

Effect of Oxygen Impurity on Corrosion in Supercritical CO₂ Environments

Jacob Mahaffey

Research Assistant
University of Wisconsin-Madison
jmahaffey@wisc.edu

David Adam

Research Assistant
University of Wisconsin-Madison
dadam@wisc.edu

Dr. Mark Anderson

Research Professor
University of Wisconsin-Madison
manderson@engr.wisc.edu

Dr. Kumar Sridharan

Research Professor
University of Wisconsin-Madison
kumar@engr.wis

Other contributors: Andrew Brittan, Muhammet Arik, Anthony Schroeder
abrittan@wisc.edu, arik2@wisc.edu, amschroeder5@wisc.edu



Jacob Mahaffey is a research assistant under Dr. Mark Anderson. His research focuses on corrosion of materials in supercritical carbon dioxide environments. He attended Carthage College where he received his BA in Physics and Chemistry in 2013.



David Adam is a research assistant under Dr. Kumar Sridharan. His research focuses on corrosion of materials in supercritical carbon dioxide environments. He attends University of Wisconsin-Madison where he will receive his Master's degree in nuclear engineering in the summer of 2016.



Dr. Mark Anderson is a research professor in the Department of Engineering Physics and Director of the University of Wisconsin's Thermal Hydraulic Laboratory. He also manages the UW - Madison Tantalus facility in Stoughton WI. Dr. Anderson studies both the physics, thermal hydraulic performance and material corrosion issues of several different fluids (salts, liquid metals, SCW, S-Co₂).



Dr. Kumar Sridharan's expertise spans a broad spectrum of areas in materials science, including nuclear reactor materials, corrosion, physical metallurgy, surface modification and coatings processes, ion implantation, plasma-based synthesis and deposition of materials, characterization and testing of materials, interfaces of materials and manufacturing, and industrial applications

ABSTRACT:

A high temperature, high pressure autoclave was constructed to withstand temperatures and pressures up to 750°C and 20Mpa respectively. Superalloys Haynes 230 (H230) and Haynes 625 (H625) were tested in research grade (99.999%) carbon dioxide, and research grade carbon dioxide doped with 100ppm of oxygen. These tests were conducted at temperatures of 650 and 750°C at a pressure of 20Mpa. These tests were completed at 200 hour intervals out to 1,000 hours. Samples were analyzed using weight change measurements along with cross sectional SEM/EDS imaging to understand the effect of oxygen on oxide growth and development.

INTRODUCTION:

The supercritical carbon dioxide (SC-CO₂) Brayton cycle is being considered for next generation energy systems, including solar, fossil, and nuclear power systems. The Brayton cycle provides higher efficiencies compared to the Rankine steam cycle as a result of higher operating temperatures and lower compressive work stemming primarily from the increased fluid density of SC-CO₂. These phenomena allow for smaller component size (e.g., turbo-machinery), fewer components, and simpler cycle design; however, materials corrosion has been identified as one of the most significant gaps in the implementation of SC-CO₂ Brayton cycle [1, 2]. Thus, it is important to understand the materials demands under realistic conditions throughout the cycle. A custom facility was constructed to test the effects of impurity doped CO₂. This facility is pictured in figure 1 below.

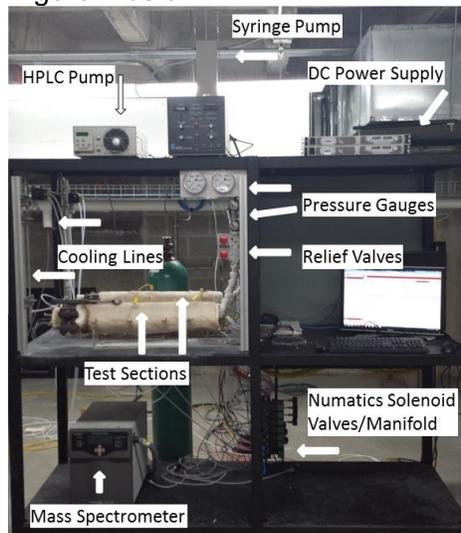


Figure 1: Supercritical CO₂ testing facility.

