ABSTRACT

In both open and closed supercritical CO\textsubscript{2} (sCO\textsubscript{2}) cycles, there is considerable interest in increasing the size and efficiency of such systems, perhaps by increasing the peak temperature. The current project is evaluating a wide range of Fe- and Ni-base alloys, which typically form protective Cr- and Al-rich surface oxides, and other candidate materials, including ceramics, with a goal of establishing maximum use temperatures in sCO\textsubscript{2} for each class of materials. A new sCO\textsubscript{2} system has been designed and built with up to 930°C (1700°F) and 55 MPa (8,000 psi) capabilities. Initial 500h experiments have been completed at 650°, 700° and 750°C with 20MPa CO\textsubscript{2}. As has been observed in other studies, higher alloyed Fe- and Ni-base alloys show protective behavior, relatively unaffected by the sCO\textsubscript{2} environment, while lower alloyed Fe-base alloys were more severely attacked. With increasing temperature, mass gains were slightly higher for the M-Cr alloys that formed protective chromia scales but some alumina-forming alloys had the highest mass gain at 650°C. Comparisons in 1 bar dry air and CO\textsubscript{2} with and without O\textsubscript{2} and H\textsubscript{2}O impurities were performed at 700°C as a baseline for the sCO\textsubscript{2} results.

INTRODUCTION

A wide range of open and closed Brayton and Rankine cycle systems employing supercritical CO\textsubscript{2} (sCO\textsubscript{2}) as the working fluid have been proposed for power generation applications [e.g. Dostal 2006, Zhang 2006, Chen 2010, Iverson 2013, Wright 2013]. The highest temperature systems, 500°-760°C (930°-1400°F) at 20-30 MPa (2900-4350 psig, 200-300 bar) develop hot gas path environments that present challenging requirements of strength and environmental resistance for the materials of construction. At these temperatures and pressures, the number of candidate alloys is extremely limited. The open cycle system (i.e. Allam cycle [Allam, 2011, 2013a, 2013b] burns fossil fuels and captures CO\textsubscript{2} with 700°-775°C (1300°-
1430°F) sCO₂ turbine exhaust temperatures and 1150°C/300 bar (2100°F/4350 psig) combustor conditions. A thermal protection system such as a ceramic thermal barrier coating [Darolia 2013] will be needed to lower the metal temperature from 1150°C to ~900°C, as no conventional structural materials can realistically operate at those peak conditions for the extended lifetimes typically required of power generation systems [Pint 2006].

While CO₂ is sometimes described as inert, the available literature on the effects of CO₂ on high temperature oxidation suggests this is an unusual use of this term. Decades old work at 1bar CO₂ [McCoy 1965] suggested that internal carburization is an issue for conventional stainless steels that normally form a protective Cr-rich external oxide or scale. More recent work has shown thick Fe-rich oxides formed on ferritic-martensitic (9-12%Cr) steels exposed to sCO₂ at 550°C [Rouillard 2011] that would normally form a thin protective scale at those temperatures. For Ni-base alloys, there is similar concern that strengthening elements that readily form carbides (e.g. W, Ta, Ti) could be internally carburized by a similar mechanism. Several groups have investigated high temperature sCO₂ compatibility over a wide range of materials [Oh 2006, Dunlevy, 2009, Tan 2011, Moore, 2012, Firouzdor 2013, He 2014].

The current project at Oak Ridge National Laboratory (ORNL) was initiated to provide a broad materials assessment of the sCO₂ compatibility of relevant Fe- and Ni-base alloys with evaluations up to 760°C/30MPa (1400°F/4500psig). A new experimental rig was developed with those capabilities and the first 500h results at 650°-750°C are reported here along with 1 bar results at 700°C to provide a baseline for comparison.

