

THE EFFECT OF IMPURITIES ON OXIDATION IN SUPERCRITICAL CO₂ AT 750°C

Bruce A. Pint

Group Leader
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6156 USA
pintba@ornl.gov

James R. Keiser

Distinguished R&D Staff Member
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6156 USA
keiserjr@ornl.gov



Bruce Pint is the Group Leader of the Corrosion Science & Technology Group in the Materials Science & Technology Division at ORNL. He received his Ph.D. from M.I.T. in Ceramic Science and Engineering in 1992 and has been at ORNL since 1994. Dr. Pint is the principal investigator for numerous R&D projects including corrosion issues in fossil energy, nuclear energy, fusion energy and combined heat and power systems. His research covers compatibility, lifetime predictions, environmental effects and coatings in all types of power generation. He is a Fellow of NACE International and ASM International.



James Keiser is a Distinguished Research and Development Staff Member and has worked in ORNL's Corrosion Science & Technology Group since 1974 where he has studied the compatibility of materials with the environments of energy producing systems. Studies have addressed the performance of metallic and ceramic materials in environments containing gaseous, liquid and supercritical corrodents. Several of his current projects concern corrosion issues in biomass liquefaction and gasification. Dr. Keiser received his B.S. in Materials Science and Ph.D. in Metallurgical Engineering and is a Fellow of NACE International and ASM International.

ABSTRACT

Both indirect- and direct-fired supercritical CO₂ (sCO₂) cycles for high efficiency power generation are expected to have impurities that may greatly alter the compatibility of structural alloys in these environments. However, the laboratory data on this subject are limited and inconclusive. For indirect applications, comparison 500-h cycles were conducted at 750°C at 1 and 300 bar with re-search grade and industrial-grade (higher possible impurities) CO₂. The mass change results suggest only limited differences between these conditions for exposures up to 5,000 h. For direct-fired or open cycles, a test rig is being assembled to conduct similar exposures at 750°C/300 bar in CO₂+1%O₂-0.25%H₂O. Commercial Fe- and Ni-base structural alloys were exposed in each environment and reaction products have been characterized after 1,000, 2,500 and 5,000 h exposures.

INTRODUCTION

Supercritical CO₂ (sCO₂) is an attractive working fluid for a range of power generation applications including nuclear, fossil, concentrated solar power (CSP), geothermal and waste heat recovery, because of its unique properties and relatively low critical point (31°C/73.8 bar) [e.g. Dostal 2006, Chen 2010, Iverson 2013, Wright 2013, Cheang 2015]. Several near-term applications including waste heat recovery have temperatures of ≤550°C, similar to the temperatures in the UK advanced gas cooled reactors operated at 43 bar [Gong 2017]. However, CSP and fossil energy applications

have targeted operation at $>700^{\circ}\text{C}$ to enable $\geq 50\%$ system efficiency [Feher, 1968] with indirect-fired or closed cycles. The proposed direct-fired or open sCO_2 cycle [Allam 2013, Wright 2013] has the potential to achieve economical, “clean” fossil energy power generation by diverting the CO_2 from combustion to sequestration or enhanced oil recovery. Impurities in the sCO_2 are a compatibility issue for both direct- and indirect-fired systems. With ppm level of impurities, most sCO_2 compatibility studies have shown protective behavior for highly alloyed Fe- and Ni-base structural alloys [Oh 2006, Dunlevy, 2009, Furukawa, 2011, Rouillard 2011, Tan 2011, Moore 2012, Cao 2012, Firouzdor 2013, Mahaffey 2014, Pint 2014a, Olivares 2015, Pint 2015a, Mahaffey 2016, Pint 2016a, Kung 2016, Pint 2017a, Pint 2017b]. Nevertheless, even closed commercial sCO_2 systems may start with lower purity CO_2 compared to what is used in most laboratory experiments. For direct-fired systems, the H_2O and O_2 residuals from the combustion of natural gas or coal-derived synthesis gas (i.e. syngas) would be incorporated into the cycle as well as possibly S and Cl if syngas were combusted.

An experimental facility to simulate 0.1-5% H_2O and 0.1-2% O_2 impurity levels under supercritical pressures is currently beginning operation at ORNL. Previously, considerable testing has been conducted at ambient pressure in CO_2 with and without H_2O , O_2 and SO_2 additions to support a variety of technologies including fuel cells, oxy-combustion of coal and the direct-fired sCO_2 cycle [Meier 1982, Kranzmann 2009, Quadakkers 2011, Gheno 2013, Nguyen 2014, Pint 2014b, Young 2014, Huczowski 2014, Yu 2016a, 2016b, Pint 2016b, Pint 2018]. In these experiments, the addition of H_2O resulted in much faster oxidation rates, especially for Fe-base alloys [Kranzmann 2009, Quadakkers 2011, Gheno 2013, Nguyen 2014, Pint 2014b, Pint 2016b, 2018]. The addition of O_2 showed both positive and negative effects as has the addition of SO_2 [Huczowski 2014, Yu 2016a, 2016b, Pint 2018]. At high pressure, O_2 additions have shown slightly negative effects [Mahaffey 2014, 2016] or little effect [Kung 2016]. It has been suggested that combinations of H_2O and O_2 at high pressure could react with Cr-rich reaction products to form volatile Cr oxy-hydroxides [Young 2006, Holcomb 2009] thereby accelerating the degradation rate (i.e rate of Cr loss) of both Fe- and Ni-base alloys [Pint 2012, Bender 2014]. This degradation would be particularly important for thin-walled structures. Impurities could also assist in C permeating the protective surface oxide (either Cr_2O_3 or Al_2O_3). While 9%Cr steels have shown severe internal carburization [Kranzmann 2009, Quadakkers 2011, Rouillard 2011, Gheno 2013, Nguyen 2014, Kung 2016, Gong 2017], higher alloyed materials at higher temperature have not shown much carbon ingress [Olivares 2015, Pint 2016a].