The testing facility consists of two autoclaves capable of simultaneous operation at independent temperatures. The autoclaves are designed to handle temperatures up to 750°C at 2900psi. The temperature are regulated within $\pm 1^\circ\text{C}$ and the pressure within $\pm 2.5\text{psi}$. The flow rate of the system is designed to refresh the CO₂ every two hours. The inlet and exit gas is measured using a trace oxygen analyzer ($\pm 1\text{ppm}$), a mass spectrometer, and a GC (CO/CH₄: $>50\text{ppb}$ ($\pm 2.5\text{ppb}$)).

Haynes 230 and Haynes 625 were tested in this study under research grade CO₂ (99.999% pure, H₂O < 3ppm, N₂ < 5ppm, THC < 1ppm, Ar+O₂+CO < 1ppm) and 100 \pm 15ppm O₂ doped research grade CO₂ fluids. The variation in oxygen concentration is due to oxygen solubility changes as CO₂ tank pressure decreased throughout the testing interval. Tests were conducted

at 650 and 750°C at 20MPa (2900psi). The compositions of the two alloys are listed in Table 1 below.

Table 1: Composition of alloys Haynes 230 and Haynes 625

	C	Mn	Fe	Si	Cu	Ni	Cr	Al	Ti	Co	Mo	Nb	W
H230	0.1	0.5	1.0	0.3	0.0	59.93	22.0	0.37	0.01	0.21	1.23		14.1
H625	0.02	0.26	5	0.25		59.63	21.9	0.22	0.29	0.28	8.59	3.51	

The goal of this work is to determine the effect that increased oxygen activity has on the oxidation of Ni-based superalloys. Previous work presented by Meier³ has been conducted on Fe-Cr alloys exposed to 1-3% oxygen additions at 550-650C. The goal of their work was to determine if increased oxygen potential could reduce the carbon activity, and therefore reduce the production of carbides in the base material. This reduction of carburization was observed, but excess oxygen also significantly increased oxidation rates [3]. The conclusions presented in the paper are also important to study with Ni-based superalloys to understand how oxygen can affect the oxidation/carburization rates. Oxidation effects are presented in this document, while ongoing work is focusing on alloy carburization

RESULTS AND DISCUSSION:

Weight change measurements obtained present a time-dependent trend of oxide development. This technique is used as a preliminary measure due to potential differences in oxide density. Weight change measurements for H230 and H625 are plotted in Figure 2 below.