EXPERIMENTAL PROCEDURE

The sCO₂ system at ORNL utilizes an autoclave fabricated from Haynes International alloy 282, a γ’-strengthened superalloy intended for high temperature structural applications. The use of this alloy gives the system a capability for operation at pressures (55 MPa, 8,000 psi) and temperatures (927°C, 1700°F) in excess of those that can be achieved by other systems used for high temperature sCO₂ studies. The autoclave is operated in a vertical orientation inside a three-zone furnace, Figure 1. The internal dimensions of the autoclave are ~266 mm (10.5 in.) x 83 mm (3.25 in.) so that it can hold a considerable number of samples, typically mounted on an alloy 282 sample rack that sits on the bottom of the autoclave, Figure 1. The specimens were held on alumina rods with alumina spacers between specimens. The supercritical fluid was continuously fed into the autoclave through a supply tube that extended to within a few mm of the
bottom of the autoclave. The fluid was supplied by a Supercritical 24 constant flow dual piston pump, which permitted the feed rate to be controlled in the range of 0.01–24.0 mL/min with 1.0 mL/min used for these experiments. The pressure in the system was controlled by use of a backpressure control valve which adjusted the orifice size as part of a feedback loop whose signal was based on the output of a pressure transducer located between the autoclave and the control valve. To prevent an inadvertent overpressurization of the system, a rupture disc and a pressure relief valve were built into the same high-pressure line between the autoclave and the control valve. For these 500 h experiments, liquid CO2 was provided from a cylinder containing CO2 with a purity of at least 99.995%. The specifications of the CO2 called for <5 ppm moisture and <5 ppm total hydrocarbons. The specimens were slowly heated to temperature over several hours, held for 500 h (with ±10°C variation across the autoclave) and then slowly cooled to room temperature. The materials used in these experiments are listed in Table 1 along with their measured compositions. Coupons were typically 1.5 mm thick and 1 x 2 cm with a final 600 grit surface finish on all sides. The specimens were ultrasonically cleaned in acetone and methanol prior to exposure. Mass change was measured on a Mettler Toledo model XP205 balance (±0.04 mg accuracy or ±0.01