To study the effect of low levels of impurities and create a performance baseline, the current work compares the behavior of several representative structural alloys in research grade (RG) and industrial grade (IG) CO_2 at 1 and 300 bar at 750°C . The ambient pressure results provide a link to the existing extensive literature at 1 atm. Experiments in laboratory air also have been conducted for comparison. The structural materials include two advanced austenitic steels, an alumina-forming Ni-based superalloy (typically used for turbomachinery) and both solid solution and precipitation-strengthened [Zhao 2003, Pike 2008, Shingledecker 2013] Ni-based alloys identified by the U.S. Advanced Ultrasupercritical Steam Consortium [Viswanathan 2005, Viswanathan 2010] for applications above 700°C . Alumina scales are thought to be less permeable to carbon (or carbonaceous species) [e.g. Jönsson 1997] and more stable in the presence of H_2O [Pint 2012]. These results provide an extensive baseline to interpret the results that will soon be generated with higher levels of impurities. The first mass change results from this new experimental equipment also are presented.

EXPERIMENTAL PROCEDURE

The chemical compositions of the structural alloys studied are shown in Table 1. Alloy coupons (~10 x 20 x 1.5mm) were polished to a 600 grit finish and ultrasonically cleaned in acetone and methanol prior to exposure. All of the exposures used 500-h cycles at 750°C. For 1 atm exposures, the coupons were placed in an alumina boat in an alumina reaction tube with end caps. The specimens were heated in RG argon to 750°C over 4 h to minimize oxidation of the samples prior to exposure to CO₂, held for 500 h in CO₂ and cooled in argon to room temperature. Gas flow rates were ~100 cc/min or ~0.1cm/s linear flow rate. For a comparison exposure in air, the specimens were heated using a similar schedule in ambient laboratory air with a relative humidity of ~50%. For the 300 bar experiments, the exposures were conducted in an autoclave fabricated from alloy 282. The vertically-oriented autoclave (~266 mm x 83 mm inner diameter) was operated inside a three-zone furnace with an alloy 282 sample rack that sat on the bottom of the autoclave. The fluid flow rate was ~2 ml/min. Additional details of the system have been provided elsewhere [Pint 2014a, 2015a, 2017a]. The specimens were slowly heated to temperature over several hours (~2°C/min) in sCO₂, held at temperature ±2°C and then cooled in sCO₂ to room temperature by lowering the furnace and using a cooling fan on the autoclave. Separate experiments were conducted for RG and IG CO₂. The H₂O content of the RG CO₂ was measured by the vendor in 6 cylinders as 4.1±0.7 ppm and, in 10 cylinders of IG CO₂, the H₂O was 18.8±16.9 ppm with a range of <1 to 57 ppm. A reliable means of measuring the low O₂ levels is still being investigated. For the first controlled impurity sCO₂ test, the O₂ level was calculated (based on gas flow) as 1.0±0.2% and the H₂O as 0.26±0.05% with most of the variation associated with the change in sCO₂ cylinders.

For all of the experiments, the specimens were weighed using a Mettler Toledo XP205 balance with an accuracy of ~±0.04 mg or 0.01 mg/cm². After exposure, samples were copper plated before being sectioned and mounted for light microscopy. Specimens were etched using aqua regia to measure internal oxidation. Both oxide thickness and internal oxidation were measured using image analysis software with ~30 measurements taken for each specimen.

Table 1. Chemical composition of the alloys measured by inductively coupled plasma and combustion analyses in mass%. UNS numbers are included where available.

Alloy	Fe	Ni	Cr	Al	Other
<i>Austenitic Fe-base chromia-forming steels</i>					
25 SS	42.6	25.4	22.3	0.03	3.4W, 3.0Cu, 1.5Co, 0.5Mn, 0.5Nb, 0.2Si, 0.2N
310HCbN (S31042)	51.3	20.3	25.5	<	0.3Co, 0.4Nb, 1.2Mn, 0.3Si, 0.3N, 0.05C
<i>Ni-base chromia-forming alloys</i>					
625 (N06625)	4.0	61.0	21.7	0.1	8.8Mo, 3.5Nb, 0.2Ti, 0.2Si, 0.2Mn, 0.1Cu, 0.1Co
230 (N06230)	1.5	60.5	22.6	0.3	12.3W, 1.4Mo, 0.5Mn, 0.4Si
617B (N06617)	1.2	54.6	22.3	1.0	11.9Co, 8.2Mo, 0.4Ti, 0.05Si, 0.04Mn, 0.005B
282 (N07208)	0.2	57.1	19.6	1.6	10.6Co, 8.6Mo, 0.04Si, 2.2Ti, 0.02Mn
740 (N07740)	0.1	49.7	24.5	1.4	20.6Co, 1.5Nb, 1.4Ti, 0.3Mn, 0.2Si
<i>Ni-base alumina-forming alloys</i>					
247 (N07247)	0.07	59.5	8.5	5.7	9.8Co, 9.9W, 0.7Mo, 3.1Ta, 1.0Ti, 1.4Hf
< indicates less than 0.01%					

RESULTS

Figure 1 shows typical data generated at 300 bar at 750°C. The boxes show the 25% and 75% values for 5-10 specimens of each alloy and the whiskers show the minimum and maximum values measured. The lines connect the median values in IG and RG sCO₂. A similar plot is shown in Figure 2 for the 1 atm results. In this case, only the median values are shown for RG CO₂ for clarity. In both cases, nearly parabolic behavior was observed. The median mass gains after 1,000 and 2,500 h (i.e. 2 and 5 cycles) for all of the alloys exposed at 750°C are shown in Figure 3. Results in air are shown for comparison. In general, the scales formed in the various CO₂ environments were not significantly different than those formed in laboratory air. In a few cases, pressure appeared to affect the results, particularly for the Fe-based alloys 25 and 310HCbN. However, in most cases, the difference between the 1 and 300 bar results was minimal. Likewise, only minimal differences were noted between IG and RG CO₂. Generally, the lowest mass gains were observed for the solid solution strengthened Ni-based alloys, 617B, 625 and 230, which have relatively low levels of Al and Ti and ~22%Cr, Table 1. The two heats of alloy 282 showed higher mass gains due to the higher levels of Al and Ti [Pint 2015a]. Both 740 and 282 have higher levels of Al and Ti to form the γ' strengthening phase. The alumina-forming superalloy 247 also showed relatively high mass gains in most cases, suggesting that a protective scale was not formed under these conditions. The greatest variability was noted for the two Fe-based alloys. Some of the highest median mass gains were observed for specimens of 310HCbN. Perhaps the high Mn content in this alloy might play a role.

