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MATERIALS CORROSION IN HIGH TEMPERATURE SUPERCRITICAL CARBON DIOXIDE

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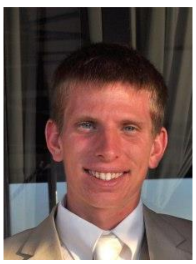

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ABSTRACT:

A high temperature, high pressure autoclave capable of testing materials corrosion in supercritical carbon-dioxide (SC-CO2) up to 750ºC (1382ºF) and 3000psi has been designed and constructed. Using this autoclave, corrosion of structural materials, 347 stainless steel, alloy 800H, and an alumina forming austenitic (AFA) alloy have been tested in research and industrial grade SC-CO2 at 550ºC (1022ºF) and 650ºC (1202ºF). At 550ºC (1022ºF) tests performed up to 1000 hours, 347 stainless steel and alloy 800H showed similarly good corrosion resistance, but the AFA alloy showed markedly higher corrosion. At 650ºC (1202ºF) performed up to 200 hours, 347 stainless steel showed evidence of oxide layer spallation, whereas alloy 800H developed a protective oxide layer. At this lower exposure time at 650ºC (1202ºF), the weight gain for AFA alloy was similar to the other two alloys. The weight gain due to corrosion of these alloys was observed to be generally similar or lower in industrial grade compared to the research grade CO_2.

INTRODUCTION:

The SC-CO2 Brayton cycle is being considered for next generation energy systems, including solar, fossil, and nuclear power systems [1,2]. The interest in SC-CO2 Brayton cycle stems from its improved economics, system simplification, and high power conversion efficiencies [2]. However, SC-CO2 has been shown to be corrosive to structural alloys that are candidates for making components of the Brayton cycle such as heat exchangers, piping, and turbines. Corrosion over the long-term can lead to reduction in effective wall thickness, reduce thermal conductivity by way of oxide layer formation, and lead to the generation of corrosion debris particulates. Evaluation of corrosion of structural materials for various components of a Brayton cycle is therefore critically important. This paper discusses the autoclave system for high temperature SC-CO2 corrosion testing and presents results of performance of austenitic materials 347 stainless steel, alloy 800H, and an AFA alloy in research and industrial grade CO2 at 550ºC (1022ºF) and 650ºC (1202ºF).

EXPERIMENTAL

A photograph of the high temperature SC-CO2 corrosion testing autoclave facility used for this research is shown in Figure 1. The autoclave is capable of withstanding tests at temperatures and pressures of 750ºC and 3000 psi, respectively. The facility is equipped with temperature, pressure, and flow rate control to ensure consistency between various tests. A 200 hour trial run at 650ºC (1202ºF) and 2900 psi was initially performed to determine any temperature and pressure variations in the system. The furthest temperature fluctuation for any part of the test section was measured to be 1.64°C. Pressure readings recorded every ten seconds with Omega brand pressure transducers showed that 95% percent of the measurements were within 2.5 psi of the targeted pressure.

The system was refreshed with CO2 every two hours in order to limit turbulence effects, while at the same time allowing enough CO2 to interact with the samples' surface without attaining equilibrium with the environment. Calculations for this two hour refresh rate showed that flow rates of 0.12 to 0.18 kg/hr would be required for temperatures between 450ºC (842ºF) and 750ºC (1382ºF). The trial run showed an average mass flow rate of 0.11 kg/hr of CO2.

Two purity grades of CO2 were used for this study, namely research grade and industrial grade, and the nominal composition specification of these gases as provided by the supplier are listed in Table 1.

Table 1: Composition of the two purity grades of CO2 as provided by the gas supplier.

CO2 Grade	Percentage Purity	Monitored Impurities
Research	99.999	H2O < 3ppm, N2 < 5ppm, THC < 1ppm, Ar+O2+CO < 1ppm
Industrial	99.95	H2O < 32ppm, Hydrocarbons < 50 ppm, O2 < 50ppm

The nominal compositions of the 347 stainless steel, alloy 800H, and AFA alloy samples used in this study are shown in Table 2. Test samples of these alloys were sectioned by electrical discharge machining (EDM) to dimensions of 0.5” x 0.5” x 0.0625” and a hole 0.125”in diameter was drilled at one of the corners for suspending the samples in the autoclave from an alumina rod holder. The samples were ground with 800 grit silicon-carbide on both sides prior to the tests. The dimensions of the samples were measured with a micrometer which had an accuracy limit of ±0.002mm. Three length and width measurements are taken along the edges, and five thickness measurements were made across different locations on the surface to calculate the entire surface area of the samples. Prior to testing the samples were weighed ten times in a balance with an accuracy limit of 2 micrograms. Between each individual sample measurement, a mass standard was weighed to ensure balance calibration.

