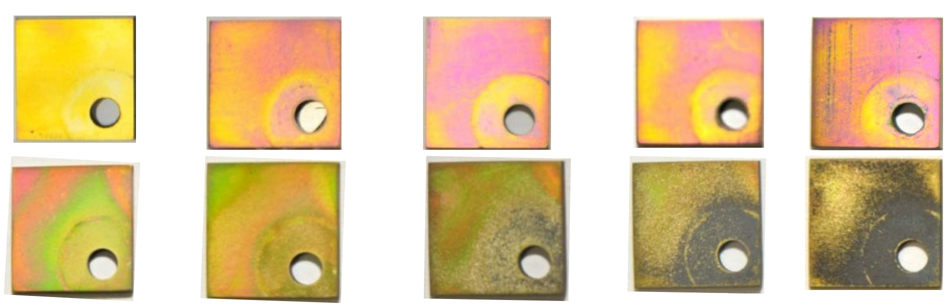
Reaction Kinetics & Surface Morphology (347SS)

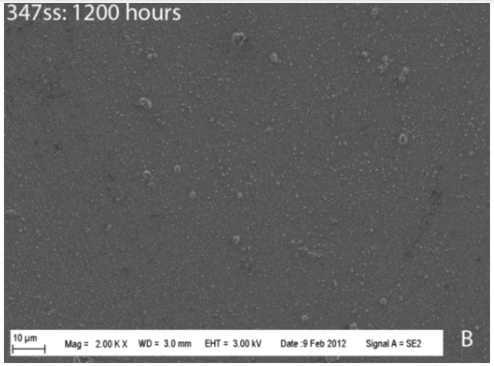


200 hrs | **400 hrs** | **600 hrs** | **800 hrs** | **1000 hrs**

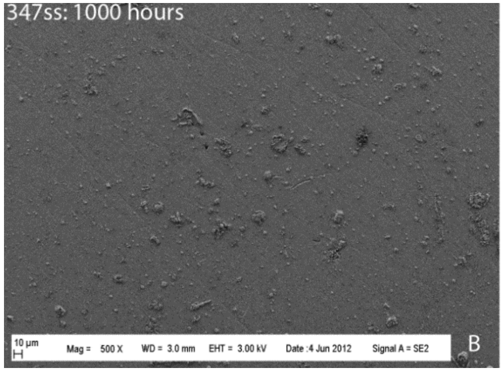
