MATERIALS PERFORMANCE IN SUPERCRITICAL CO₂ IN COMPARISON WITH ATMOSPHERIC PRESSURE CO₂ AND SUPERCRITICAL STEAM

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Abstract

To facilitate the development of supercritical CO2 (sCO2) power plants, a comparison of the oxidation behavior of austenitic stainless steel and Ni-base alloys in sH2O and sCO2 was made. Experiments were conducted at 730°C/207 bar (sCO2) and 726°C/208 bar (sH2O). Ni-base alloys in sCO2 did not exhibit much change with pressure. Ni-base alloys in sH2O had an increase in corrosion rate and the log of the parabolic rate constant was proportional to pressure. Austenitic stainless steels in sCO2 and sH2O were less protective with pressure as the dense protective chromia scale was replaced with faster growing Fe-oxide rich scales.

Introduction

Heat engine power cycles, using a working fluid of supercritical carbon dioxide (sCO2) have the potential for high thermodynamic efficiencies when configured as a (indirect) recompression Brayton cycle [1]. Direct cycles, where pressurized oxy-combustion flue gas is utilized as the working fluid in an open loop, are also in development [2]. These sCO2 cycles are projected to have higher efficiencies compared to steam cycles due to lack of phase change in working fluid within the working envelope, recompression of sCO2 near liquid densities, and high heat recuperation. In addition to lowering the environmental impact due to the higher efficiencies, dry or reduced water cooling in direct and indirect cycles, and producing storage ready CO2 in direct cycles, will also lower the environmental impact. Furthermore, compact turbo machinery and simple configurations of the sCO2 cycles could result in lower capital cost.

While the compactness of the turbo machinery presents the possibility of using more costly alloys (Ni-base superalloys) in fabrication of components to achieve higher efficiency targets, economics dictates to utilize less costly materials to their limits. Materials selection for components exposed to specific sCO2 power cycles is challenging since materials have not been commonly tested under these conditions. However, materials selected for advanced ultra-supercritical (A-USC) steam (sH2O) systems are a good starting point for sCO2 cycles. Required key properties of materials employed in fossil fuel sCO2 cycles will depend on the application temperature, pressure and environment. In this study, the oxidation behaviour of austenitic stainless steels and Ni-base alloys in sCO2 and sH2O will be compared.
Table 1 shows representative proposed inlet and outlet temperatures and pressures for the heater, turbine, and heat exchanger (HX) components of indirect- [3] and direct-cycle [2] sCO2 power systems. In indirect-cycle systems, the working fluid to expand in the turbine will be relatively pure CO2. In direct-cycle systems, the working fluid to expand in the turbine will be CO2-rich combustion gases (for example, CO2 with 1-5 vol% O2 and 2-10% vol% H2O). The work presented here is on environments representative of indirect-cycle systems, with emphasis on the temperatures and pressures associated with the turbine inlet.

Table 1. Representative temperatures and pressures of components in indirect- [3] and direct-cycle [2] sCO2 power systems. Indirect turbine inlet conditions are the emphasis of the work presented here.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Component</th>
<th>Inlet T, °C</th>
<th>Inlet P, bar</th>
<th>Outlet T, °C</th>
<th>Outlet P, bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indirect</td>
<td>Heater</td>
<td>450-535</td>
<td>10-100</td>
<td>650-750</td>
<td>10-100</td>
</tr>
<tr>
<td></td>
<td>Turbine</td>
<td>650-750</td>
<td>200-300</td>
<td>550-650</td>
<td>80-100</td>
</tr>
<tr>
<td></td>
<td>HX</td>
<td>550-650</td>
<td>80-100</td>
<td>100-200</td>
<td>80-100</td>
</tr>
<tr>
<td>Direct</td>
<td>Heater</td>
<td>750</td>
<td>200-300</td>
<td>1150</td>
<td>200-300</td>
</tr>
<tr>
<td></td>
<td>Turbine</td>
<td>1150</td>
<td>200-300</td>
<td>800</td>
<td>30-80</td>
</tr>
<tr>
<td></td>
<td>HX</td>
<td>800</td>
<td>30-80</td>
<td>100</td>
<td>30-80</td>
</tr>
</tbody>
</table>