Table 2: Elemental composition (wt %) of the alloys investigated in the work.

	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	-

Corrosion testing was performed at 550ºC (1022ºF) for 1000 hours with the samples being taken out every 200 hours for weight change measurements and electron microscopy. Testing at 650ºC (1202ºF) was performed only up to 200 hours as spallation was detected in 347 stainless steel.

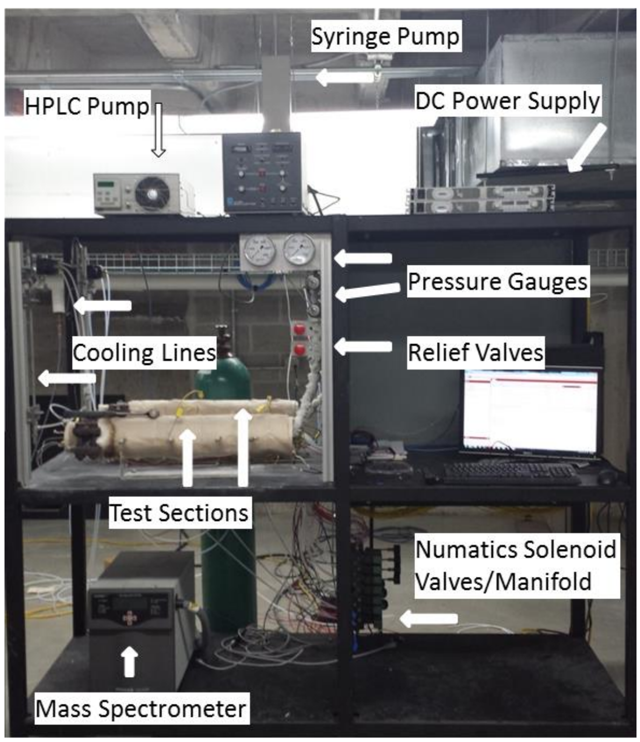

Figure 1: Autoclave system for evaluation of materials corrosion in high temperature SC-CO2 environment in the present study.

RESULTS AND DISCUSSION

The weight change data for the three alloys at 550ºC (1022ºF) are shown in Figure 2. As is evident from this data both 347 stainless steel and alloy 800H showed approximately similar weight gains and a self-limiting oxide growth behavior. The purity grade of CO2 did not have a significant effect on corrosion of 347 stainless steel, but for alloy 800H weight gain due to corrosion was higher for research grade than the industrial grade. For AFA alloy the weight gain due to corrosion was higher than the other two alloys, and furthermore the purity grade of the gas used had a pronounced effect. Samples of AFA alloy exposed to industrial grade CO2 showed a relatively low self-limiting oxide growth behavior, but those exposed to research grade CO2 exhibited high corrosion rates indicative of break-away oxidation. Statistical significance of the data was established by performing a t-test on both industrial and research grade SC-CO2 test results. The results of these t-test calculations are shown in Table 3. The t-critical values were calculated using a 95% confidence interval and the number of samples examined for that particular test. The results show a statistically lower weight gain for alloy 800H and AFA alloy samples that were exposed to industrial grade SC-CO2 compared to those exposed to research grade SC-CO2, while no such difference was observed for 347 stainless steel. It is clear from Table 1 that the concentration of the oxidizing species such as O2 and H2O are higher in the industrial grade gas which would promote oxidation hence weight gain. However, we speculate that the lower weight gains observed in samples in industrial grade CO2 may be due to the presence of the of hydrocarbon impurities which have a reducing effect. Separate effects tests by intentionally adding known quantities of these reducing impurities will be performed in our research program in the near-future to confirm this mechanism.

Figure 2: Weight gain data for tests performed in SC-CO2 at 550ºC and 2900psi, (a) 347 stainless steel (b) alloy 800H and (c) AFA-OC6.

A power law fit based the equation $\Delta W = at^b$ was applied to each of the data sets. The parameters are also shown in Table 3. The equations for the power fit can be used to determine if there is a fundamental change in the shape of the curve, and hence the time dependence of corrosion. The 'b' parameter for alloy 800H and AFA alloy shows a distinct difference between industrial and research grade CO2, whereas it does not change for 347 stainless steel.