Table 1. Chemical composition of the alloys measured by inductively coupled plasma and combustion analyses in mass%.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Al</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gr.91</td>
<td>89.7</td>
<td>0.1</td>
<td>8.3</td>
<td>&lt;</td>
<td>1Mo,0.3Mn,0.1Si</td>
</tr>
<tr>
<td>Save12</td>
<td>83.4</td>
<td>0.3</td>
<td>9.6</td>
<td>0.01</td>
<td>2.6Co,3W,0.4Mn,0.1Si</td>
</tr>
<tr>
<td>410SS</td>
<td>86.9</td>
<td>0.1</td>
<td>11.8</td>
<td>0.04</td>
<td>0.5Mn,0.4Si</td>
</tr>
<tr>
<td>EBrite</td>
<td>72.6</td>
<td>0.1</td>
<td>25.8</td>
<td>&lt;</td>
<td>1.0Mo,0.2Si,0.1V</td>
</tr>
<tr>
<td>AL294C</td>
<td>66.1</td>
<td>0.2</td>
<td>28.6</td>
<td>0.07</td>
<td>3.7Mo,0.2Mn,0.3Si,0.4Ti,0.3Nb</td>
</tr>
<tr>
<td>201SS</td>
<td>70.8</td>
<td>4.1</td>
<td>16.2</td>
<td>&lt;</td>
<td>6.7Mn,0.9Cu,0.3Mn,0.5Si,0.2Co</td>
</tr>
<tr>
<td>347HFG</td>
<td>66.0</td>
<td>11.8</td>
<td>18.6</td>
<td>0.01</td>
<td>1.5Mn,0.8Nb,0.4Si,0.2Mo,0.2Co</td>
</tr>
<tr>
<td>304H+SP</td>
<td>70.4</td>
<td>8.4</td>
<td>18.4</td>
<td>&lt;</td>
<td>1.6Mn,0.3Mn,0.4Cu,0.3Si</td>
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<tr>
<td>310HCbN</td>
<td>51.3</td>
<td>20.3</td>
<td>25.5</td>
<td>&lt;</td>
<td>0.3Co,0.4Nb,1.2Mn,0.3Si,0.3N</td>
</tr>
<tr>
<td>NF709</td>
<td>49.0</td>
<td>25.0</td>
<td>22.3</td>
<td>0.02</td>
<td>1.5Mo,0.2B,1.0Mn,0.4Si</td>
</tr>
<tr>
<td>800H</td>
<td>43.2</td>
<td>33.8</td>
<td>19.7</td>
<td>0.7</td>
<td>1.0Mn,0.3Si,0.5Ti,0.3Cu</td>
</tr>
<tr>
<td>HR120</td>
<td>35.0</td>
<td>37.6</td>
<td>24.7</td>
<td>0.1</td>
<td>0.7Mn,0.6 Nb,0.3Mo,0.2Si</td>
</tr>
<tr>
<td>AFA OC4</td>
<td>49.1</td>
<td>25.2</td>
<td>13.9</td>
<td>3.5</td>
<td>2.5Nb,2W,1.9Mn,2Mo,0.5Cu,0.2Si</td>
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<tr>
<td>Ohm40</td>
<td>81.7</td>
<td>0.5</td>
<td>12.7</td>
<td>3.6</td>
<td>0.4Mn,0.3Ti,0.2Si,0.1V</td>
</tr>
<tr>
<td>APMT</td>
<td>69.2</td>
<td>0.2</td>
<td>21.1</td>
<td>5.0</td>
<td>0.2Hf,0.1Mn,2.8Mo,0.6Si,0.3Y,0.1Zr</td>
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<tr>
<td>PM2000</td>
<td>74.1</td>
<td>0.02</td>
<td>19.1</td>
<td>5.5</td>
<td>0.5Ti,0.4Y,0.25O</td>
</tr>
<tr>
<td>IN718</td>
<td>18.8</td>
<td>52.8</td>
<td>18.2</td>
<td>0.6</td>
<td>5Nb,3Mn,1Ti,0.3Mn,0.1Si</td>
</tr>
<tr>
<td>Hastelloy X</td>
<td>17.9</td>
<td>46.8</td>
<td>22.1</td>
<td>0.09</td>
<td>9.5Mo,1.8Co,0.6W,0.3Si,0.7Mn</td>
</tr>
<tr>
<td>IN625</td>
<td>4.0</td>
<td>60.6</td>
<td>21.7</td>
<td>0.09</td>
<td>9.4Mo,3.6Nb,0.2Ti,0.2Si,0.1Mn</td>
</tr>
<tr>
<td>HR230</td>
<td>1.5</td>
<td>60.5</td>
<td>22.6</td>
<td>0.3</td>
<td>12.3W,1.4Mo,0.5Mn,0.4Si</td>
</tr>
<tr>
<td>CCA617</td>
<td>0.6</td>
<td>59.9</td>
<td>21.6</td>
<td>1.3</td>
<td>11.3Co,8.6Mo,0.4Ti,0.1Si</td>
</tr>
<tr>
<td>HR282</td>
<td>0.2</td>
<td>58.0</td>
<td>19.3</td>
<td>1.5</td>
<td>10.3Co,8.3Mo,0.06Si,2.2Ti,0.1Mn</td>
</tr>
<tr>
<td>IN740</td>
<td>1.9</td>
<td>48.2</td>
<td>23.4</td>
<td>0.8</td>
<td>20.2Co,2.1Nb,2.0Ti,0.3Mn,0.5Si</td>
</tr>
<tr>
<td>HR224</td>
<td>27.2</td>
<td>47.0</td>
<td>20.3</td>
<td>3.8</td>
<td>0.3Co,0.34Mn,0.39Si,0.37Ti</td>
</tr>
<tr>
<td>HR214</td>
<td>3.5</td>
<td>75.9</td>
<td>15.6</td>
<td>4.3</td>
<td>0.2Mn,0.1Si,0.02Zr</td>
</tr>
<tr>
<td>NM105</td>
<td>0.8</td>
<td>53.0</td>
<td>15.5</td>
<td>4.9</td>
<td>19.0Co,4.7Mo,1.4Ti,0.1Mn,0.1Si,0.12Zr</td>
</tr>
<tr>
<td>713LC</td>
<td>0.03</td>
<td>74.2</td>
<td>12.1</td>
<td>6.2</td>
<td>4.5Mo,2.1Nb,0.7Ti,0.06Zr</td>
</tr>
<tr>
<td>CM247</td>
<td>0.07</td>
<td>59.5</td>
<td>8.5</td>
<td>5.7</td>
<td>9.8Co,9.9W,0.7Mo,3.1Ta,1.0Ti,1.4Hf</td>
</tr>
<tr>
<td>PWA1483</td>
<td>0.03</td>
<td>60.6</td>
<td>12.0</td>
<td>3.4</td>
<td>8.8Co,5.2Ta,4.0Ti,4.1W,1.9Mo</td>
</tr>
<tr>
<td>NiCrAlYHf</td>
<td>0.01</td>
<td>72.2</td>
<td>15.5</td>
<td>12.0</td>
<td>0.14Hf,0.05Y</td>
</tr>
<tr>
<td>CVD SiC</td>
<td>&lt;</td>
<td>0.01</td>
<td>&lt;</td>
<td>&lt;</td>
<td>69.8Si,30.2C,0.003O</td>
</tr>
</tbody>
</table>