A few comments on nomenclature are in order for steam power plants. The pressures and temperatures of a pulverized coal (PC) power plant are commonly reported as in this example for the Isogo 1 ultra-supercritical pulverized coal plant: 4060 psi/1050°F/1110°F (280 bar/566°C/599°C) [4]. The pressure and first temperature refer to conditions in superheater tubing and the inlet of the high pressure turbine; the second temperature refers to conditions in the reheater tubing and inlet of the intermediate pressure turbine. The terms subcritical, supercritical (SC), ultra-supercritical (USC), and advanced ultra-supercritical (A-USC) refer to the pressure and temperature of the superheater and inlet of the high pressure turbine. While there are no universally accepted definitions of these terms, they arise out of power plant design and the alloy categories required for operation. Table 2 shows one set of definitions for the steam conditions for each, along with typical net plant efficiency. Due to their high creep strengths at high temperatures, nickel-base superalloys are required for A-USC pulverized coal power plants. Advanced ferritic-martensitic steels and austenitic stainless steels are used in USC power plants. The U.S. convention for net plant efficiency calculations is to use higher heating value (HHV), which includes the heat of steam condensation. The European convention is to use lower heating value (LHV), which does not include the heat of steam condensation—resulting in higher reported efficiencies [5].

Table 2. Steam conditions and net plant efficiencies for various categories of pulverized coal power plants (adapted from ref [5]).

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Typical Conditions</th>
<th>Net Plant Efficiency (HHV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subcritical</td>
<td>2400 psi/1050°F/1050°F (165 bar/566°C/566°C)</td>
<td>35%</td>
</tr>
<tr>
<td>Supercritical (SC)</td>
<td>3600 psi/1050°F/1075°F (248 bar/566°C/579°C)</td>
<td>38%</td>
</tr>
<tr>
<td>Ultra-Supercritical (USC)</td>
<td>&gt;3600 psi/1100°F/1150°F (&gt;248 bar/593°C/621°C)</td>
<td>&gt;42%</td>
</tr>
<tr>
<td>Advanced Ultra-Supercritical (A-USC)</td>
<td>4000-5000 psi/1300-1400°F (276-345 bar/704-760°C)</td>
<td>&gt;45%</td>
</tr>
</tbody>
</table>

A comparison of the temperatures and pressures for indirect turbine inlet conditions in sCO2 (Table 1) and A-USC conditions (Table 2), show how similar the systems are, and why a good starting point for candidate alloys for sCO2 systems are the ones proposed for A-USC power plants. Bordenet et al.
[6] reported long-term testing of Ni-base and austenitic stainless steels under A-USC temperatures from a reheat steam line (21-41 bar), and both the fireside and steamside results showed very low corrosion and oxidation losses. This result, and others (for example in ref [5]), show how these candidate alloys should perform well with respect to steam oxidation in A-USC conditions.

The purpose of this communication is to present and compare results from exposures in sCO₂ and sH₂O. A direct comparison was made for three alloys (austenitic stainless steel 347H and nickel-base superalloys 625 and 282) exposed for (nominally) 500 h at 730°C/207 bar to sCO₂ and sH₂O, and to atmospheric pressure CO₂ (aCO₂) for 500 h at 730°C/1 bar. These results are combined with literature results in both sCO₂ and sH₂O for a comparison of oxidation kinetics in these two systems.

Experimental Procedures

Three alloys were selected for direct comparison in sCO₂, sH₂O and aCO₂. The alloys were 347H austenitic stainless steel and Ni-base alloys 625 and 282. The compositions of each alloy, as determined by wavelength dispersive x-ray fluorescence (WDXRF) using a Rigaku ZSX Primus II spectrometer, are shown in Table 3.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Co</th>
<th>Mo</th>
<th>Si</th>
<th>Ti</th>
<th>Al</th>
<th>Mn</th>
<th>Cu</th>
<th>V</th>
<th>Nb</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>347H</td>
<td>Bal</td>
<td>17.6</td>
<td>9.1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>1.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.7</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>282</td>
<td>0.2</td>
<td>19.4</td>
<td>Bal</td>
<td>10.1</td>
<td>8.7</td>
<td>2.2</td>
<td>1.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>625</td>
<td>3.4</td>
<td>22.1</td>
<td>Bal</td>
<td>8.9</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
<td>3.3</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Triplicate specimens were made of each alloy for each exposure type. The samples were machined as compact tension specimens with overall dimensions of approximately 23 × 22 × 3 mm. Surfaces were ground to a 600 grit (CAMI, Coated Abrasive Manufacturers Institute, now part of the Unified Abrasives Manufacturers' Association) finish, which is equivalent to a P1200 (FEPA, Federation of European Producers of Abrasives) finish. The samples were then ultrasonically cleaned in isopropyl alcohol, dried, and weighed.