550°C

650°C

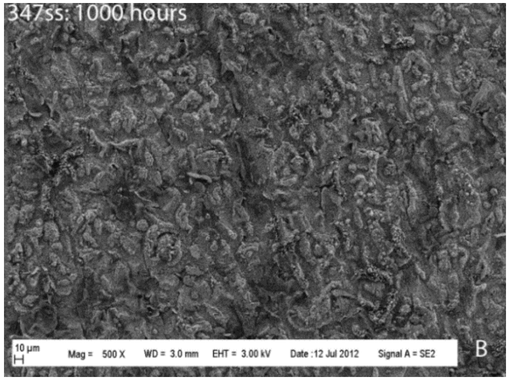




450°C

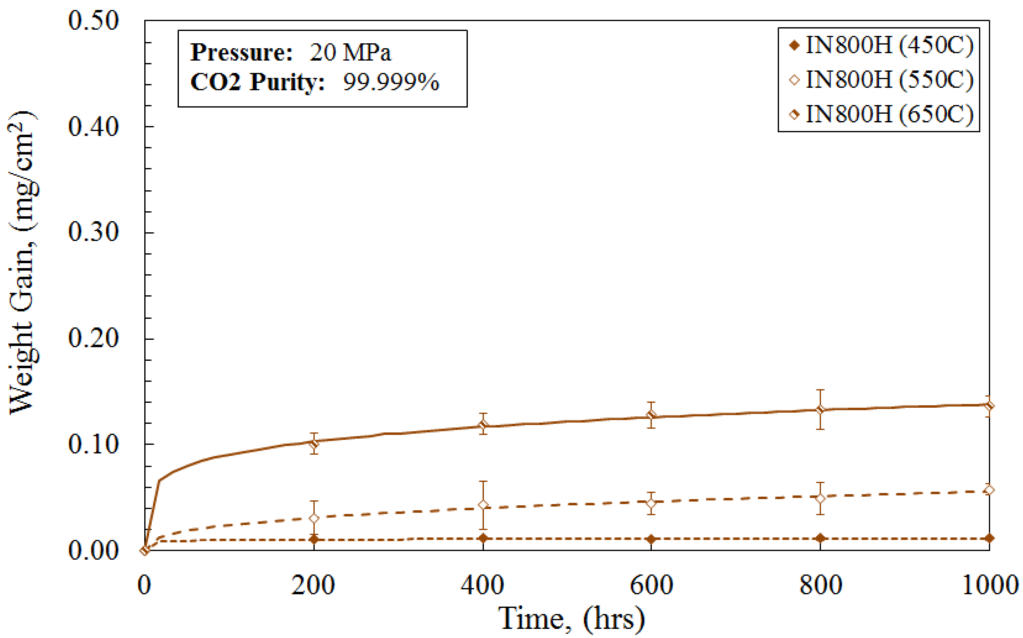


550°C



650°C

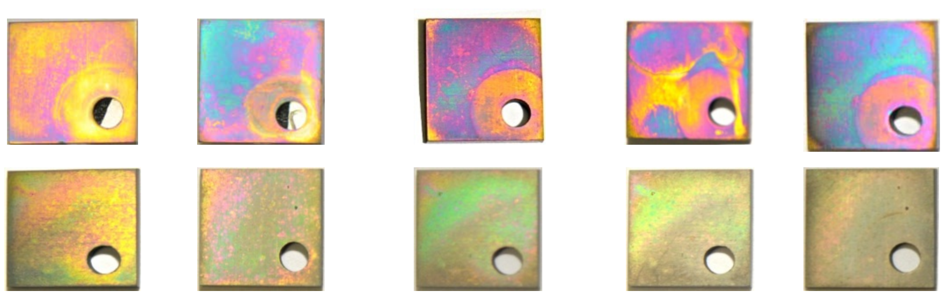
Reaction Kinetics & Surface Morphology (IN800H)