< indicates less than 0.01%
mg/cm²). Similar specimens were exposed at 1 bar in a horizontal alumina tube with end caps within a 3-zone furnace for better temperature control. Under these conditions, 500 h experiments were conducted at 700°C, in dry air, high-purity CO₂, CO₂ with 0.15%O₂ and a mixed CO₂+10vol.%H₂O with 10 specimens (bold in Table 1) in each test held in an alumina boat. After exposure, specimens were Cu-plated to protect the surface oxide and metallographically mounted and imaged with light microscopy.

RESULTS

Figures 2-7 summarize the mass change data from the 7 conditions studied. In the 1 bar experiments, only the 10 alloys shown in Figure 2 were exposed. These alloys were selected to represent the major alloy classes denoted in Table 1, Fe- and Ni-base alloys that form chromia and alumina scales. For most of the alloys, the mass gains were small suggesting protective scale formation under these conditions and only minor effects of the CO₂ environment after these 500 h exposures. In general, the chromia-forming alloys (310H, 230, 740, 282) showed slightly higher mass gains after 700° and 750°C in 200 bar CO₂ compared to 650°C, as would be expected with the higher temperatures. The alloy 282 specimen exhibited a higher mass gain after the 750°C sCO₂ exposure, Figure 2. In two cases mass losses were observed: the ferritic steel E-Brite specimen at 700°C in 200 bar CO₂ and the austenitic steel 347HFG specimen in CO₂-10%H₂O. High mass gains were exhibited for the lowest alloyed material, Gr.91 steel and occasionally for 347HFG. The mass gains for Gr.91 are somewhat unreliable as the thick oxides can spall on cooling due to the strain energy associated with the CTE mismatch between the alloy and oxide.

Figure 3 summarizes the mass change data for the ~30 specimens exposed at 650°, 700° and 750°C in 200 bar CO₂ as a function of their Cr content. Again, the majority of specimens showed a low mass change and only the lowest-alloyed Fe-base alloy specimens exhibited high mass gains suggesting the rapid formation of FeOₓ under these conditions. As was noted above, when a thick oxide formed, the exact value of the mass gain is unreliable as the oxide is likely to spall. The CVD SiC specimen exhibited little or no mass change at these temperatures after 500 h. Two trends are noted between the temperatures (1) some alloys that had higher mass gains at 650°C (e.g. 410SS, AFA) showed less mass gain at 700° and 750°C; this can be attributed to faster Cr or Al diffusion in the substrate at the higher temperature enabling the
formation of a protective scale and (2) several alloys experienced a mass loss at 700°C whereas no mass losses were noted at 650° or 750°C. Further characterization is needed to explain the 2nd trend.

Figures 4-6 expand the y-axis of Figure 3 for the 650°-750°C data, respectively, in order to observe the behavior of the more highly-alloyed materials. The conventional austenitic (347HFG, 304H) and high Mn (201) stainless steels exhibited higher mass gains at 650°C compared to higher alloyed stainless steels.

Figure 3. Specimen mass change as a function of alloy Cr content after 500h exposures in 200 bar CO$_2$ at 650° (open), 700°C (half-filled) and 750°C (filled symbols).