For each condition, specimens were removed after 1,000 and 2,500 h for characterization. Figure 4 shows example light microscopy cross-sections of the specimens removed after 2,500 h. In general, the cross-sections show that the scale was generally thin, which is consistent with the low mass gains observed in Figures 1-3. Also as expected, little internal oxidation was observed

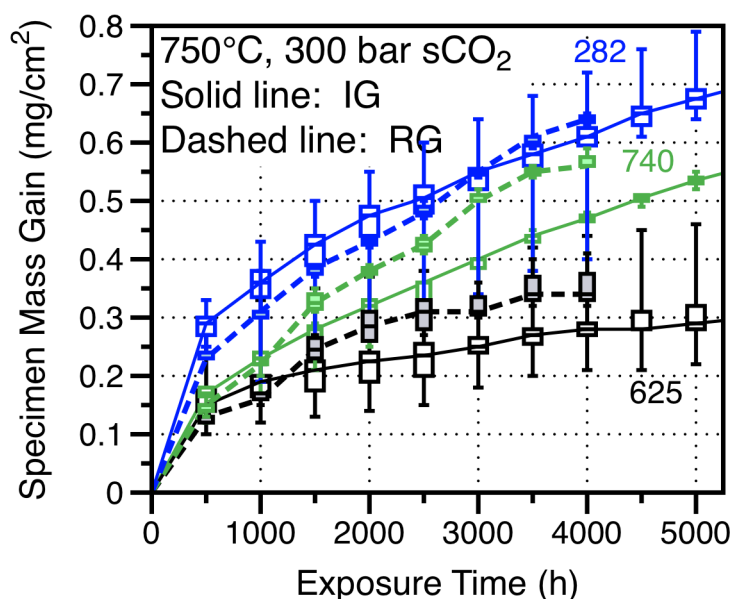


Figure 1. Specimen mass gain data for 500-h cycles at 750°C in 300 bar IG and RG sCO₂. Box and whisker plots show data for 5-10 specimens exposed with solid lines connecting the median values of the IG data. Shaded boxes and dashed lines indicate the RG data.

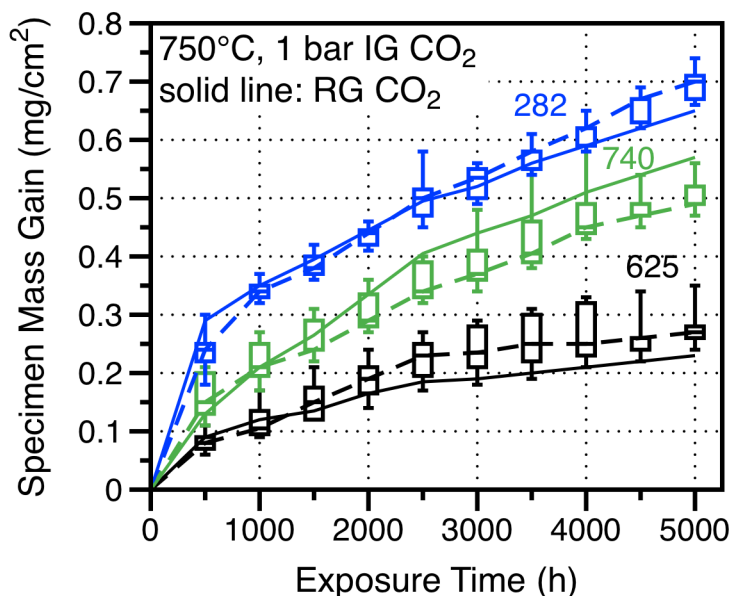


Figure 2. Specimen mass gain data for 500-h cycles at 750°C in 1 bar IG and RG CO₂. Box and whisker plots show data for 5-10 specimens exposed with dashed lines connecting the median values of the IG data. Solid lines indicate the RG data.

for alloys 25 and 625. While much more internal oxidation was observed for precipitation strengthened alloys 740 and 282, the scale also appears thicker, which has been attributed to an effect of the Ti addition [Ennis 1985, Brady 2006, Pint 2014c]. Significant internal oxidation also