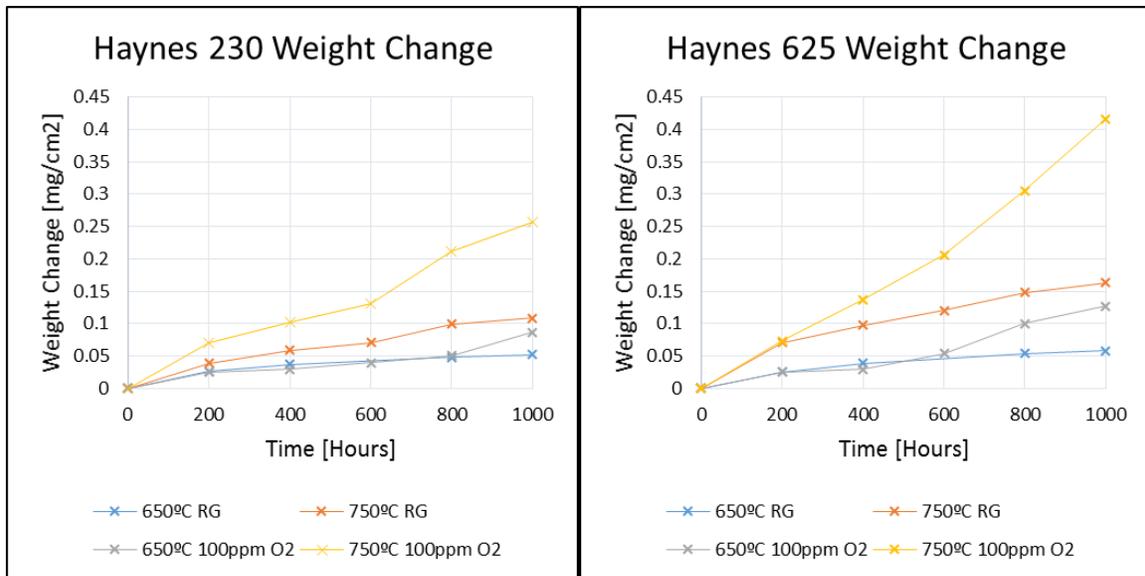


Figure 2: Weight change measurements for H230 (left) and H625 (right) after exposure to CO₂ at 650°C and 750°C in RG and Doped (100ppm O₂) conditions.

Weight change in figure 2 suggests that oxygen has a significant effect on oxidation rates. This is most evident as temperatures increase from 650 to 750°C. One concerning feature in the weight change data is the lack of protective behavior of the oxide formation on samples exposed