

Compatibility of Steels in Supercritical CO₂ at 450°-650°C

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ABSTRACT

Supercritical CO₂ (sCO₂) power cycles, particularly direct-fired cycles, have the possibility of revolutionizing clean fossil energy. However, in the lower temperature sections of the cycle, lower cost steels are needed in order to lower the cost of the sCO₂ technology. Representative 9 and 12%Cr steels and conventional and advanced austenitic steels are being evaluated at 450-650°C using mass change, bulk carbon (C) content and room temperature tensile properties to determine the maximum use temperatures for both direct- and indirect-fired sCO₂ cycles. After 1000 h exposures in research grade (RG) sCO₂ at 300 bar and RG sCO₂ with 1% O₂ and 0.1% H₂O additions, the results suggest that increasing the Cr content from 9 to 12% yielded no significant benefit under these conditions but the higher Cr and Ni contents in S31025 provided better compatibility in RG sCO₂ at 650°C but limited benefit at 550°C with impurities. For S31609, the formation of Fe-rich oxide after exposure to RG sCO₂ at 650°C resulted in both an increase in the bulk C content and a large drop in room temperature ductility. The evidence suggests thin, protective oxides prevented C ingress in these conditions.

Keywords: supercritical carbon dioxide, thermal cycling, lifetime model

INTRODUCTION

Several power generation technologies are exploring the use of supercritical CO₂ (sCO₂) including fossil, nuclear, geothermal, concentrating solar power (CSP) and waste heat recovery, because of its unique properties and relatively low critical point (31°C/73.8 bar)¹⁻⁶. Several recent studies focused on sCO₂ operating temperatures of ≥700°C⁷⁻¹², where greater than 50% thermal efficiency is predicted¹³. However, for sCO₂-based cycles to be commercially competitive, lower cost steels are needed in the lower temperature components in the cycle. There is concern about the use of steels in sCO₂ because prior experience of K90941 (Grade 9) in the UK advanced gas cooled reactors (AGRs) operated with 43 bar CO₂ (sub-critical conditions) at ≤550°C where severe internal carburization could occur under those conditions¹⁴. A recent review concluded that creep-strength enhanced ferritic (CSEF) steels were

limited to 450°C in sCO₂¹⁵, significantly lower than the 580°-600°C limit in supercritical steam¹⁶. A nuclear fuel cladding study found that a stainless steel such as S32750 (type 316FR) had much better oxidation resistance than 9-12%Cr CSEF steels but began to show accelerated oxidation at 600°C¹⁷. Another factor in assessing sCO₂ steel compatibility is the presence of impurities in the sCO₂. At 750°C, little difference in reaction rates was noted between research grade (RG) sCO₂ and industrial grade sCO₂¹⁰. However, the higher impurity levels expected for direct-fired cycles^{3,5}, compared to indirect-fired or closed cycles, has been shown to affect reaction rates^{8,10}. Also, the additions (CH₄, H₂O, etc.) in the AGR CO₂ used to prevent oxidation of the graphite moderator may have affected performance.

The current work has exposed two CSEF steels and two austenitic steels to 300 bar RG sCO₂ at 450°-650°C for 1000 h (two 500-h cycles) to begin to determine the maximum use temperatures for these materials. An initial 1000 h experiment also has been conducted at 550°C with controlled O₂ and H₂O additions¹⁰ to simulate the Allam cycle. In addition to mass change and oxide thickness, room temperature tensile properties and bulk C content^{18,19} have been measured to assess internal carburization.

EXPERIMENTAL PROCEDURE

The chemical composition of the four steels investigated in this study are shown in Table 1. Alloy coupons (~12 x 20 x 1.5mm) were polished to a 600 grit finish and tensile specimens (SS-3 type: 25.4 mm long, 0.76 x 5 mm gauge) were prepared with a similar finish. All specimens were ultrasonically cleaned in acetone and methanol prior to exposure. For the 500-h cycles in 300 bar RG sCO₂, the exposures were conducted in an autoclave fabricated from N07208. The vertically-oriented autoclave (~266 mm x 83 mm inner diameter) was operated inside a three-zone furnace with an N07208 sample rack that sat on the bottom of the autoclave. The fluid flow rate was ~2 ml/min and additional details are provided elsewhere^{9,10,20}. 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 using a cooling fan on the autoclave. For the controlled impurity sCO₂ experiments, three pumps were used for the sCO₂, O₂, and H₂O, and the O₂ was delivered as a CO₂-O₂ gaseous mixture. The O₂ was calculated (based on gas flow) as 1.0 ± 0.2% and the H₂O content as 0.1 ± 0.05% with most of the variation associated with the change in sCO₂ cylinders (typically twice per 500-h cycle) and operational issues such as filter plugging and valve leakage.