Figure 4. Specimen mass change as a function of alloy Cr content after a 500h exposure in 200 bar CO$_2$ at 650°C (1200°F): Fe-Cr alloys (circle), Ni-Cr (diamonds), M-Cr-Al (triangles).
such as NF709 and type 310, Figure 4. All of the chromia-forming Ni-base alloys performed similarly at 650°C with very low mass gains. Most of the alumina-forming alloys had higher mass gains than the chromia-forming Ni-Cr alloys and several had much higher mass gains. The AFA specimen as well as the “lean” FeCrAl, Ohmalloy 40, and a cast model superalloy bond coating alloy, NiCrAlYHf, all showed much higher mass gains, suggesting somewhat non-protective behavior.

In Figures 5 and 6, most of the Ni-Cr alloys performed similarly with relatively low mass gains. Figure 7 compares just the Ni-Cr alloys at 650°-750°C. While all of these alloys appeared to form a protective Cr-
rich oxide, it is not surprising that the mass gain increased as the temperature increased. The two exceptions were the mass loss observed for alloy X specimen at 700°C and the higher mass gain for the alloy 282 specimen at 750°C (neither specimen has been characterized at this time to determine the reason for this behavior). In contrast to the Ni-Cr alloys, many of the alumina-forming alloys exhibited lower mass gains at 700° and 750°C (compare Figures 4-6). Typically, alumina-forming alloys are selected for applications above 900°C (1650°F) where their slower oxidation kinetics are more significant for long-term component lifetime. At 650°C, many alumina-forming alloys with only 3-5% Al have difficulty forming an alumina scale because of the slow reaction kinetics to form alumina and the relatively slow Al diffusion in the substrate, which inhibits selective oxidation of Al to form alumina. However, as the temperature increased thereby increasing oxidation and Al diffusion (in the alloy) rates, alumina formation was easier [Pint 1999]. Another aspect in Figure 5 is that the dashed lines note that several alloys exhibited mass losses at 700°C: X, E-Brite, Ohmalloy 40 and 224. Characterization of these specimens is in progress to explain this selective behavior. In Figure 6, the dashed line was removed for the Fe-Cr alloys because of the range of behavior, such as the higher mass gain of the high Mn type 201 stainless steel specimen. It should be noted that the low mass gains for some of the alloys (410SS, 347HFG, 304H) at 750°C could be an indication of more protective behavior or a net result of a thicker scale with some spallation. Further characterization is needed to understand these most recent results. Furthermore, these promising results may be related to the 500h exposure time. Longer exposures are needed to verify that these materials remain compatible.

Examples of the initial microstructural characterization are shown in Figures 8-13. Figure 8 shows cross-sections from Gr.91 at several conditions. Prior work had exposed a specimen of this alloy for 5,000 h (10, 500-h cycles) at 650°C in laboratory air. Figure 8c shows that a thin protective scale was formed on a majority of the surface after this extended exposure. In contrast, after only 500 h at 700°C in dry air, Gr.91 formed a thick, duplex oxide that is typical of Fe-based alloys that are unable to form a protective Cr-rich oxide, Figure 8d. A duplex oxide is formed in many environments (air, steam, liquid metals, CO₂, etc.) and its hallmark is an outer Fe-rich oxide, typically free of Cr and either Fe₃O₄ or Fe₂O₃ depending on the oxygen partial pressure; and an inner Cr-rich oxide layer that may contain unoxidized metal precipitates [Otsuka, 1989]. The Gr.91 exposures in CO₂ suggest that it is particularly attacked by the presence of 200 bar CO₂ both at 650°C (Figure 8a) and 700°C (Figure 8b). In 1 bar CO₂ at 700°C, the thick oxide was not continuous.
on the surface and some regions were able to retain a protective scale after 500h. However, what begins as oxide nodules with a duplex structure, grows laterally leading to a complete coverage of the thick oxide after longer times. In 200 bar CO₂, the duplex oxide was continuous, Figure 8b. One previously suggested explanation for this breakdown is that internal carburization of Cr in the presence of CO₂ prevents Cr from participating in the formation of a protective Cr-rich oxide [Quadakkers 2011]. Pressure, temperature and environment may affect the structure of the duplex scale and further characterization of these thick oxides is required.

Similar reaction products were sometimes observed for 347HFG in Figure 9. In this case, protective behavior, i.e. a thin Cr-rich oxide, was observed at 700°C in dry air, Figure 9c, but thick duplex oxide nodules began to form at 700°C in 1 bar CO₂, Figure 9d. At higher magnification of the same specimen in Figure 9e, the duplex oxide structure appeared somewhat different in CO₂ at 700°C/1 bar compared to 650°C/200 bar in Figure 9a. However, nodule formation was not observed after exposure in 200bar CO₂ at 700°C.