to oxygen doped CO₂. This is observed in for both H230 and H625 samples at 750C. Instead of having a parabolic relation, the weight gain continuously increases, or have sudden

increase at later time exposures. In order to study the oxide further, cross-sectional SEM images were produced. Cross sections for H230 and H625 exposed to RG CO₂ and oxygen doped CO₂ are shown in Figure 3 below.

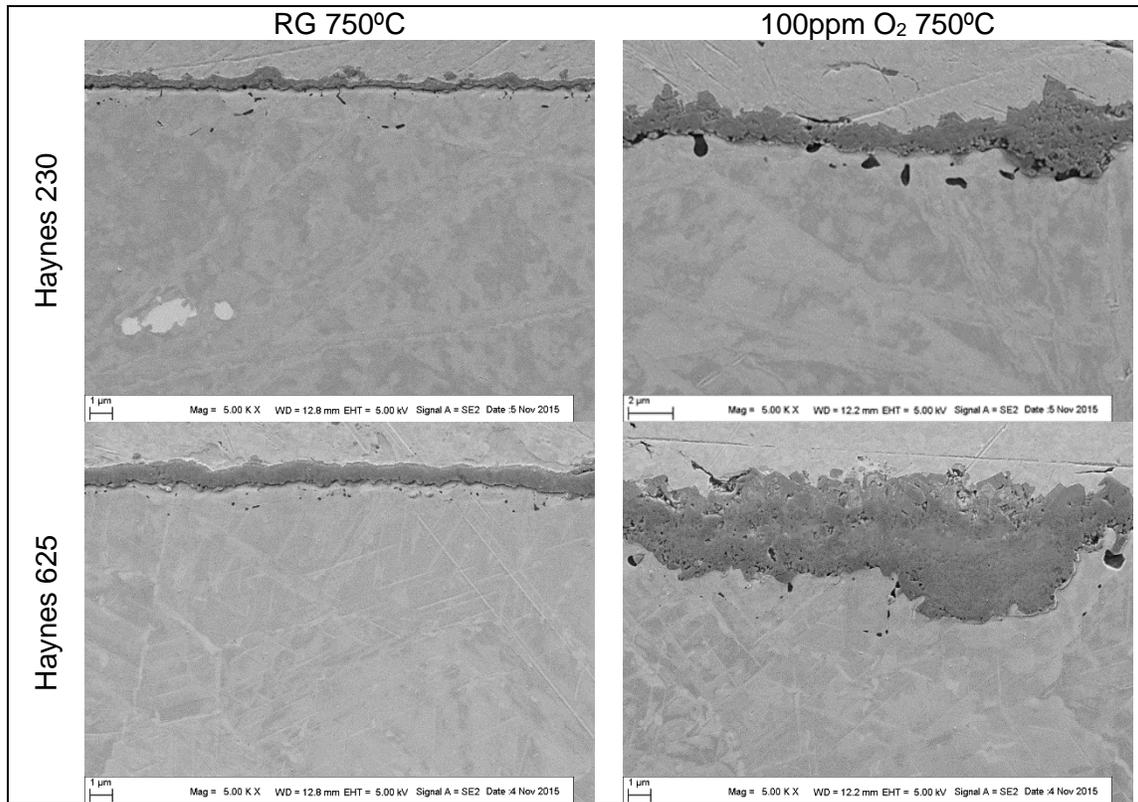
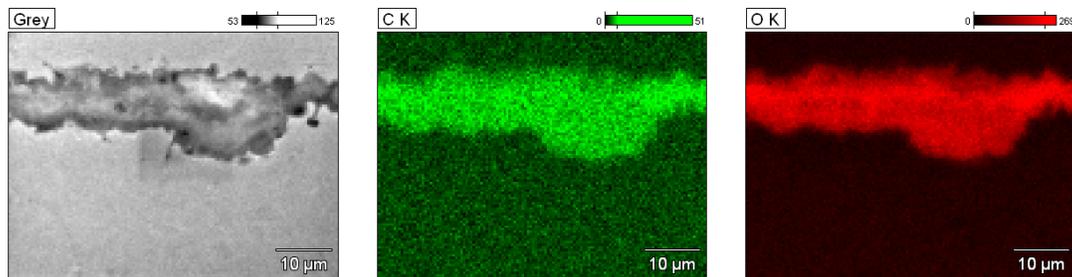


