Oxidation behavior of Fe- and Ni-base alloys in supercritical CO$_2$ and related environments

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Introduction
Heat engine power cycles, using a working fluid of supercritical carbon dioxide (sCO$_2$), have the potential for high thermodynamic efficiencies when configured as a (indirect) recompression Brayton cycle. Two aspects of the oxidation behavior of alloys were compared between several indirect- and direct-cycle related environments.
- The critical Cr content needed in Ni alloys to achieve a compact and protective chromia scale.
- The effect of surface finish on the oxidation behavior of Grade 91 ferritic-martensitic steel.

### sCO$_2$ Power Cycles - Indirect

<table>
<thead>
<tr>
<th>Test Gas composition</th>
<th>Gas Notes</th>
<th>Alloys</th>
<th>T, °C</th>
<th>P, bar</th>
<th>Flow rate at T/P, cm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ + 1% O$_2$</td>
<td></td>
<td>Ni-xCr</td>
<td>700</td>
<td>200</td>
<td>25</td>
</tr>
<tr>
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### Critical Cr Content in Ni Alloys

- The oxidation responses of Ni-xCr model alloys (where x varied from 5 to 24 wt%) were compared in six high temperature environments.
- When H$_2$O or O$_2$ was part of the gas phase, a transition to protective kinetics occurred somewhere between 5-12Cr in DF4, DF4S and air, and at 14Cr in sH$_2$O.
- The oxygen activity in sCO$_2$ and sH$_2$O were similar, so H$_2$O was more aggressive than CO$_2$ for the Ni-5Cr alloy.
- The ability to remain protective at low Cr values indicates that nickel base superalloys may be resilient to damage that exposes near-surface alloy that is depleted Cr—especially in pure CO$_2$.

### Surface Finish of Grade 91 Ferritic Steel

- The mass gains in air were much lower than in CO$_2$ environments.
- The Ni-5Cr alloy in pure CO$_2$ environments (sCO$_2$ and aCO$_2$) was at least somewhat protective, while it was unprotective in the other environments.

### Summary

- The oxidation responses of Ni-xCr model alloys (where x varied from 5 to 24 wt%) were compared in six high temperature environments.
- The Ni-5Cr alloy in pure CO$_2$ environments (sCO$_2$ and aCO$_2$) was at least somewhat protective, while it was unprotective in the other environments.
- When H$_2$O or O$_2$ was part of the gas phase, a transition to protective kinetics occurred somewhere between 5-12Cr in DF4, DF4S and air, and at 14Cr in sH$_2$O.
- The oxygen activity in sCO$_2$ and sH$_2$O were similar, so H$_2$O was more aggressive than CO$_2$ for the Ni-5Cr alloy.
- The ability to remain protective at low Cr values indicates that nickel base superalloys may be resilient to damage that exposes near-surface alloy that is depleted Cr—especially in pure CO$_2$.
- The oxidation responses of ferritic steel Grade 91, with three different surface finishes, were compared in three different environments at 550 °C.
- The mass gains in air were much lower than in CO$_2$ environments.
- The benefits of near surface cold work were observed—the samples with the most cold work had the smallest mass gains in all three environments.
- This indicates that surface enhancements to induce more residual stress, such as shot peening, may be of benefit for 9-12Cr ferritic-martensitic steels in sCO$_2$.

### Acknowledgements

This work was performed in support of the US Department of Energy’s Fossil Energy Crosscutting Technology and Advanced Turbine Research Programs. The Research was executed through NETL Research & Innovation Center’s Advanced Alloy Development Field Work Proposal. Research performed by AECOM Staff was conducted under the RES contract DE-FE-0004000.

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• Recompression $sCO_2$ Brayton Cycle
  • Widely proposed for Concentrated Solar and Nuclear Energy due to their relatively narrow temperature range requirements
  • The split recuperator allows a portion of the high pressure $sCO_2$ to bypass the LTR to balance its heat duty and improve efficiency
  • For Fossil Energy applications, consideration must be given to use the significant thermal energy remaining in the combustion flue gas after passing through the PHX

HTR high-temperature recuperator, LTR low-temperature recuperator, MC main compressor, PC primary cooler, PHX primary heat exchanger, RC recycle compressor, T turbine
Semi-open sCO₂ Brayton Cycle
- Oxycombustion using O₂ instead of air to burn fuel
- More akin to gas turbines (indirect cycles more akin to steam turbines)
- Higher turbine inlet temperatures and thus higher efficiencies
- High pressure sCO₂ output allows for CO₂ transport and sequestration
- Working fluid not pure CO₂, but contains other combustion products including H₂O

ASU air separation unit, C compressor, HTR high-temperature recuperator, LTR low-temperature recuperator, T turbine
HTR high-temperature recuperator, LTR low-temperature recuperator, MC main compressor, PC primary cooler, PHX primary heat exchanger, RC recycle compressor, T turbine

ASU air separation unit, C compressor, HTR high-temperature recuperator, LTR low-temperature recuperator, T turbine