Exposures in sCO₂ were performed in a horizontal autoclave constructed from alloy 625. The autoclave inside diameter was 4.3 cm. The sample rack and exposure specimens are shown in Fig. 1. A SSI Supercritical 24 constant flow dual piston pump was used to inject 99.999% pure CO₂ into the autoclave at a rate of 0.035 kg/hr. At test conditions this resulted in a fluid velocity of 0.4 cm/min through the autoclave, which corresponded to a test section volume change every 2 h. Nominally the test lasted 500 h at 730°C/207 bar. However, there was a loss in pressure from a leak 497.9 h into the test. The autoclave heaters were turned off after 500.5 h of exposure. The temperature averaged 730.4 ± 1.4 °C and the pressure averaged 206.6 ± 0.6 bar.

Fig. 1. Sample rack and samples for sCO₂ exposure in a horizontal autoclave. The rack was made from alloy 625 with alumina spacers.
Exposures in $\text{sH}_2\text{O}$ were performed in a vertical autoclave constructed from alloy 230. The autoclave inside diameter was 6.35 cm. The sample rack and samples are shown in Fig. 2. A Lab Alliance constant pressure dual-piston pump was used to inject deionized water into the autoclave at a rate of 0.27 kg/h. At test conditions this resulted in a fluid velocity of 0.21 cm/min through the autoclave, which corresponded to a test section volume change every 2.4 h. Nominally the test lasted 500 h at 726°C/208 bar. The temperature averaged 725.9 ± 2.4 °C and the pressure averaged 208 ± 3 bar.

Exposures in $\text{aCO}_2$ were performed in a horizontal alumina tube furnace. The tube inside diameter was 6.81 cm. The sample rack and samples are shown in Fig. 3. Carbon dioxide, with a purity of 99.99%, was fed into the tube chamber at a rate of 370 cm$^3$/min, or 0.040 kg/hr. At test conditions this resulted in a fluid velocity of 33 cm/min through the autoclave, which corresponded to a test section volume change every 16 s. Nominally the test lasted 500 h at 730°C/1 bar. A hairline crack was observed in the alumina tube after the test was complete. Subsequently, an oxygen sensor was placed in the tube with the same conditions as the test, except for temperature, which was set at 800°C to enable the stabilized zirconia oxygen sensor to operate. The oxygen partial pressure was measured as 0.25%. Assuming the source of the oxygen was from the atmosphere, a nitrogen partial pressure of 0.93% was inferred.

There was a large difference in linear velocity within the test chambers between the tests at high pressure (0.4 cm/min for $\text{sCO}_2$ and 0.21 cm/min for $\text{sH}_2\text{O}$) and the test at atmospheric pressure (33 cm/min for $\text{aCO}_2$). However, when expressed in terms of the Reynolds number, Re, the test...
conditions were much more comparable, primarily due to the much higher densities at high pressure. Eq. 1 is the expression for Re,

\[ Re = \frac{\rho u L}{\eta} \]  

where \( \rho \) is the density, \( u \) is the velocity, \( L \) is a characteristic dimension (chamber diameter in this case), and \( \eta \) is the absolute viscosity. Table 4 summarizes the three direct comparison tests. All of the Re numbers were quite low, indicating laminar flow.