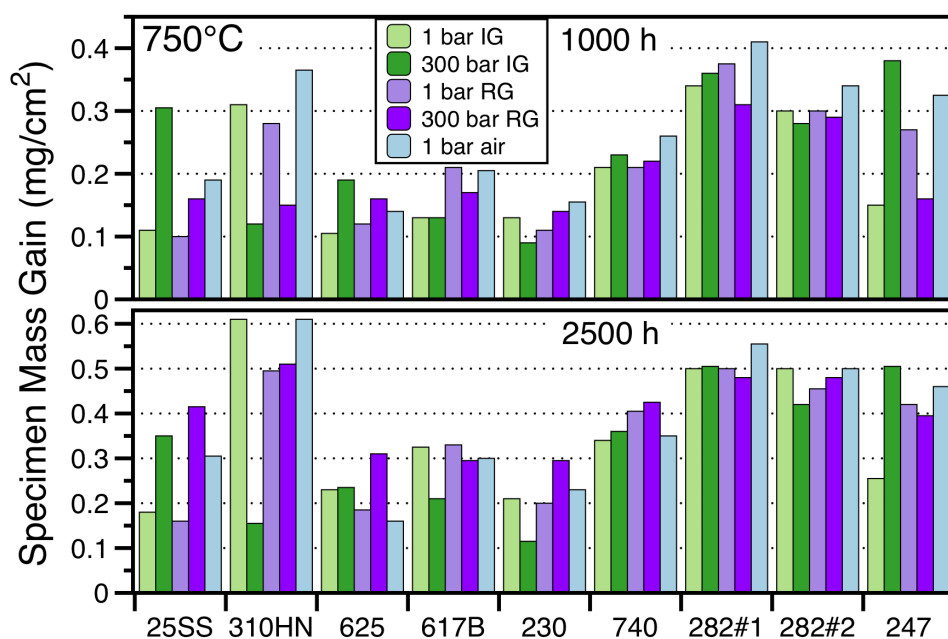


Figure 3. Median specimen mass gain values after 1,000 and 2,500 h exposures at 750°C in five different environments.

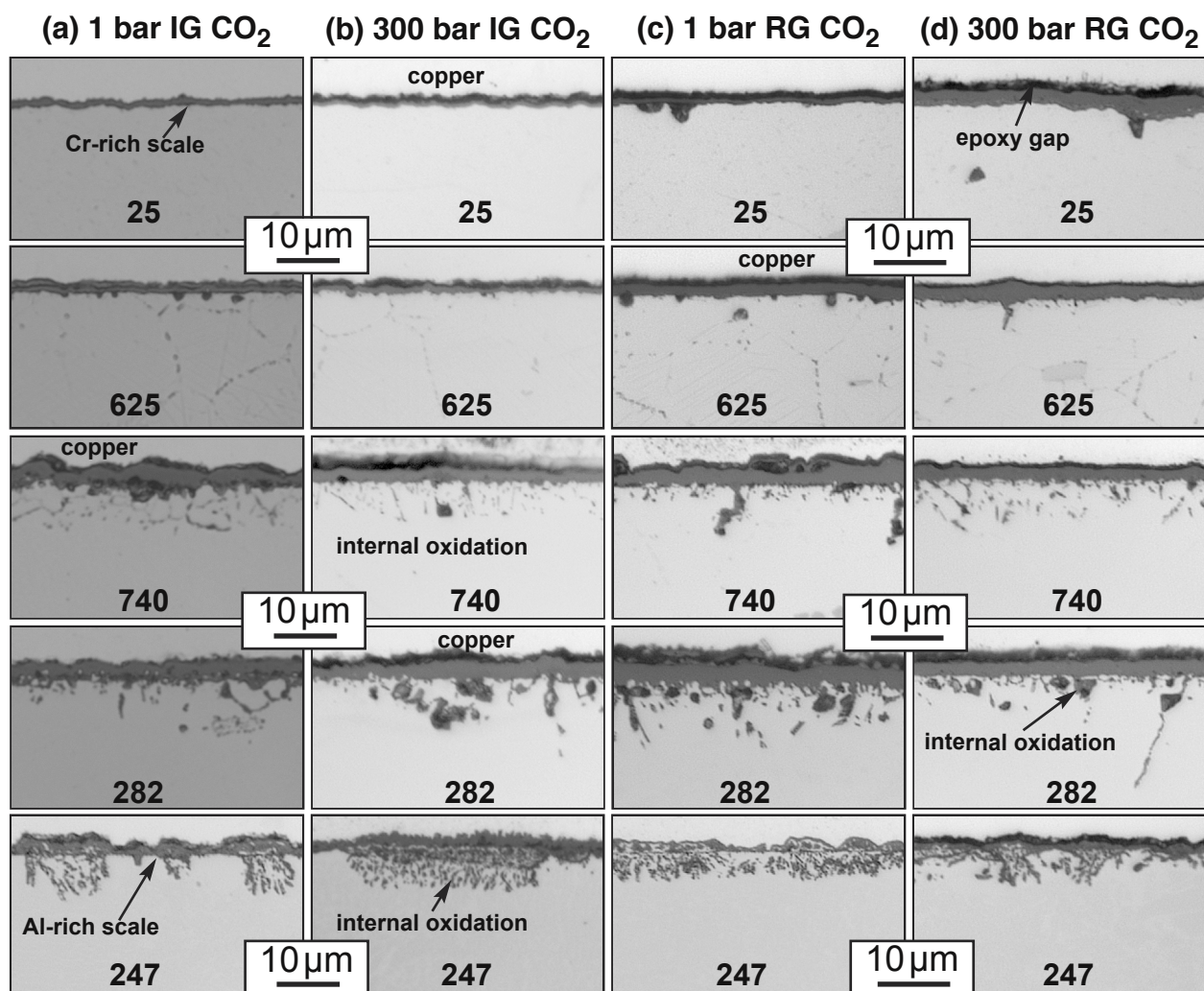


Figure 4: Light microscopy of polished cross-sections of specimens exposed for 2,500 h at 750°C in four different environments. Sections are shown of the 282 #1 heat.

was observed for alloy 247, which is consistent with the high mass gains for this alloy. Some of the internal oxidation may be due to the 1%Hf addition in this alloy [Pint 2015a]. An exposure temperature of 750°C is somewhat low for forming an alumina-scale. Further characterization is needed but it appears that the alloy was not able to form a continuous alumina scale in these conditions.

Figure 5 shows box and whisker plots of the measured oxide thickness and depth of internal attack for three of the Ni-based alloys after exposure in air and IG CO₂. Consistent with the mass change data and the cross-sections in Figure 4, the reaction products formed in these different environments were very similar. Surprisingly, there is some indication that the 300 bar IG sCO₂ condition resulted in slightly less reaction product.