For the higher alloyed chromia-forming alloys, Figure 10 shows examples of two of the alloys, 310HCbN stainless steel and Ni-base alloy 740, that exhibited low mass gains in the presence of 200 bar CO₂ at 650°C (Figures 10a and 10c) and 700°C (Figure 10b and 10d). A thin, Cr-rich scale was observed in all cases, with only an occasional oxide nodule observed. After the 700°C exposure, the oxide scale appeared somewhat thicker than was observed at 650°C. Similar oxides were observed in the other 700°C conditions but not shown here.

As suggested by the mass gain data in Figures 1, 4 and 5, Figure 11 shows examples for alloy APMT where an alumina-forming alloy formed a thinner scale at the higher temperature. Similar observations were apparent for alloy 214, a Ni-base alumina-forming alloy, Table 1. A more complicated reaction product was observed for alloy 247, Figure 12. This DS superalloy was specifically included because of its high Hf content. The light microscopy suggested some internal oxidation, perhaps associated with the Hf-rich precipitates in the alloy, which appear to have been internally oxidized in all of the environments (including dry air at 700°C) whenever the precipitates were at or near the reaction interface.

Finally, Figure 13 shows two unique specimens exposed to 200 bar CO₂ at 650°C. Figure 13a shows the reaction product formed on cast NiCrAlYHf. Rather than the protective alumina scale that forms on this alloy at 1000°-1150°C (1800°-2100°F) [Unocic 2013], this specimen formed a thick reaction product with...
internal oxidation in the presence of sCO₂ at 650°C. Figure 13b shows the shot peened ID of a 304H tube specimen. While shot peening has been effective on the steamside of stainless steel tubes in commercial coal-fired boilers [Pint 2012] and in laboratory testing in steam at 620°C (1150°F) [Tossey, 2011] and 650°C (1200°F) [Pint 2014a], it did not appear to be effective in the presence of sCO₂ at 650°C where a non-protective duplex scale formed on the shot-peened ID. As suggested by the mass change data, both alloys performed better at higher temperatures.

**DISCUSSION**

![Figure 9. Light microscopy of polished cross-sections of type 347HFG stainless steel after 500 h at (a) 650°C in 200 bar CO₂, (b) 700°C in 200 bar CO₂, (c) 700°C in 1 bar dry air and (d,e) 700°C in 1 bar CO₂ (two magnifications).](image)

![Figure 10. Light microscopy of polished cross-sections of alloys 310 (a,b) and 740 (c,d) after 500 h at (a,c) 650°C in 200 bar CO₂ and (b,d) 700°C in 200 bar CO₂.](image)
Initial results are presented from the new ORNL sCO$_2$ test rig. Future work will continue this 500 h experiment series to different temperatures as needed and vary the pressure from 12.5-30 MPa (1800-4350 psi). These conditions were selected in order to repeat prior conditions covered by other research groups at MIT and Wisconsin, while expanding to higher pressures at 750°C than have previously been explored. The current results with thick reaction products for low-alloyed stainless steels are consistent with prior observations [e.g. Rouillard 2011]. Similar observations with thin reaction products for higher-alloyed materials, also have been observed previously [e.g. Dunlevy, 2009].

For the present results, more characterization is needed, such as electron probe microanalysis, in order to better understand the various reaction products. Based only on the mass change data, the effect of CO$_2$ pressure appears minimal at 700°C (1 vs. 200 bar), Figure 2. One of the key mechanistic issues to be further explored is the ingress of C through the external scale and whether pressure affects this mechanism. While the carbon activity in the gas is low in these environments (10$^{-44}$ at 700°C in 1bar CO$_2$), McCoy [1965] and others have seen examples of internal carburization. The most likely explanation for the internal attack is that C penetrates the scale and its activity increases at the low O activity at the metal-scale interface where Cr/Cr$_2$O$_3$ or Al/Al$_2$O$_3$ equilibrium exists. The traditional view has been that alumina scales are less permeable to C than chromia scales (with the opposite true for N$_2$) [Jönsson 1997]. Thus, at some high temperature sCO$_2$ conditions, alumina-forming alloys may be the primary candidates. However, for high pressures at 700°C-750°C, precipitation strengthened Ni-base superalloys like 740 [Zhao 2003, Shingledecker 2013] and 282 [Pike 2008] are likely candidates with the former alloy recently gaining ASME boiler and pressure vessel code qualification and a similar code case starting for alloy 282 in 2015.