<table>
<thead>
<tr>
<th>Test</th>
<th>( T, ^\circ C )</th>
<th>( P, \text{ bar} )</th>
<th>( \rho, \text{ g/cm}^3 )</th>
<th>( u, \text{ cm/min} )</th>
<th>( L, \text{ cm} )</th>
<th>( \eta, \text{ Pa*s} )</th>
<th>Re</th>
</tr>
</thead>
<tbody>
<tr>
<td>sCO₂</td>
<td>730</td>
<td>207</td>
<td>1.04×10⁻¹</td>
<td>0.40</td>
<td>6.35</td>
<td>4.26×10⁻⁵</td>
<td>10.4</td>
</tr>
<tr>
<td>sH₂O</td>
<td>726</td>
<td>208</td>
<td>4.77×10⁻²</td>
<td>0.21</td>
<td>4.30</td>
<td>3.89×10⁻⁴</td>
<td>1.8</td>
</tr>
<tr>
<td>aCO₂</td>
<td>730</td>
<td>1</td>
<td>5.28×10⁻⁴</td>
<td>33.0</td>
<td>6.81</td>
<td>4.14×10⁻⁵</td>
<td>4.8</td>
</tr>
</tbody>
</table>

Data collected included mass change measurements, glancing angle (1.5°) x-ray diffraction (XRD), scanning electron microscopy (SEM) of the surfaces of exposed samples using secondary electrons (SE) and back-scattered electrons (BSE), and microanalysis using energy dispersive spectroscopy (EDS). The SEM was a FEI Inspect F50, the EDS was an Oxford INCA, and the XRD was a Rigaku Ultima III.

**Results**

Mass change results are shown in Table 5. In sCO₂, all three alloys had small mass gains—indicative of the formation of a thin protective chromia scale. In sH₂O, the mass gains for alloy 347H were very high for two of the replicates, and small for the third replicate. Examination of the surface of the third replicate with a small mass gain showed evidence of spalling (i.e., areas where some of the oxide remained and areas without the thick oxide layer). The two Ni-base alloys had higher mass gains in sH₂O than in sCO₂, and with more variability, but these mass increases were relatively small. In aCO₂, the negative mass change values for alloy 347H was clear evidence of oxide spalling. The mass change values for the two Ni-base alloys for aCO₂ were similar to those found for sCO₂.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>sCO₂</th>
<th>sH₂O</th>
<th>aCO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>347H</td>
<td>0.10</td>
<td>8.44</td>
<td>-2.47</td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>0.79</td>
<td>-3.23</td>
</tr>
<tr>
<td>282</td>
<td>0.36</td>
<td>0.87</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>1.25</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>0.39</td>
<td>0.37</td>
</tr>
<tr>
<td>625</td>
<td>0.16</td>
<td>2.73</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.53</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>0.21</td>
<td>0.31</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Surface SE SEM results are shown in Fig. 4 for alloy 347H. In sCO₂ (Fig. 4a), most of the surface was a thin Cr-rich oxide. However, there were also areas of thicker oxides that were either Mn-rich or Nb-rich, as well as some areas without oxide indicative of a spall. Glancing angle XRD showed the surface to contain Cr₂O₃ and Mn₃O₄ phases. The exposures in sH₂O and aCO₂ (Figs. 4b-4c) consisted of Fe₂O₃ with small amounts of Cr, Mn, and Ni (based on combined XRD and EDS analysis).

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1 The XRD signal from MnFe₂O₄, Mn₃O₄, Fe₂NiO₄, Mn₂NiO₄ and Fe₃O₄ are all quite similar, so reporting as M₃O₄ is generally more accurate.
Cross-section BSE SEM results are shown in Fig. 5 for alloy 347H. A thin and protective chromia scale formed in sCO$_2$, as seen in Fig. 5a. Thick oxide scales formed in both sH$_2$O and aCO$_2$, Fig. 5b and Fig. 5c, respectively. Elemental mapping for sH$_2$O shows an outer iron oxide scale (~40 µm). Below that was a mixed oxide region (~30 µm) that was overall rich in Cr and Mn, poor in Fe, with both rich and poor areas of Ni, as well as a few Nb regions. Patches of an internal oxidation region of 39O-37Fe-13Cr-11Ni were observed. The mass loss measurements in aCO$_2$ indicated that the outer portion of the scale spalled. While Fig. 5c was representative of most of the surface, there were small areas with retained outer oxide, which was pure iron oxide about 20-25 µm thick. The remaining scale in aCO$_2$ had several composition (at%) bands: 1) nearest the outer surface, to a depth of about 8 µm, was 67O-17Fe-11Cr-4Ni, 2) below that, with a thickness of about 15 µm, was 62O-16Fe-14Cr-6Ni, 3) below that was a thin (~3 µm) layer of 64O-17Fe-18Cr, and 4) an internal oxide layer (~8 µm thick) with 42O-32Fe-13Cr-11Ni. Internal oxidation is likely in the form of chromia.