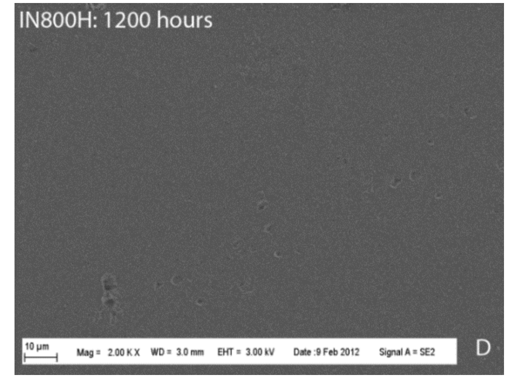


200 hrs | **400 hrs** | **600 hrs** | **800 hrs** | **1000 hrs**

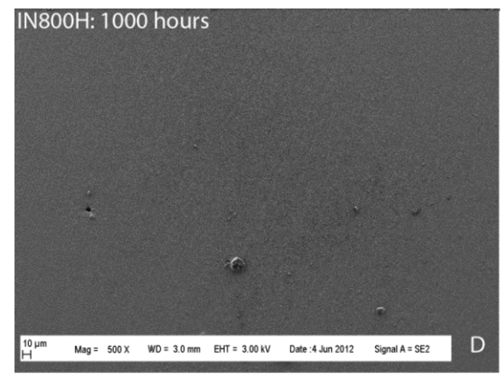
550ºC

650ºC

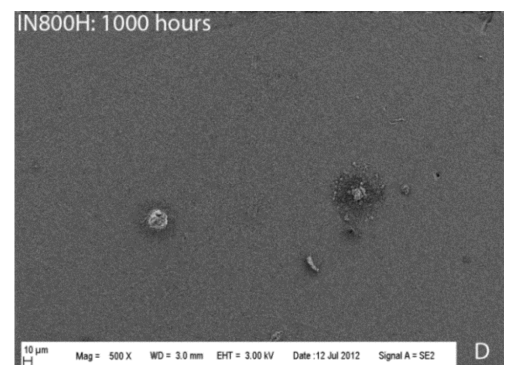




450ºC



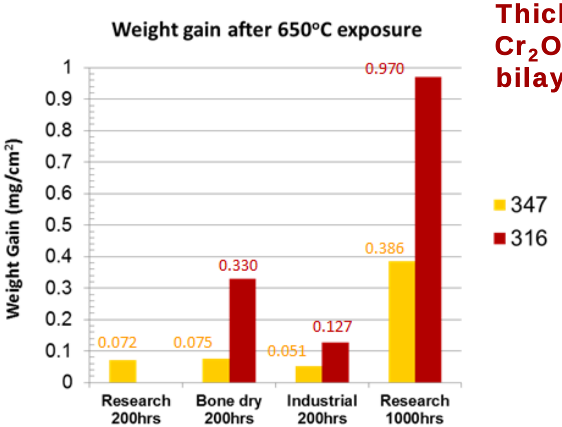
550ºC



650ºC

Slight changes in alloy composition can effect corrosion rates

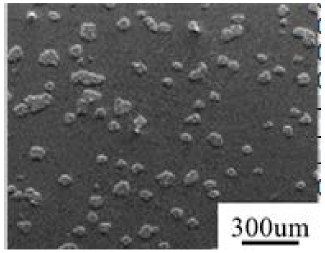
	316	347
Fe	Bal.	Bal.
Cr	17.4	17.67
Ni	13.3	9.62
Al	-	-
Mn	1.7	1.66
Nb	-	0.72
Cu	-	0.38
Mo	2.7	0.38
Si	0.43	0.77
C	0.045	0.051
W	-	-
Ti	-	-
V	-	-
P	-	0.027
N	0.044	-



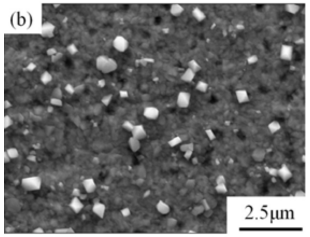
316ss

Fe oxide on surface

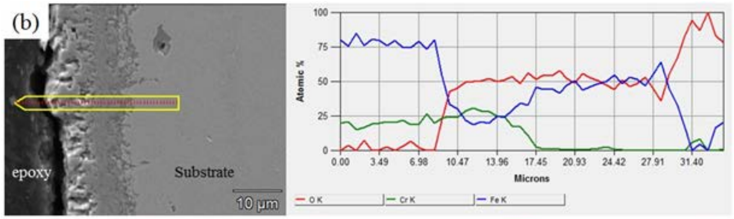
Thickness 20 µm
Fe_3O_4 and Fe-Cr –O Spinel
bilayer scale