Figure 6 shows the first results with controlled impurities of 1%O₂ and 0.26%H₂O at 300 bar to simulate the direct-fired cycle. For comparison, average mass gains from the IG and RG sCO₂ experiments are shown with the whisker showing one standard deviation. Three specimens of each alloy were exposed in this experiment and larger variations were noted for some alloys

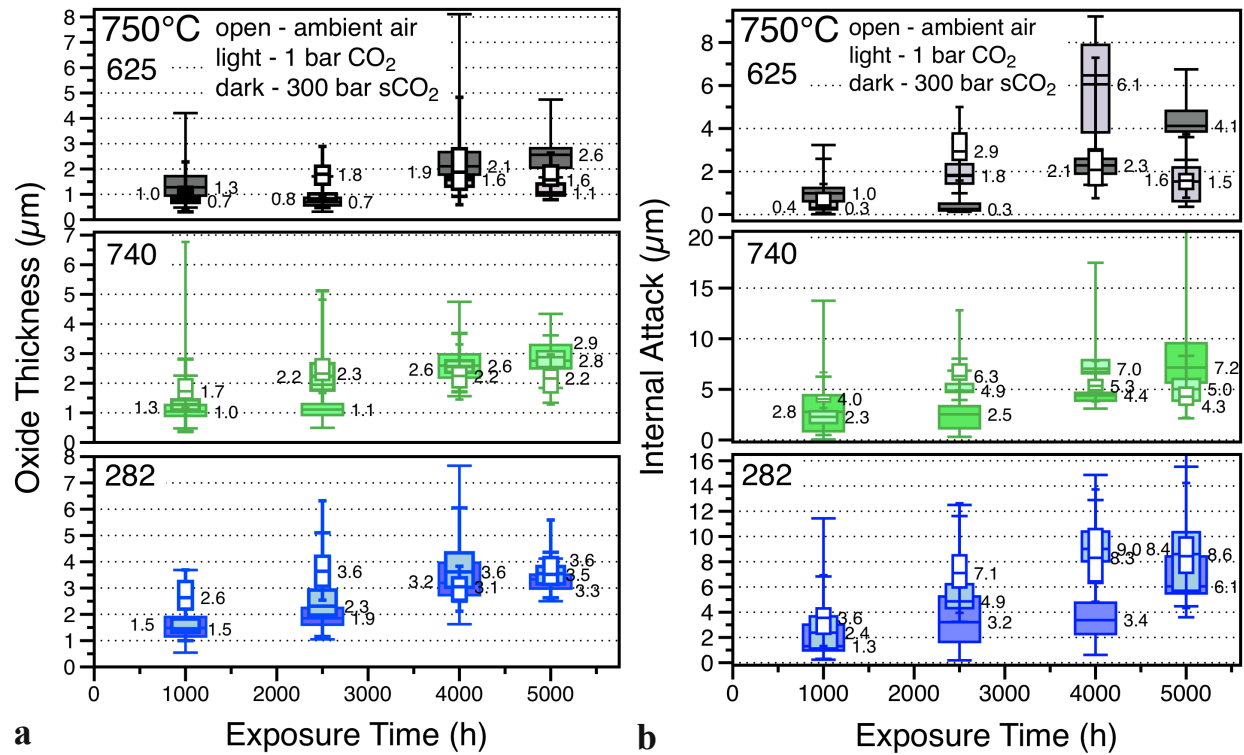


Figure 5. Box and whisker plots of (a) oxide thickness and (b) depth of internal oxidation for 625, 740 and 282 specimens exposed at 750°C in air and 1 and 300 bar IG sCO_2 .

compared to the RG and IG conditions. Additional cycles are in progress that will help to establish relative reaction rates and specimens will be removed at similar time intervals for comparison to

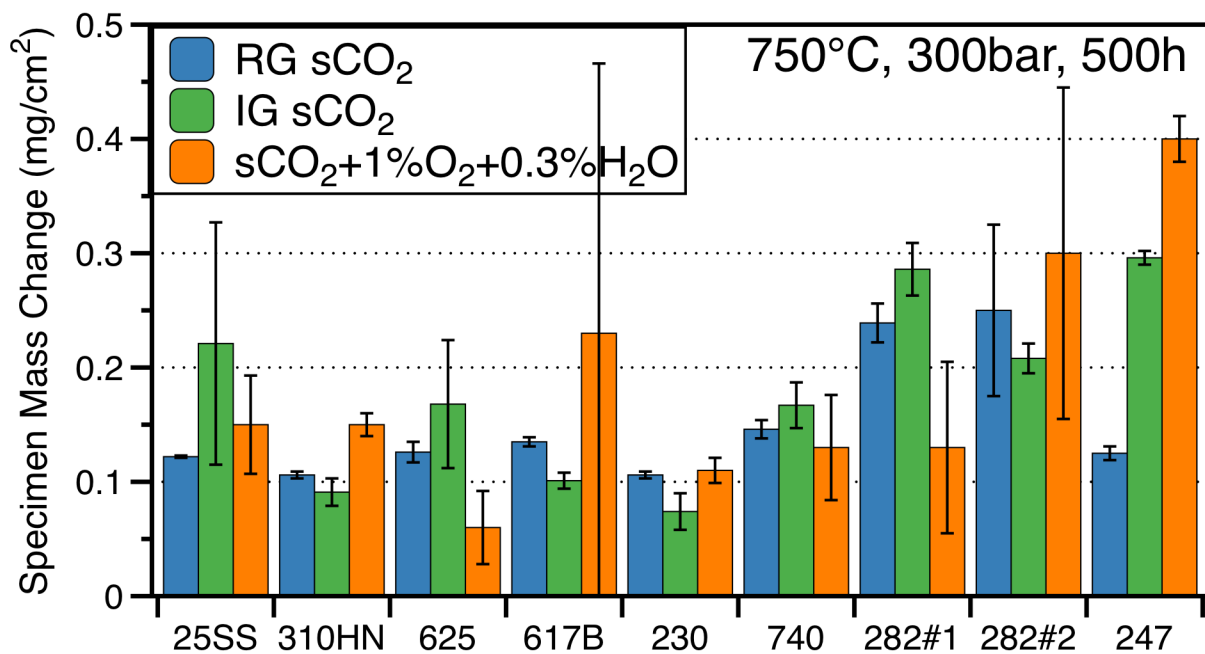


Figure 6. Mean specimen mass gain values after 500 h exposures at 750°C/300 bar in three different sCO_2 environments.

the other conditions.