Surface SE SEM results are shown in Fig. 6 for alloy 282. The surfaces of all three exposures were similar in appearance, with small sub-micron oxide particles. Glancing angle XRD showed the primary surface phases to be Cr$_2$O$_3$ and TiO$_2$, which is in agreement with EDS analysis.
Cross-section BSE SEM results are shown in Fig. 7 for alloy 282. The structures in sCO$_2$ and aCO$_2$ were similar to each other. The oxide scale was thicker in sH$_2$O than in CO$_2$, while internal oxidation was deeper in CO$_2$. In CO$_2$, the oxide scale was primarily Cr oxide (glancing angle XRD indicated Cr$_2$O$_3$), with Ti oxide (TiO$_2$) as a secondary component. In sH$_2$O, the oxide scale had thin Cr-rich layers. Where Cr was not enriched, it also had Ni, Co, and Ti oxides. Internal oxidation consisted of Al and Ti oxides, with Ti oxide found near the alloy/oxide interface and Al oxide found at all internal oxide locations. The alloy matrix was depleted in Cr, Al and Ti to a depth about 50-100% deeper than the internal oxidation depth. This is shown in Fig. 8 for exposure in sCO$_2$. Alloy 282 is strengthened by gamma prime, Ni$_3$(Al,Ti), so loss of Al and Ti will lower alloy strength to this depth, and not just by metal thickness loss.
Surface SE SEM results are shown in Fig. 9 for alloy 625. The surfaces look similar to that for alloy 282 in Fig. 6, except that some of the oxide particles in aCO2 (Fig. 9c) were larger in size. Glancing angle XRD showed the primary surface phase to be Cr2O3, which is in agreement with EDS analysis.

Cross-section BSE SEM results are shown in Fig. 10 for alloy 625. The oxide scale in both sCO2 (Fig. 10a) and aCO2 (Fig. 10c) were Cr oxides (Cr2O3) with some Ni and a trace amount of Mn. Bright second phases were Nb/Mo rich. There was enrichment of Nb and Mo in the alloy near the oxide scale. Some portions of the aCO2 cross-section had thicker scales than in Fig. 10(c), especially along the original edges. In sH2O, Table 5 shows two results with very low oxidation rates and one with a high oxidation rate. Figure 10b is the cross-section of the high oxidation rate sample, showing a very thick oxide scale (note the scale marker change). The composition of the scale had metal ratios similar to that of the alloy, indicating that a protective scale was not formed. The other two samples of alloy 625 in sH2O had very low oxidation rates and Cr2O3 was detected at the surface by glancing
angle XRD. This indicates that these two samples established and maintained a chromia scale. It is not known what triggered the change in behaviour among the sH2O samples.

![Images of samples](image1.png)

(a) sCO2, +0.16 mg/cm²  (b) sH2O, +2.73 mg/cm²  (c) aCO2, +0.09 mg/cm²

Fig. 10. Cross-section BSE SEM results for alloy 625 after 500 h of exposure. The mass change values identify the specific sample imaged from Table 5.