For the high combustion temperatures 1100°-1150°C (2000°-2100°F) envisioned for the open Allam cycle [Allam 2013a], even the most oxidation resistant alloys will likely require protective coatings. In air- and

![Figure 11. Light microscopy of polished cross-sections of FeCrAl alloy APMT after 500 h at (a) 650°C in 200 bar CO$_2$ and (b) 700°C in 200 bar CO$_2$.](image)

![Figure 12. Light microscopy of polished cross-sections of Ni-base superalloy 247 after 500 h at (a) 650°C in 200 bar CO$_2$ and (b) 700°C in 200 bar CO$_2$. Arrow in (a) marks an apparent crack.](image)
land-based turbines, the highest performance alumina-forming single-crystal superalloys (e.g. 1483) are coated with alumina-forming metallic coatings (like the cast, model NiCrAlYHf specimens) to increase durability and low thermal conductivity ceramic top coatings (e.g. Y$_2$O$_3$-stabilized ZrO$_2$) are used to lower the metal temperature. For aero-engines, metal temperatures may reach 1100°-1150°C (2000°-2100°F) during takeoff and landing for ~5-10% of ~15,000 h commercial engine wing time but the majority of operation is at hundreds of degrees lower temperature. To achieve continuous 1150°C gas temperature, a TBC will be required to significantly lower the metal temperature. Essentially, the coating is then life limited by interdiffusion between the Al-rich coating and the substrate. Initial ORNL work on TBC lifetime in 1bar 90%(CO$_2$-0.15O$_2$)-10%H$_2$O found no detrimental effect of this environment on TBC lifetime in furnace cyclign tests [Pint 2014b].

Future experiments will consider the effect of impurities in the CO$_2$ on the reaction kinetics. The initial 1 bar experiments with O$_2$ and H$_2$O additions are the first step in creating a baseline for those experiments. A more sophisticated pumping system will be required for controlled impurities in sCO$_2$ and construction of an experimental rig for creating controlled impurity exposures has been proposed for 2015. In addition, future experiments will include small (25mm, 1") tensile bars to evaluate (ex-situ) the effect of the sCO$_2$ environment on alloy mechanical properties. Obviously, much more work is needed to understand sCO$_2$ material compatibility for higher temperature/pressure conditions and longer lifetime applications needed for high efficiency power generation systems.

CONCLUSIONS

Initial sCO$_2$ results have been generated with 500 h exposures at 650°-750°C (1200°-1380°F) in 20 MPa (2900 psi) CO$_2$. A wide range of Fe- and Ni-base alloys, which form protective Cr- and Al-rich surface oxides, has been evaluated. Many of the higher alloyed materials and SiC exhibited low mass changes and thin reaction products at all three temperatures with expected thicker reaction products at 700° and 750°C. As has been observed in other studies, lower alloyed steels can form non-protective Fe-rich oxides in the presence of CO$_2$ when normally thin protective Cr-rich oxides from under other oxidizing conditions. Similarly, some alumina-forming alloys were not as protective at 650°C as at 700°-750°C likely because of the difficulty in selectively forming an alumina scale at the lower temperature. Baseline data at 1 bar acquired at 700°C for comparison suggested that many of these materials were relatively unaffected by the sCO$_2$ environment and that pressure (1 vs. 200 bar) had a minimal effect after 500 h of exposure. More characterization is in progress to understand the mass losses for a few specimens at 700°C and the mass change results presented at 750°C. Further evaluation of the reaction products formed under all of these conditions is needed.

NOMENCLATURE

AFA = alumina-forming austenitic steel (Grade OC4 investigated in this study)
APMT = Advanced Powder Metallurgy Tube (Sandvik/Kanthal FeCrAl alloy)
CTE = Coefficient of Thermal Expansion
REFERENCES


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