Figure 3: Comparison of oxide thicknesses for Haynes 625 and Haynes 230 after 1000 hours in RG and doped CO₂

Figure 3 compares oxide behavior for Haynes 230 and Haynes 625 for an oxygen-doped environment (100ppm) and a RG environment at 750°C. It is observed that the oxide thickness on samples exposed to the oxygen doped system is both much greater and more variable than on samples exposed to RG CO₂. These images also show that Haynes 230 has a smaller oxide thickness than Haynes 625. Both alloys exposed to oxygen doped CO₂ at 750°C also show void formation in the bulk material, possibly indicating the Kirkendall Effect which is the diffusion into the oxide faster than through the sample matrix. Further investigation needs to be completed to definitively prove this. In order to show the composition of the oxides for different exposures, both EDS surface mapping and line scans were completed. These are shown in Figures 7 below.



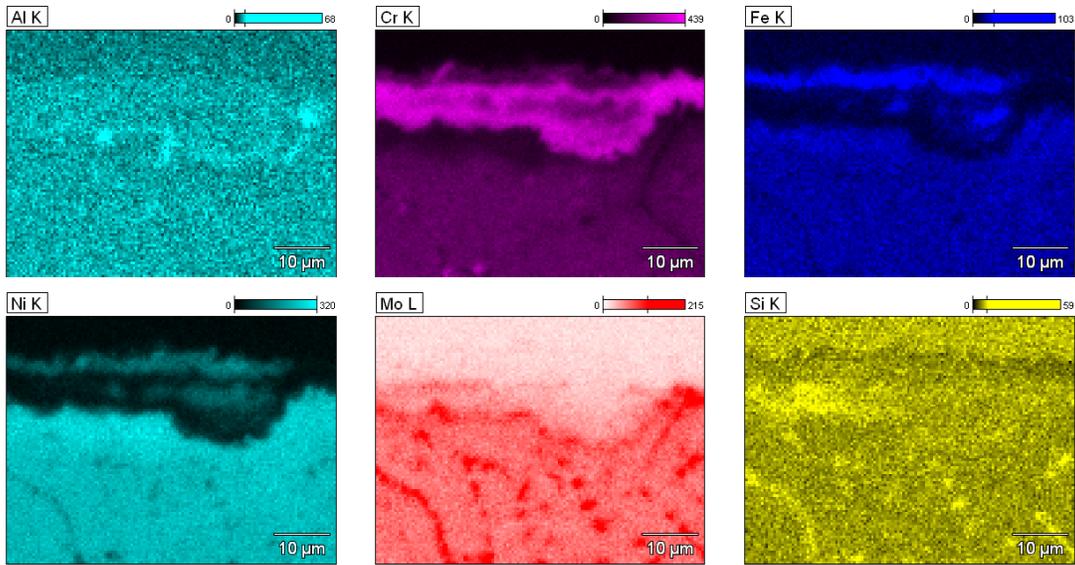


Figure 4: 2D EDS cross sectional mapping of alloy Haynes 625 after 1000 hours of exposure to CO₂ doped with 100 ppm O₂ at 750°C

Figure 4 shows the EDS mapping of Haynes 625 exposed to doped CO₂ at 750°C for 1000 hours. The oxide that is developed on this sample contains features not observed in past studies completed at the University of Wisconsin. Of particular note is the concentration of nickel and iron within the oxide surfaces. These metal oxides were not observed in samples exposed to pure RG CO₂. It is proposed that the increase in partial pressure of oxygen allows the formation of oxides that were otherwise thermodynamically unfavorable in RG CO₂. It is also theorized that chromium diffusion to the oxide becomes more rate limiting as the oxidation rate increases as a result of the increased oxygen potential. This is also supported by the appearance of large chromium depletion zones underneath the oxide. Additionally, increased concentration of molybdenum and silicon were mapped along grain boundaries, most likely due to the formation of their respective carbides along said grain boundaries. This is shown in more detail by the EDS line scans presented in Figure 6.