DISCUSSION

The results here appear to confirm both that low impurity levels have limited effects on compatibility and that pressure (1 vs. 300 bar) has little effect on the oxidation rate. Longer exposures are required to draw a similar conclusion about high impurity levels at 300 bar. Since the oxides formed at 750°C are relatively thin, Figure 4, there is not much to learn from the polished cross-sections. Currently, transmission electron microscopy is being conducted on 625 specimens exposed for 5,000 h in air, 1 bar IG CO₂ and 300 bar IG sCO₂ in order to look for differences in the microstructure that might help explain some of the observations. For example, if there is a difference in oxide scale porosity between 1 and 300 bar. There was no indication of C ingress in this work (based on metallography, microscopy and GDOES [Lance 2018]), which suggests that these materials are relatively compatible with sCO₂ despite the high C activity created at the metal-scale interface in a CO₂ environment [Fujii 1967, Young 2011]. The internal oxidation observed, particularly for the 740 and 282 specimens, is also observed when these alloys are oxidized in air and steam. The rates of internal oxidation have been studied extensively at 800°C and were found to be acceptably low [Pint 2015b]. The oxidation rates at higher temperatures in a range of environments is relevant for the primary heat exchanger on indirect-fired systems.

One of the reasons for studying both 1 and 300 bar is that there are limited capabilities for studying compatibility at supercritical pressures, particularly with controlled impurity levels. However, an effect of pressure is to increase the amount of impurities and that may not be captured in an ambient pressure experiment. For example, the formation of CrO₂(OH)₂ is limited by the amount of H₂O and O₂ present to react with the Cr₂O₃ scale [Young 2006]. The amount of reaction at 1 bar may be negligible but not at 300 bar in a flowing test. This type of degradation is a particular concern for thin-walled components in heat exchangers.

CONCLUSIONS

Impurities are a concern for both direct- and indirect-fired supercritical CO₂ (sCO₂) cycles for high efficiency power generation. For indirect applications, comparison 500-h cycles were conducted at 750°C at 1 and 300 bar with research grade and industrial grade CO₂. Commercial Fe- and Ni-base structural alloys were exposed in each environment and reaction products were characterized after 1,000 and 2,500 h exposures. Only minor differences were noted between these two grades of CO₂ after 2,500 h and little effect of pressure was observed. For direct-fired or open cycles, a test rig has been built to conduct similar exposures at 750°C/300 bar in CO₂+1%O₂-0.25%H₂O and the first mass change results were presented.

NOMENCLATURE

CSP	=	Concentrated Solar Power
GDOES	=	Glow Discharge Optical Emission Spectroscopy
IG	=	Industrial Grade
ORNL	=	Oak Ridge National Laboratory
RG	=	Research Grade
UK	=	United Kingdom

REFERENCES

- Allam, R. J., Palmer, M. R., Brown Jr., G. W., Fetvedt, J., Freed, D., Nomoto, H., Itoh, M., Okita, N., Jones Jr., C., 2013, "High efficiency and low cost of electricity generation from fossil fuels while eliminating atmospheric emissions, including carbon dioxide," *Energy Procedia* 37, 1135–1149.
- Bender, M. D., Klug, R. C., 2014, "Comparison of Ni-Based 625 Alloy and ATI 20-25+Nb™ Stainless Steel Foils After Long-Term Exposure to Gas Turbine Engine Exhaust," ASME Paper #GT2014-25334, presented at the International Gas Turbine & Aeroengine Congress & Exhibition, Düsseldorf, Germany, June 16–20, 2014.
- Brady, M. P., Pint, B. A., Lu, Z. G., Zhu, J. H., Milliken, C. E., Kreidler, E. D., Miller, L., Armstrong, T. R., Walker, L. R., 2006, "Comparison of Oxidation Behavior and Electrical Properties of Doped NiO- and Cr₂O₃-Forming Alloys for Solid Oxide Fuel Cell Metallic Interconnects," *Oxid. Met.* 65, 237-261.
- Cao, G., Firouzdor, V., Sridharan, K., Anderson, M., Allen, T. R., 2012, "Corrosion of austenitic alloys in high temperature supercritical carbon dioxide," *Corros. Sci.* 60, 246-255.
- Cheang, V., Hedderwick, R. A., McGregor, C., 2015, "Benchmarking supercritical carbon dioxide cycles against steam Rankine cycles for Concentrated Solar Power," *Solar Energy*, 113, 199-211.
- Chen, H., Goswami, D. Y., Stefanakos, E. K., 2010, "A review of thermodynamic cycles and working fluids for the conversion of low-grade heat," *Renewable & Sustainable Energy Reviews* 14, 3059-3067.
- Dostal, V., Hejzlar, P., Driscoll, M. J., 2006, "The supercritical carbon dioxide power cycle: Comparison to other advanced power cycles," *Nuclear Technology*, 154(3), 283-301.
- Dunlevy, M. W., 2009, "An Exploration of the Effect of Temperature on Different Alloys in Supercritical Carbon Dioxide Environment," M.Sc. Thesis, MIT, Cambridge, MA.
- Ennis P. J., Quadakkers, W. J., 1985, "Corrosion and Creep of Nickel-Base Alloys in Steam Reforming Gas," in *High Temperature Alloys, Their Exploitable Potential*, eds. J. B. Marriott, M. Merz, J. Nihoul and J. Ward, Elsevier, London, p.465-74.
- Feher, E. G., 1968, "The Supercritical Thermodynamic Power Cycle," *Energy Conversion*, 8, 85-90.
- Firouzdor, V., Sridharan, K., Cao, G., Anderson, M., Allen, T. R., 2013, "Corrosion of a stainless steel and nickel-based alloys in high temperature supercritical carbon dioxide environment," *Corrosion Science* 69, 281-291.
- Fujii, C. T., Meussner, R. A., 1967, "Carburization of Fe-Cr Alloys During Oxidation in Dry Carbon Dioxide," *J. Electrochem. Soc.*, 114, 435-442.
- Furukawa, T., Inagaki, Y., Aritomi, M., 2011, "Compatibility of FBR structural materials with supercritical carbon dioxide," *Progress in Nuclear Energy* 53, 1050–1055.
- Gheno, T., Monceau, D., Young, D. J., 2013, "Kinetics of breakaway oxidation of Fe-Cr and Fe-Cr-Ni alloys in dry and wet carbon dioxide," *Corros. Sci.* 77, 246-256.
- Gong, Y., Young, D. J., Kontis, P., Chiu, Y. L., Larsson, H., Shin, A., Pearson, J. M., Moody, M. P., Reed, R. C., 2017, "On the breakaway oxidation of Fe9Cr1Mo steel in high pressure CO₂," *Acta Materialia*, 130, 361-374.
- Holcomb, G. R., 2009, "Steam Oxidation and Chromia Evaporation in Ultrasupercritical Steam Boilers and Turbines," *J. Electrochem. Soc.* 156 (9), C292-C297.