**Discussion**

Mass gain results were put into parabolic form for ease of comparison with literature values for these and similar alloys. The validity and some of the limitations of this approach has been discussed in Holcomb et al. [7]. Equation 2 shows how the parabolic rate constant, $k_p$, was defined, where $\Delta m$ is mass change and $t$ is time. This calculation was not done when there was evidence of spalling.

$$k_p = \frac{(\Delta m)^2}{2t}$$

**sH2O Environments**

A comparison of the parabolic rates for the experimental results in sH2O with those in the literature for 300 series stainless steels (nominally Fe-18Cr-8Ni) is made in Fig. 11. Averages of triplicate experimental test results are shown. Some of the earlier experimental test results are shown [7,9], including those for E-Brite, a high Cr ferritic stainless steel. At atmospheric pressure, parabolic rates for fine-grained alloys align with that of a pure chromia scale—the PMCr data [8]. Coarse-grained alloys oxidize much faster and do not maintain a dense and compact chromia scale. At higher pressures, Fig. 11 shows most results for fine-grain alloys having higher corrosion rates than at atmospheric pressure; in some cases similar to what would be expected for coarse-grain alloys. The experimental test alloys had ASTM grain sizes of 7 for 304H, 10 for alloy 347H, and 9 for E-Brite. While there is no definitive definition, a grain size of 5 or greater is the general dividing point for these alloys to be considered fine-grained. The high pressure test data for fine-grained 304H show the full range of results, from values close to the PMCr line to those of the coarse-grained atmospheric pressure line. E-Brite, with a higher Cr value and a very fine grain size, was close to the PMCr line in both cases. Examination of the surfaces of samples with SEM showed that very low oxidation rate surfaces were primarily chromia, and very high oxidation rate surfaces were primarily iron oxides (containing a small amount of chromium). Surfaces with oxidation rates between the two extremes had nodules, or islands, of iron oxide against a chromia background. The breakdown in the protective chromia scale resulted in the nucleation of sites with faster growing iron oxides that grow laterally to eventually cover the surface. Nucleation events can vary with time, leading to the range in oxidation behavior observed in Fig. 11. In summary, elevated pressure exposures of fine-grained 300 series stainless steels increased the oxidation rate, making them behave more like coarse-grained alloys.
Fig. 11. Arrhenius plot of parabolic oxidation of 300 series austenitic stainless steels (nominally Fe-18Cr-8Ni alloys) in steam, updated from Holcomb [9] and Holcomb et al. [7], which was adapted from the compilation of Wright and Dooley [10] with numerous sources for coarse-grain alloys: 241 bar (304 and 347 at 538°C) [11], 240 bar (316 at 500°C) [12], 105 bar (304 at 482 and 538°C) [13], 41 bar (304, 316, 321, and 347) [14], and 1 bar (304 at 650°C, -10.4 log(g²cm⁻⁴s⁻¹)) [15]; and fine-grain alloys: 105 bar (304HFG and 347HFG at 571°C) [16], 17 bar (347HFG, CF8C and S304H) [8], and 1 bar (all other 1 bar data, 304H, 347HFG, S304H) [17]. The 17 bar PMCr data [8] is for a pure chromia forming alloy. CF8C is a cast version of 347. The C and F labels indicate coarse- and fine-grain alloys when away from the coarse-grain fit and PMCr lines. Test data at both 208 and 209 bar are labeled as 209 bar.

A comparison of the parabolic rates for the experimental results in sH₂O with those in the literature for Ni-base alloys is made in Fig. 12. Averages of triplicate experimental test results are shown, along with some from earlier tests [7, 9]. At atmospheric pressure, parabolic rates align with that of a pure chromia scale—the PMCr data [8]. The high pressure test data, 190 bar and above, showed significantly higher oxidation rates. One result, for alloy 625 at 670°C and 267 bar, showed a much higher oxidation rate. As described in Holcomb [9], the scale was very thick and had metal composition ratios (not including oxygen) similar to that of the alloy. This is similar to what was observed in Fig. 10b. Grain size, composition, and expected phases were examined as possible sources of the difference between alloy 625 and the other alloys, but no conclusions were established. Long-term exposure of alloy 625 in a power plant test of over 8000 h [18] showed very good oxidation behavior (the lower of the two 190 bar data points in Fig. 12). That, combined with a failure to reproduce such high oxidation rates in subsequent tests, has led to considering the very high oxidation result for alloy 625 at 267 bar to be an outlier. Another apparent outlier is the 41 bar result for alloy 600 [14]. This alloy has 15.5% Cr, which is less than the other alloys shown in Fig. 12. This could have contributed to the development of a less protective oxide scale. The oxides grown on Ni-base alloys at high pressures were thicker than at low pressures, but were still primarily chromia scales. In summary, elevated pressure exposures of Ni-base alloys increased the oxidation rate by 1-2 orders of magnitude. It should be noted that these are still relatively low oxidation rates, and would not preclude the successful use of Ni-base alloys in A-USC power plant applications.
Fig. 12. Arrhenius plot of parabolic oxidation of Ni-base alloys in steam, updated from Holcomb [9] and Holcomb et al. [7], which was adapted from the compilation of Wright and Dooley [8] from numerous sources: 241 bar (600, 601, 718) [11], 105 bar (617) [13], 41 bar (600) [14], 17 bar (230, 617, 718, 740, 263, 80A, PMCr) [8], and 1 bar (230, 617, 740, and 263 [17]. In addition, long-term industrial exposures of 625 and Waspalloy at 1 bar (750°C) and 190 bar (713°C) were added [18]. The 17 bar PMCr data [8] is for a pure chromia forming alloy. Test data at both 208 and 209 bar are labeled as 209 bar.