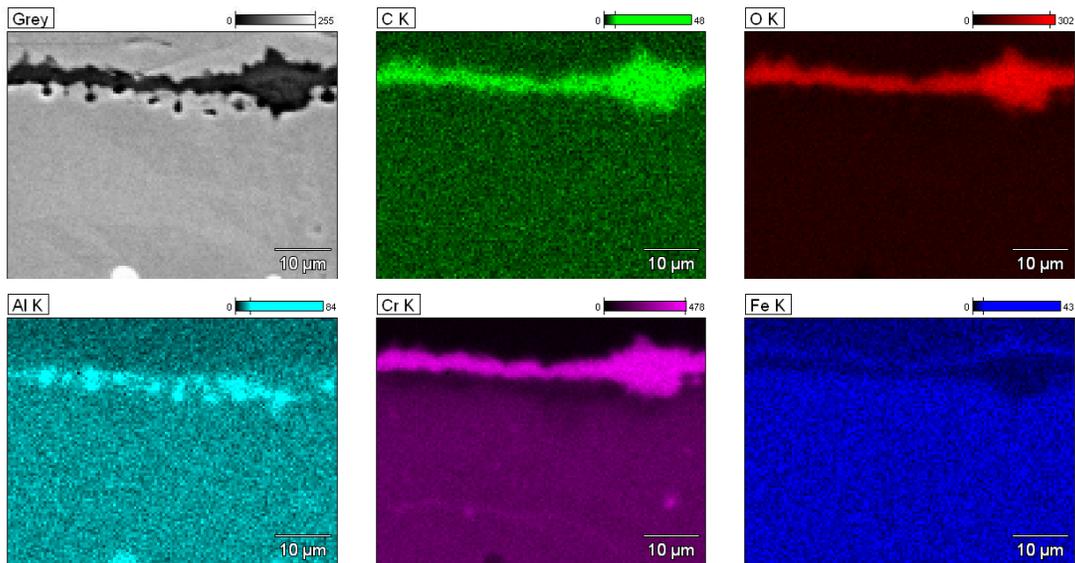
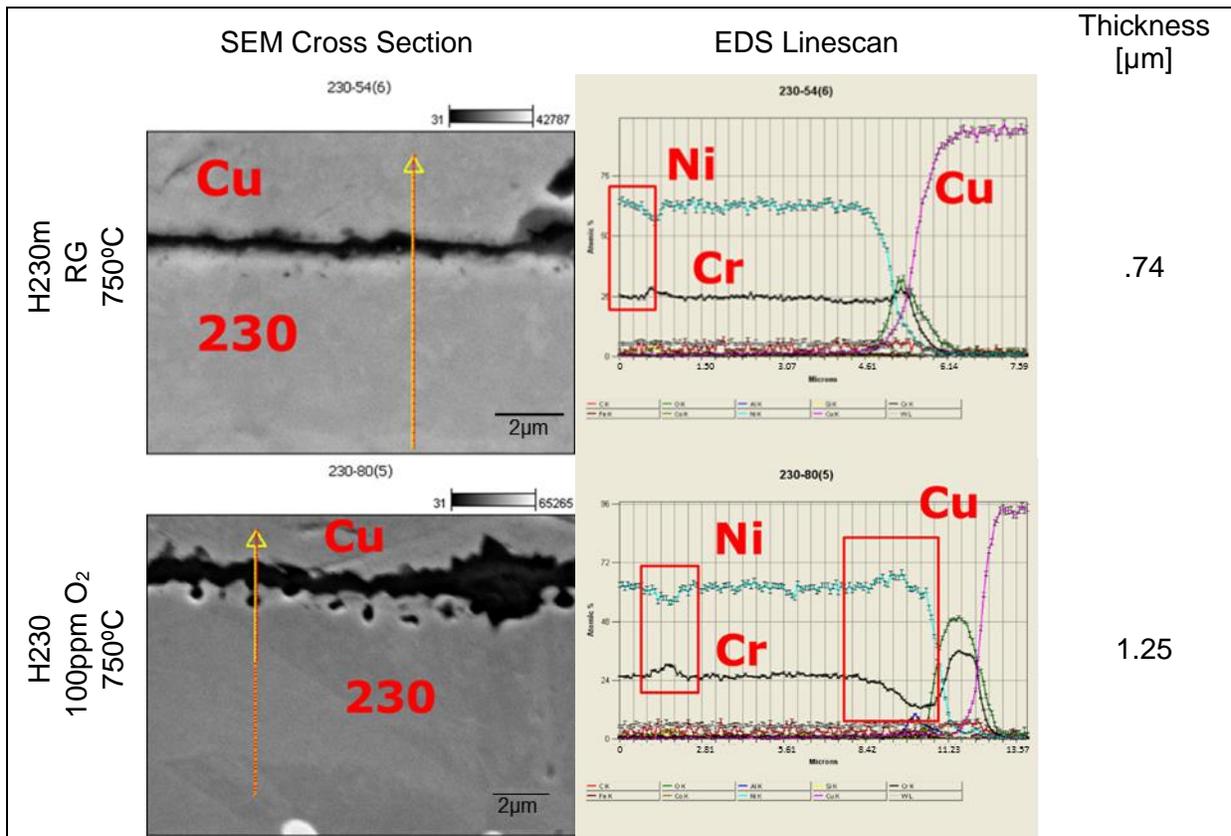


Figure 5: 2D EDS cross sectional mapping of alloy Haynes 230 after 1000 hours of exposure to CO₂ doped with 100 ppm O₂ at 750°C

Figure 5 shows EDS surface mapping for Haynes 230 exposed to oxygen doped CO₂ at 750°C. Figure 5 very closely matches the trends observed in figure 4. The main differences from Haynes 625 are the lack of molybdenum along the grain boundaries (not shown above) and the presence of aluminum in the void induced region. This aluminum/alumina layer is not as well defined for Haynes 625. These are due to compositional differences in the base material, listed in Table 1. Another characterization of these effects is shown in the EDS line scans in Figure 8 below.