- Huczowski, P., Olszewski, T., Schiek, M., Lutz, B., Holcomb, G. R., Shemet, V., Nowak, W., Meier, G. H., Singheiser, L., Quadakkers, W. J., 2014, "Effect of SO₂ on oxidation of metallic materials in CO₂/H₂O-rich gases relevant to oxyfuel environments," *Materials and Corrosion* 65, 121-131.
- Iverson, B. D., Conboy, T. M., Pasch, J. J., Kruizenga, A. M., 2013, "Supercritical CO₂ Brayton cycles for solar-thermal energy," *Applied Energy*, 111, 957-970.
- Jönsson, B., Svedberg, C., 1997, "Limiting Factors for Fe-Cr-Al and NiCr in Controlled Industrial Atmospheres," *Mater. Sci. Forum*, 251-254 (1997) 551-558.
- Kranzmann, A., Huenert, D., Rooch, H., Urban, I., Schulz, W., Oesterle, W., 2009, "Reactions at the interface between steel and oxide scale in wet CO₂ containing atmospheres," NACE Paper 09-265, Houston, TX, presented at NACE Corrosion 2009, Atlanta, GA, March 2009.
- Kung, S. C., Shingledecker, J. P., Thimsen, D., Wright, I. G., Tossey, B. M., Sabau, A. S., 2016, "Oxidation/Corrosion in Materials for Supercritical CO₂ Power Cycles," in *Proceedings of the 5th International Symposium on Supercritical CO₂ Power Cycles*, San Antonio, TX, Paper #9.
- Lance, M. J., Leonard, D. N., Pint, B. A., 2018, "The Use of Glow Discharge Optical Emission Spectroscopy to Quantify Internal Carburization in Supercritical CO₂," in *Proceedings of the 6th International Symposium on Supercritical CO₂ Power Cycles*, Pittsburgh, PA, Paper #117.
- Mahaffey, J., Kaira, A., Anderson, M., Sridharan, K., 2014 "Materials Corrosion in High Temperature Supercritical Carbon Dioxide," in *Proceedings of the 4th International Symposium on Supercritical CO₂ Power Cycles*, Pittsburgh, PA, Paper #2.
- Mahaffey, J., Adam, D., Brittan, A., Anderson, M., Sridharan, K., 2016, "Corrosion of Alloy Haynes 230 in High Temperature Supercritical Carbon Dioxide with Oxygen Impurity Additions," *Oxidation of Metals* 86, 567-580.
- Meier, G. H., Coons, W. C., Perkins, R. A., 1982, "Corrosion of Iron-, Nickel- and Cobalt-Base Alloys in Atmospheres Containing Carbon and Oxygen," *Oxidation of Metals* 17, 235-262.
- Moore, R., Conboy, T., 2012, "Metal Corrosion in a Supercritical Carbon Dioxide – Liquid Sodium Power Cycle," Sandia National Laboratory Report SAND2012-0184.
- Nguyen, T. D., Zhang, J. Q., Young, D. J., 2014, "Water vapour effects on corrosion of Fe-Cr and Fe-Cr-Ni alloys containing cerium and manganese in CO₂ gas at 818°C," *Corros. Sci.* 89, 220-235.
- Oh, C. H., Lillo, T., Windes, W., Totemeier, T., Ward, B., Moore, R., Barner, R., 2006, "Development Of A Supercritical Carbon Dioxide Brayton Cycle: Improving VHTR Efficiency And Testing Material Compatibility," Idaho National Laboratory Report INL/EXT-06-01271.
- Olivares, R. I., Young, D. J., Marvig, P., Stein, W., 2015, "Alloys SS316 and Hastelloy-C276 in Supercritical CO₂ at High Temperature," *Oxid. Met.* 84, 585–606.
- Pike, L. M., 2008, "Development of a Fabricable Gamma-Prime (γ') Strengthened Superalloy," in *Superalloys 2008*, R. C. Reed et al. eds TMS, Warrendale, PA, 2008, p.191-200.
- Pint, B. A., Dryepontdt, S., Rouaix-Vande Put, A., Zhang, Y., 2012, "Mechanistic-Based Lifetime Predictions for High Temperature Alloys and Coatings," *JOM*, 64, 1454-1460.
- Pint, B. A., Keiser, J. R., 2014a, "The Effect of Temperature on the sCO₂ Compatibility of Conventional Structural Alloys," in *Proceedings of the 4th International Symposium on Supercritical CO₂ Power Cycles*, Pittsburgh, PA, September 2014, Paper #61.
- Pint, B. A., Thomson, J. K., 2014b, "Effect of oxy-firing on corrosion rates at 600°-650°C," *Materials*

and Corrosion 65, 132-140.