sCO₂ Environments

To supplement the sCO₂ experimental results for a comparison with sH₂O, mass loss data from the literature was examined. The examination was limited to results using research grade CO₂ (at least 99.99% pure) and at 200-220 bar. Many results were performed for a single time interval. These were treated in the same manner as the experimental results, with kp values estimated using Eq. 2. Other results had a series of times and mass changes. In cases where initial oxidation does not follow parabolic kinetics, it is preferable to calculate the parabolic rate constant from the slope of Δm vs the square root of t, rather than directly from Δm² vs t [19]. The Δm vs the square root of t procedure was used here. Initial oxidation may include either the formation of non-protective scales prior to the establishment of a more protective scale, or the transition from a short-lived more protective oxide to a less protective oxide. In some cases the data fit parabolic kinetics better after an initial period of time rather than starting at time equal to zero. Excluding some of the initial mass change data can improve the determination of kp. To consistently quantify the decision to obtain kp after an initial period of time, the F-statistic (using the Linest function in Excel) was used [20]. The literature data sets with 4 or more data points were examined with the F-statistic using all the data prior to any maximum in mass change (which would indicate spalling and non-parabolic behavior). Subsequently, all but the first data point was analyzed, then all but the first two data points, and so on. The data set with at least four data points and with the maximum F-statistic was used to obtain kp, with the proviso that a majority of the data were used.

A comparison of the parabolic rates for the experimental results in sCO₂ with those in the literature for 300 series stainless steels (nominally Fe-18Cr-8Ni alloys) is made in Fig. 13. For ease in making comparisons with the sH₂O data in Fig. 11, the PMCr 17 bar data in steam [8] indicating protective chromia formation and coarse-grained behavior in atmospheric pressure steam [10] indicating less-
protective iron oxide formation are repeated in Fig. 13. The effect of pressure in sCO$_2$ was very similar to the effect in sH$_2$O—usually a substantial increase in oxidation rate above what would be expected for a very protective chromia scale. One difference was that no rates reached as high as the coarse-grained behavior line in sCO$_2$, while they did in sH$_2$O.

Fig. 13. Arrhenius plot of parabolic oxidation of 300 series austenitic stainless steels (nominally Fe-18Cr-8Ni alloys) in sCO$_2$, all with pressures between 200-220 bar. Literature values were derived from [21-27]. For comparison with sH$_2$O, the 17 bar PMCr data in steam [8] for a pure chromia forming alloy was included, along with the coarse-grained line in steam [10].

A comparison of the parabolic rates for the experimental results in sCO$_2$ with those in the literature for Ni-base alloys is made in Fig. 14. At temperatures above 600-650°C, the oxidation behavior was close to that for a protective chromia scale. This was different than was found for sH$_2$O, where a substantial increase in oxidation rates were observed at these high pressures. At lower temperatures a chromia scale may have been harder to establish and the rates were higher than the extrapolation of the chromia formation curve.
Fig. 14. Arrhenius plot of parabolic oxidation of Ni-base alloys in sCO$_2$ at 200-207 bar. Literature values were derived from [23, 26-31]. For comparison purposes, the 17 bar PMCr data in steam [8] for a pure chromia forming alloy was included.