The oxide growth appears to be significantly thicker on the Haynes 625 samples (most obvious in the oxygen doped case). Ongoing testing has provided some evidence that initial stage spallation may have occurred in the oxygen doped system, followed by the formation of a stable oxide. If this occurred, the reduced thickness in the H230 sample could be a result of spallation of the oxide. Another difference between the two alloys is the presence of large tungsten carbides present in H230 and molybdenum carbides in the H625 samples. Further investigation of the carburization of the samples is being studied.



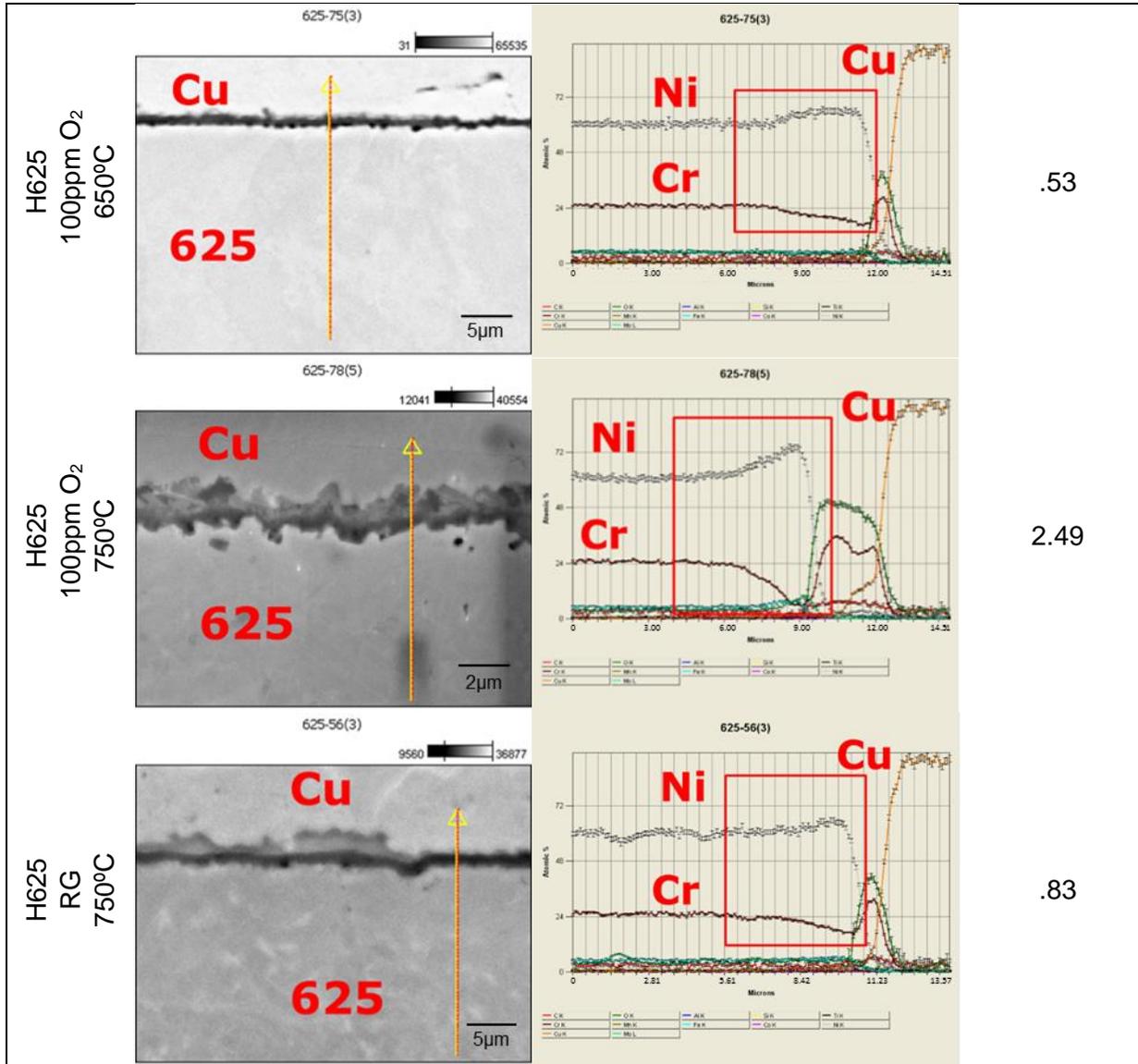


Figure 6: SEM cross section with corresponding EDS line scans for Haynes 230 and H625 after 1000 hours of exposure in different CO₂ conditions.

These line scans shown above in Figure 6 are labeled with red boxes to show chromium depletion zones, and in some cases (top 2) chromium spikes. These spikes in chromium indicate the formation of chromium carbides along the grain boundaries. Further characterization of concentration and depth of carburization is currently being investigated. The chromium depletion zones are much more pronounced in the samples exposed to oxygen-doped CO₂. This is a result of the increased corrosion rate due to the high oxygen potential. In oxygen-doped environments, it is proposed that chromium diffusion becomes rate limiting in the corrosion process, and therefore leads to the formation of other oxides such as iron and nickel. The line scans also suggest the presence of carbon in all oxide layers present, along with small spikes in aluminum for samples exposed to oxygen-doped CO₂ at 750°C.

Conclusions

Weight change measurements and SEM work were conducted to characterize oxide thickness and composition for alloys Haynes 230 and Haynes 625 for RG and 100ppm O₂ doped CO₂ at temperatures ranging from 650-750°C. Based on SEM images, samples exposed to oxygen doped CO₂ (100ppm) showed significantly larger oxide thickness, and