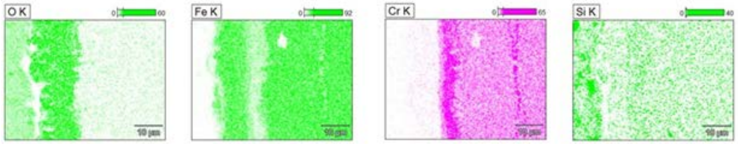


Larger size less amount of Cr-Mn rich oxide



Looser Oxide Scale primarily Fe_3O_4



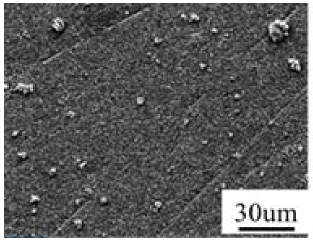


316 ss exposed to research grade s-CO_2 at 650C for 1000 hou

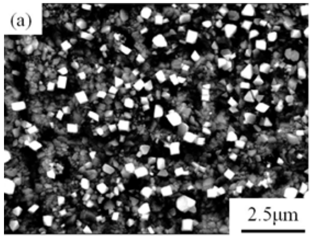
347ss

Nb oxide present on surface

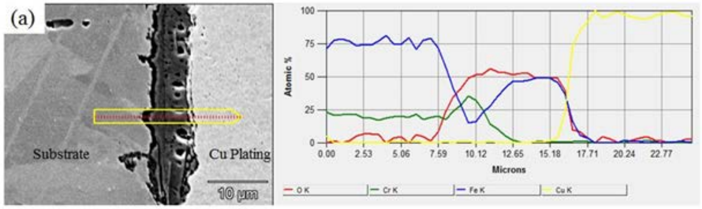
Thickness 10 µm
Cr_2O_3 / Fe_3O_4
bilayer scale

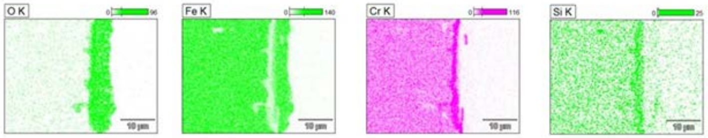


Smaller size higher amount of Cr-Mn rich Oxide



Denser Oxide Scale slower growth – less spall





347 ss exposed to research grade s-CO_2 at 650C for 1000 hou

Si enrichment in the inner layer and presence of Nb Oxide

Alloys	Oxide	Number Density	overall corrosion rate	Comments
IN740	Elongated Nb-Ti rich oxide cluster (50um)	Low	~1um-2um/year	Excellent corrosion resistnace/ good strength at temp
	Cr rich oxide (<1um)	High		
H 282	No Current SEM data		Not enough data to make a reasonable guess	Excellent corrosion resistance up to 550C. More testing needed for higher temperatures
H 625	Cr rich oxide present		450C - <1um/year	Good corrosion resistance. Needs to be looked at for higher temps.
	Similar oxide layer to Hanes 230 alloy, more testing needed		550C - <1um/year	
			650C –1-4um/year	
H230	Elongated W rich oxide cluster (30um)	Medium	450C - <1um/year	Good corrosion resistance. Needs to be looked at for higher temps.
			550C - <1um/year	
	Cr rich oxide (<1um)	High	650C - 2-5um/year	
IN800H	Ti oxide cluster (20um)	Low	450C - 1-2um/year	Performed similar to 347 but cost is considerable higher
	Cr-Mn rich oxide (<1um)	High	550C- 5 um/year	
	Octahedral Fe oxide cluster (30um)	Medium	650C - 30 um/year	
347SS	Nb oxide (<1um)	Medium	450C - 5um/year	Alloy performed pretty well at most temps - started to fall off at 650 not suitable for higher temps
	Needle Cr-Mn rich oxide scale	Some spallation	550C- 5um/year	
	Octahedral Fe oxide cluster (20um)	High	650C - 35um/year	
316L	Octahedral Fe oxide scale	70% of surface	450 C - 10um/year	Ok for lower temperatures 347 performed
			550 C - 30-50um/year	
	Octahedral Cr-Mn rich oxide scale	30% of surface	650 C- 100um/year	

Summary and Discussion of 316 vs. 347

Oxidation in both 347 and 316 increase with decrease gas impurity level.

Fe_2O_3 tends to form in high impurity gas while Fe_3O_4 tends to form in low impurity gas.

After corrosion test, 316 shows higher weight gain than 347 despite of their similar composition.

Continuous Cr_2O_3 was found in 347 steel in all 3 impurity grade gas, while hardly seen in 316 steel.

Higher Cr content in 347 is responsible for its better corrosion resistance, while addition of Nb and Si may also make contributions. Besides, different grain boundary distribution in 347 and 316 could also affect the corrosion behaviors.