**aCO$_2$ Environments**

The very low mass change results for the two Ni-base alloys in aCO$_2$ and sCO$_2$ (Table 5) were very similar and showed little variability with pressure. Figure 14 shows that the kinetics in sCO$_2$ were consistent with protective chromia scale formation. The kinetics in aCO$_2$ were as well. The similar kinetics, combined with the similar surface scale morphologies (Figs. 6 and 9), show that pressure had very little influence on the oxidation behavior of Ni-base alloys—at least within the first 3000 h (the longest duration of the tests reported in Fig. 14 [27]).

The results in aCO$_2$ for the austenitic alloy 347H was markedly different than in sCO$_2$. In sCO$_2$, a thin protective chromia scale covered much of the surface, Fig. 4a. In aCO$_2$, the mass change results (Table 5) indicated spalling occurred. The observable scale was primarily iron oxide, Fig. 4c. This result is consistent with the variable effect of pressure shown in Fig. 13. At times iron-rich nodules can form, which spread to cover the surface. These iron-rich oxides are less protective than the chromia scales, and grow much thicker. Thick oxides are more prone to spallation than thin oxides, so the mass loss found in aCO$_2$ was not a surprising result.

**Effect of Pressure on Oxidation Kinetics**

To isolate and estimate the pressure effect in steam from the experimental and literature results at different pressures and temperatures, the activation energy for chromia formation using the PMCr 17 bar data [8] was determined (207 kJ/mol). Since oxide scales remained essentially pure chromia at high pressure, Arrhenius behavior was assumed and the activation energy used to estimate what the data in Fig. 12 would be at 700°C.

For Ni-base alloys the estimates on a 700°C basis are shown in Fig. 15. The two outliers in the data set (data points denoted by × in Fig. 15) were not used to fit the data. In Fig. 15a, the log $k_p$ values are
shown in terms of log $P_T$. There was a large amount of scatter in the data, and the $R^2$ value was 0.33. In Fig. 15b, the log $k_p$ values are shown in terms of $P_T$. The fit was better, with an $R^2$ value of 0.60. The fit was better largely due to less pressure dependence in the data at 17 bar. Based on this analysis, the effect of pressure on log $k_p$ appears to be proportional to $P_T$.

![Graphs showing oxidation kinetics of Ni-base alloys](image)

(a) 700°C Basis Obtained using an Activation Energy of 207 kJ/mol  
(b) 700°C Basis Obtained using an Activation Energy of 207 kJ/mol

Fig. 15. Oxidation kinetics of Ni-base alloys as a function of pressure using an activation energy of 207 kJ/mol to estimate the data on a 700°C basis.

**Conclusions**

A comparison of the oxidation behavior of austenitic stainless steels and Ni-base alloys in sH$_2$O and sCO$_2$ was made. Experiments were conducted at 730°C and 207 bar (sCO$_2$) and 726°C and 208 bar (sH$_2$O).

Ni-base alloys in sCO$_2$ did not exhibit much, if any, effect on oxidation behavior with pressure. Dense and protective chromia scales were formed. In contrast, Ni-base alloys in sH$_2$O had an increase in corrosion rates and parabolic rate constants as a function of pressure. Chromia scales still formed, but were less protective. It should be noted that these are still relatively low oxidation rates, and would not preclude the successful use of Ni-base alloys in A-USC power plant applications. A relationship of log $k_p$ being proportional to $P_T$ in sH$_2$O was found from an examination of the experimental and literature data.

Austenitic stainless steels in sCO$_2$ and sH$_2$O responded similarly with pressure. In both cases the dense protective chromia scale that formed at atmospheric pressure was replaced by faster growing Fe-oxide rich scales. Variability in the nucleation of Fe-oxide nodules on the surface led to a lot of variability in the oxidation kinetics.

The oxidation behavior of candidate A-USC alloys was found to be as good as, or better, in sCO$_2$ than in sH$_2$O. So it was confirmed, based on relatively short-term oxidation tests, that these alloys are also good candidates for indirect sCO$_2$ power system components.

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References