contained multiple oxides that were not present in other conditions. As expected, samples exposed to higher temperatures showed increases in oxide thickness. SEM also showed preferential carburization along grain boundaries, along with uniform carbon deposits throughout the oxide for samples exposed to all conditions. As a result of these findings, it is advised oxygen should be limited in the CO₂ environment to reduce oxide growth.

Future/Ongoing Work

Current testing is being completed on samples exposed to CO₂ containing 7ppm of oxygen. Preliminary results give evidence towards initial stage spallation of the oxide, followed by a subsequent re-oxidation. The oxide formed after the spallation creates a more stable oxide layer similar to what was observed on the samples exposed to 100ppm of oxygen. Further investigation of the initial stage oxidation in oxygen doped systems needs to be studied in order to make these conclusions. Substantial work needs to be completed on studying the carbon concentration throughout the oxide, and ingress into the base material. Future work will be focused on characterizing this carbon migration.

REFERENCES

- [1] Gomez, Judith. "Degradation Mechanisms and Development of Protective Coatings for TES and HTF Containment Materials." *National Renewable Energy Laboratory* (2012): 1-35. Print.
- [2] Ma, Zhiwen, and Turchi, C., "Advanced Supercritical Carbond Dioxide Power Cycle Configurations for Use in Concentrating Solar Power Systems." *Proceeds of the Supercritical CO2 Power Cycle Symposium*, Boulder, CO. 2011. Supercritical
- [3] Meier, Gerald H., Keeyoung Jung, Nan Mu, Nazik M. Yanar, Frederick S. Pettit, J. Pirón Abellán, Tomasz Olszewski, L. Nieto Hierro, Willem J. Quadackers, and Gordon R. Holcomb. "Effect of Alloy Composition and Exposure Conditions on the Selective Oxidation Behavior of Ferritic Fe–Cr and Fe–Cr–X Alloys." *Oxid Met Oxidation of Metals* 74.5-6 (2010): 319-40.

Acknowledgements

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.