Pint, B. A., 2014c, "The Use of Model Alloys to Study the Effect of Alloy Composition on Steam and Fireside Corrosion," NACE Paper 14-4279, Houston, TX, presented at NACE Corrosion 2014, San Antonio, TX.

Pint B. A., Keiser, J. R., 2015a, "Initial Assessment of Ni-Base Alloy Performance in 0.1 MPa and Supercritical CO₂," JOM 67(11), 2615-2620.

Pint, B. A., Thiesing, B. P., 2015b, "Effect of Environment on the Oxidation Behavior of Commercial and Model Ni-Base Alloys," NACE Paper C2015-5919, Houston, TX, presented at NACE Corrosion 2015, Dallas, TX.

Pint, B. A., Brese, R. G., Keiser, J. R., 2016a, "The Effect of Temperature and Pressure on Supercritical CO₂ Compatibility of Conventional Structural Alloys," in Proceedings of the 5th International Symposium on Supercritical CO₂ Power Cycles, San Antonio, TX, Paper #56.

Pint, B. A., Brese, R. G., Keiser, J. R., 2016b, "The Effect of Impurities on Supercritical CO₂ Compatibility of Structural Alloys," in Proc. 8th Inter. Conf. on Advances in Materials Technology for Fossil Power Plants, ASM International, Materials Park, OH, 2016, pp.845-855

Pint, B. A., Brese, R. G., Keiser, J. R., 2017a, "Effect of Pressure on Supercritical CO₂ Compatibility of Structural Alloys at 750°C," Materials and Corrosion, 68, 151-158.

Pint, B. A., Brese, R. G., Keiser, J. R., 2017b, "Effect of Pressure and Thermal Cycling on Compatibility in CO₂ for Concentrated Solar Power Applications," ASME Paper #GT2017-65066, for the International Gas Turbine & Aeroengine Congress & Exhibition, Charlotte, NC.

Pint, B. A., Brese, R. G., Keiser, J. R., 2018, "The effect of impurities and pressure on oxidation in CO₂ at 700°-800°C," NACE Paper C2018-11199, Houston, TX, presented at NACE Corrosion 2018, Phoenix, AZ.

Quadakkers, W. J., Olszewski, T., Piron-Abellan, J., Shemet, V., Singheiser, L., 2011, "Oxidation of Metallic Materials in Simulated CO₂/H₂O-rich Service Environments Relevant to an Oxyfuel Plant," Mater. Sci. Forum 696, 194-199.

Rouillard, F., Charton, F., Moine, G., 2011 "Corrosion Behavior of Different Metallic Materials in Supercritical Carbon Dioxide at 550°C and 250 bars," Corrosion 67(9), 095001

Shingledecker, J. P., Pharr, G. M., 2013, "Testing and Analysis of Full-Scale Creep-Rupture Experiments on Inconel Alloy 740 Cold-Formed Tubing," J. Mater. Eng. Performance, 22, 454-462.

Tan, L. Anderson, M., Taylor, D., Allen, T. R., 2011, "Corrosion of austenitic and ferritic-martensitic steels exposed to supercritical carbon dioxide," Corrosion Science 53, 3273-3280.

Viswanathan, R., Henry, J.F., Tanzosh, J., Stanko, G., Shingledecker, J., Vitalis, B., Purgert, R., 2005, "U.S. Program on Materials Technology for Ultra-Supercritical Coal Power Plants," J. Mater. Eng. Performance 14(3), 281-285.

Viswanathan, R., Shingledecker, J., Purgert, R., 2010, "Evaluating Materials Technology for Advanced Ultrasupercritical Coal-Fired Plants," Power, 154(8), 41-45.

Wright, I. G., Pint, B. A., Shingledecker, J. P., Thimsen, D., 2013, "Materials Considerations for Supercritical CO₂ Turbine Cycles," ASME Paper #GT2013-94941, presented at the International Gas Turbine & Aeroengine Congress & Exhibition, San Antonio, TX, June, 3-7, 2013.

Young D. J., Pint, B. A., 2006, "Chromium Volatilization Rates from Cr₂O₃ Scales Into Flowing

Gases Containing Water Vapor,” *Oxid. Met.*, 66, 137-153.

Young, D. J., Zhang, J., Geers, C., Schütze, M., 2011, “Recent advances in understanding metal dusting: A review,” *Mater. Corros.* 62, 7-28.

Young, D. J., Nguyen, T. D., Felfer, P., Zhang, J., Cairney, J. M., 2014, “Penetration of protective chromia scales by carbon,” *Scripta Materialia* 77, 29–32.

Yu, C., Nguyen, T. D., Zhang, J., Young, D. J., 2016a, “Sulfur Effect on Corrosion Behavior of Fe-20Cr-(Mn, Si) and Fe-20Ni-20Cr-(Mn, Si) in CO₂-H₂O at 650°C,” *Journal of The Electrochemical Society*, 163, 3 (2016): pp.C106-C115.

Yu, C., Zhang J., Young, D. J., 2016b, “High temperature corrosion of Fe-Cr-(Mn/Si) alloys in CO₂-H₂O-SO₂ gases,” *Corrosion Science* 112, 214–225.

Zhao, S. Q., Xie, X. S., Smith, G. D. Patel, S. J., 2003, “Microstructural stability and mechanical properties of a new nickel based superalloy,” *Mater. Sci. Eng. A* 355, 96-105.

ACKNOWLEDGEMENTS

The authors would like to thank M. Howell, M. Stephens, T. M. Lowe, R. G. Brese and T. Jordan for assistance with the experimental work. Material was provided by Haynes International, Special Metals and Sandvik. S. S. Raiman provided helpful comments on the manuscript. This research was sponsored by the U.S. Department of Energy, Office of Fossil Energy, Crosscutting Technology Program and the Office of Energy Efficiency and Renewable Energy, Solar Energy Technology Program: SuNLaMP award number DE-EE0001556. This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).