Before and after each 500-h cycle, the specimens were weighed using a Mettler Toledo XP205 balance with an accuracy of ±0.04 mg or ~0.01 mg/cm². After exposure, tensile specimens were tested at room

Table 1
Alloy chemical compositions (weight %)(¹)

Alloy	UNS#	Fe	Cr	Ni	Mo	Mn	Si	C	S(ppm)	Other
Gr.91	K90901	88.8	8.6	0.3	0.9	0.46	0.35	0.10	6	0.2V,0.06Nb,0.045N
12CrCoW		83.3	11.5	0.4	0.4	0.38	0.42	0.12	3	1.6W,1.5Co,0.2V,0.04N
316H	S31609	69.5	16.3	10.0	2.0	0.84	0.46	0.041	6	0.3Cu,0.3Co,0.04N
709	S31025	51.3	20.1	25.2	1.5	0.89	0.41	0.064	3	0.2Nb,0.06Cu,0.15N

(¹) measured by inductively coupled plasma analysis and combustion analysis
< indicates below the detectability limit of <0.01%

temperature with a strain rate of 0.015/min per ASTM E8-13. The bulk C uptake was measured using combustion analysis. For metallography, specimens were Cu plated before sectioning. Reaction product thickness was measured using image analysis software with ~30 measurements per specimen.

RESULTS

Figure 1 shows the coupon mass change data in 300 bar RG sCO₂. Box and whiskers are used to show the results from 5-6 specimens of each alloy at each condition and the median values are shown. One specimen of each alloy was removed after each cycle for characterization. As expected, the 9-12%Cr steels showed higher mass gains at each temperature. At 650°C, scale spallation was evident for these specimens which affected the values and distribution, Figure 1b. The two median data points were used to calculate parabolic rate constants by plotting them vs. the square root of time²¹. Figure 2 shows that the rates (large open symbols) were very similar to those previously measured¹⁷ and changing from 8.6% to 11.5% Cr had little effect on the rates in this temperature range where Cr mobility is limited²². For the stainless steels, the mass gain were very low at 450° and 550°C and only the 550°C mass gains are shown in Figure 1a. At 650°C, the mass gains also were very low for the S31025 specimens. However, a much thicker oxide was observed for the S31609 specimens, which also is consistent with prior work^{17,23}. The rates for S31609 were consistent with prior literature values¹⁷, Figure 2. No prior results were found for S31025 in sCO₂ but the rates near 10⁻¹⁶ g²/cm⁴s are as low as can be measured with 0.01 mg/cm² accuracy and are similar to rates measured for chromia-forming Ni-based alloys²⁴.

Figure 3 shows the mass change data at 550°C with and without controlled impurity additions. The shaded boxes show the results with 1%O₂+0.1%H₂O additions. For the CSEF steels, no statistically significant change in mass gain was observed with the addition of impurities. In contrast, both austenitic steels experienced higher mass gains. The larger change for the S31025 specimens was observed after the second 500-h cycle. After the first cycle, median values of 0.02 mg/cm² were measured in both conditions. The measured rates are shown as closed symbols at 550°C in Figure 2.

To avoid relying solely on mass change data, specimens were removed from these experiments after each cycle for characterization of the reaction products. Figure 4 shows examples of the reaction products for each alloy after one 500-h cycle at each condition. Consistent with the mass change data

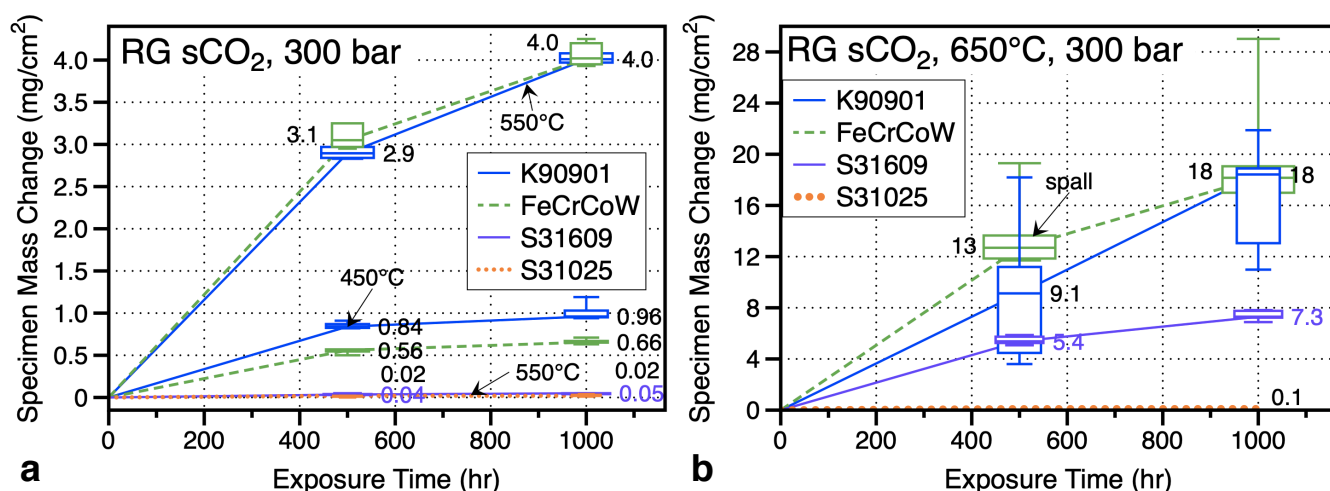


Figure 1. Specimen mass gain during 500-h cycles in 300 bar RG sCO₂ (a) 450° and 550°C and (b) 650°C. Box and whisker plots show data for 5-6 specimens exposed and the median values are shown.