Table 3: Statistical fit parameters for weight change measurements for 347 stainless steel, alloy 800H, and AFA alloy in 550ºC (1022ºF) tests (RG: Research Grade, and IG: Industrial Grade).

Conditions	a	b	R^2	T-Value	T-Crit (95%)	Conclusion
347 IG	0.000894	0.563	0.998	2.985	4.303	FALSE
347 RG	0.000898	0.563	0.998			
AFA-OC6 IG	0.00109	0.575	0.997	10.821	4.303	TRUE
AFA-OC6 RG	0.00267	0.635	0.996			
800H IG	0.000969	0.568	0.999	6.211	4.303	TRUE
800H RG	0.00117	0.58	0.999			

Weight change data for 650ºC (1202ºF) tests for 200 hours is shown in Figure 3, and t-test values are shown in Table 4. At 650ºC (1202ºF), there is a significant increase in the weight change of the alloys in comparison to the 550ºC (1022ºF) tests at 200 hours. Here again, the weight gain data is higher for research grade compared to industrial grade SC-CO2 tests even for 347 stainless steel, an effect that may be again due to the reducing effect of the hydrocarbon impurities. T-test calculations shown in Table 4 indicate these differences to be statistically significant.

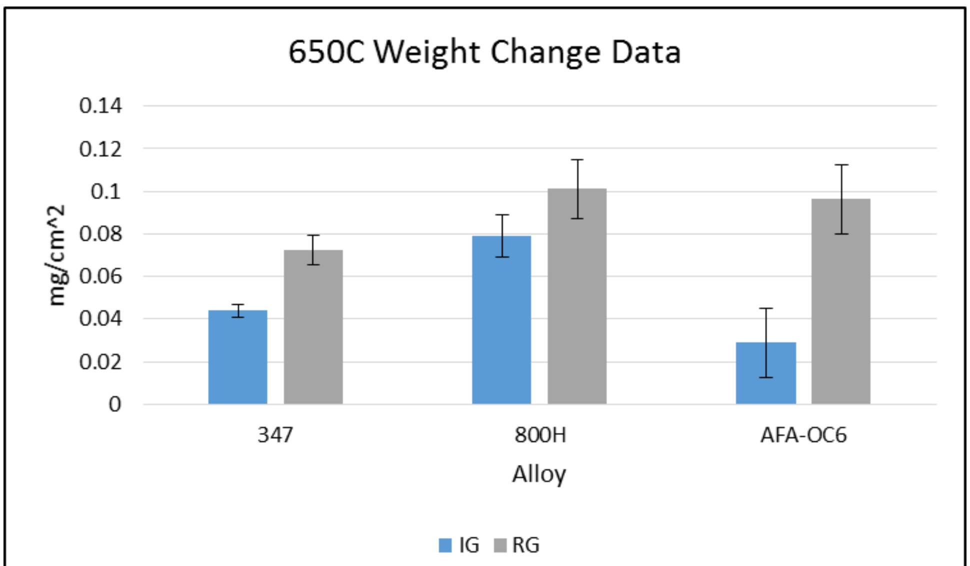

Figure 3: Weight change data for tests performed at 650ºC (1202ºF) for 200 hours for 347 stainless steel and alloy 800H.

Table 4: Statistical t-test values for 650ºC (1202ºF)/200 hour tests

	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									

Figure 4 shows the SEM surface images of the samples for 347 stainless steel, alloy 800H, and AFA-OC6 after 650ºC (1202ºF) tests. For 347 stainless steel, evidence of initiation of oxide layer spallation is clearly observed, whereas alloy 800H even after 1000 hours exposure clearly retains a protective oxide layer.

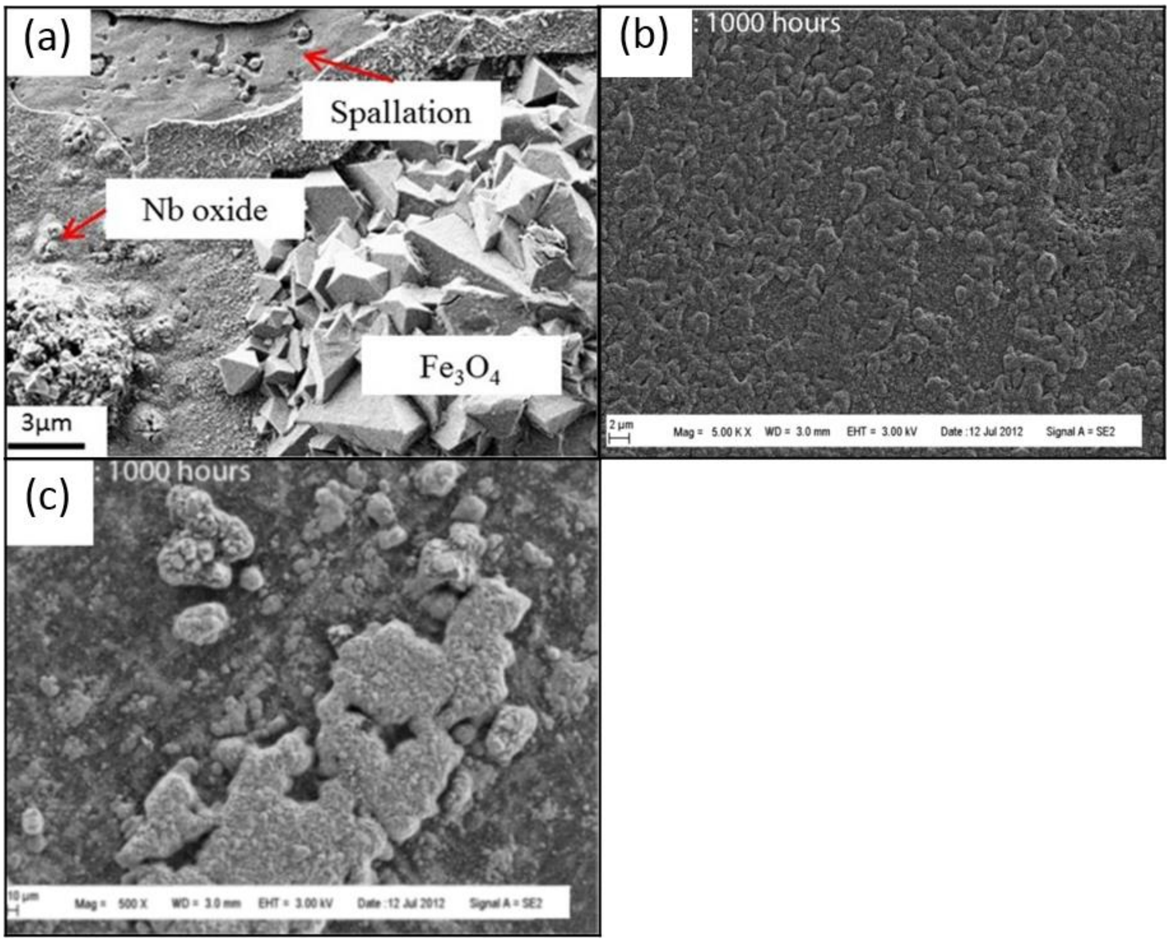

Figure 4: SEM surface image of samples after corrosion tests in high temperature research grade SC-CO2 tests at 650ºC (1202ºF) (a) 347 stainless steel after 200 hours exposure (b) Alloy 800H and (c) AFA-OC6 after 1000 hour exposure.

CONCLUSIONS AND ONGOING WORK:

Corrosion testing of 347 stainless steel, Alloy 800H, and an alumina forming austenitic (AFA) alloy have performed at 550ºC (1022ºF) (up to 1000 hours) and 650ºC (1202ºF) (up to 200 hours) in industrial and research grade SC-CO2. At 550ºC (1022ºF). 347 stainless steel and alloy 800H showed good corrosion resistance, while the AFA alloy showed less than expected corrosion resistance. Also at this temperature, for alloy 800H and AFA alloy, the research grade CO2 resulted in higher weight gain due to corrosion compared to the industrial grade CO2, the effect being particularly notable for the AFA alloy. There was no difference in corrosion between the two grades for 347 stainless steel. In 650ºC (1202ºF) performed up to 200 hours, higher weight gain was observed in research grade CO2 for all three alloys. 347 stainless steel exhibited oxide spallation while alloy 800H showed a dense protective oxide layer. The results shown in this paper represent an ongoing work in the area of high temperature CO2 corrosion in a broad spectrum of alloys including Haynes 230, Haynes 626, Inconel 617, Inconel 718, 347ss, 316ss, and Inconel 800H. Future experiments will also focus on developing a more fundamental understanding of the effects of gas purity on corrosion by performing separate effects test by adding known quantities of hydrogen and hydrocarbon impurities.

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Acknowledgements

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