

Compatibility of Steels at 450°-650°C in Supercritical CO₂ with O₂ and H₂O Additions

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ABSTRACT

Direct-fired supercritical CO₂ (sCO₂) power cycles are being commercialized to revolutionize the use of fossil fuels as a low-emission power source. However, the cycle will increase O₂ and H₂O in the sCO₂ and the implications of these additions have not been fully studied, particularly for lower cost steels that are needed in the lower temperature segments of the plant. Representative 9 and 12%Cr ferritic-martensitic (FM) steels and conventional and advanced austenitic steels were evaluated at 450-650°C in sCO₂ with 1%O₂ and 0.1%H₂O at 300 bar to determine their maximum use temperatures. Compared to research grade (low impurity) sCO₂ in indirect-fired cycles, the mass gains and scale thickness were not significantly changed for FM steels: both formed thick duplex Fe-rich scales with and without impurities. For austenitic steels, higher mass gains were observed at all temperatures with increased Fe-rich oxide nodule formation. After 1000 h at 650°C, the measured bulk C content was high for all of the steels with the addition of impurities suggesting a lower maximum operating temperature for steels. The impact of the environment on the post-exposure room temperature tensile properties was also evaluated and compared to 1000 h Ar anneals.

Keywords: supercritical carbon dioxide, steels, impurities, carbon ingress

INTRODUCTION

Using supercritical CO₂ (sCO₂) as a working fluid is being explored for a number of power generation technologies including fossil, nuclear, geothermal, concentrating solar power (CSP) and waste heat recovery¹⁻⁷. The various sCO₂ cycles are attractive because of the low critical point (31°C/73.8 bar) and the reduced work of compression compared to an ideal gas. While CO₂ is sometimes described as inert, there is a long history of component degradation in subcritical and supercritical CO₂ and a particular concern about internal carburization⁸⁻¹⁶. Recent work has found that Ni-based alloys appear to have good compatibility with sCO₂ up to 800°C^{14,17-21}. However, less expensive steels would be desirable for components operating at ≤650°C. Prior experience with low-alloy and ferritic-martensitic (FM) steels (e.g. Grade 9, K90941) in the UK advanced gas cooled reactors (AGRs) showed breakaway

oxidation associated with internal carburization for operation in 43 bar CO₂ at <550°C^{15,22}. A recent review concluded that 9-12%Cr creep-strength enhanced FM steels were limited to 450°C in sCO₂¹⁶, substantially lower than the 580°-600°C limit in supercritical steam²³. However, CO₂ additions (CH₄, H₂O, etc.) used in AGRs to prevent oxidation of the graphite moderator may have negatively affected performance by increasing the C activity compared to low impurity CO₂.

For combusting fossil fuels, the direct-fired oxy-combustion or Allam cycle^{3,5,7} represents a potentially attractive strategy for carbon capture, utilization and storage. However, the high O₂ and H₂O impurity levels compared to indirect-fired closed sCO₂ cycles is a further concern. Initial studies of the effect of sCO₂ impurities at >650°C indicated that impurities accelerate reaction rates^{18,20}. To further explore the effects of impurities and establish maximum operating temperatures in sCO₂, the current ongoing study exposed two FM steels and two austenitic steels to 300 bar RG sCO₂ at 450°-650°C for 1000 h (two 500-h cycles) with and without controlled O₂ and H₂O additions²⁰ to simulate expected conditions in the Allam cycle. Mass change, oxide thickness, room temperature tensile properties, bulk C content^{8,9} and C profiles were measured to assess reaction kinetics and internal carburization with and without impurities.

EXPERIMENTAL PROCEDURE

Table 1 lists the measured chemical composition of the four steels used in this study. Steel coupons (~12 x 20 x 1.5mm) were machined and polished to a 600 grit finish and SS-3 type²⁴ dogbone tensile specimens (25.4 mm long, 0.76 x 5 mm gauge) were prepared with a similar finish. Specimens were ultrasonically cleaned in acetone and methanol prior to exposure. The 500-h exposures at 300 bar were conducted using research grade (RG) CO₂ in a vertically-oriented autoclave (~266 mm x 83 mm inner diameter) fabricated from N07208. Specimens were held in an N07208 sample rack and the fluid flow rate was ~2 ml/min with additional details provided elsewhere^{17,20,21}. The specimens were slowly heated to temperature in sCO₂ over several hours (~2°C/min) using a three-zone furnace. After holding at temperature ±1°C for 500 h, the autoclave was then cooled to room temperature. The controlled impurity experiments used two pumps for sCO₂ and H₂O, and O₂ was added as a CO₂-O₂ gaseous mixture from a high pressure cylinder. Based on gas flow rates, the O₂ was calculated as 1.0 ± 0.2% and the H₂O content as 0.1 ± 0.05% with the largest variations associated with issues with filters, valves and changing sCO₂ cylinders (usually twice per 500-h cycle).

The specimens were weighed before and after exposure using a Mettler Toledo model XP205 balance with an accuracy of ±0.04 mg or ~0.01 mg/cm². Room temperature tensile tests used a strain rate of 0.015/min per ASTM E8-13. Bulk C was measured using combustion analysis and C profiles were

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

Alloy	UNS#	Fe	Cr	Ni	Mo	Mn	Si	C	S(ppm)	Other
Gr.91	K91560	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%

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acquired via electron microprobe analysis (EPMA) using a JEOL model 8200 equipped with 5 tunable wavelength dispersive spectrometers. EDS spectra were acquired and processed using a Thermo Scientific Pathfinder EDS system. The accelerating voltage was set to 20 kV and the beam current was 50 nA. Pure standards were used to calibrate all elements. Unknown and standard intensities were corrected for deadtime. Standard intensities were corrected for standard drift measured between the beginning and end of the run. Interference corrections were applied to Mn K_{α} for interference by Cr K_{β} and a ZAF algorithm was used²⁵. For thin reaction products, Cu plating was used before sectioning for metallography. Reaction product thickness was measured using image analysis software with ~30 measurements per specimen.

RESULTS

Examples of the mass change data in 300 bar RG sCO₂ are shown in Figure 1. The 550°C data were previously presented²⁶. The results from 5-6 specimens of each alloy at each condition are presented using box and whisker plots with the median values shown. One specimen of each alloy was removed after 500 h for characterization. The 9-12%Cr steel specimens showed the highest mass gains at each temperature. The addition of impurities (shaded boxes) resulted in an initial mass increase at 450°C compared to the mass change without impurities for all of the alloys. At 650°C, scale spallation was evident for these specimens which affected the values and distribution, Figure 1b. For the S31609 specimens, a uniform mass loss was observed with the addition of impurities. Even for the S31025 specimens, increases were observed at both temperatures with the addition of impurities.

Parabolic rate constants were calculated by plotting the median data points vs. the square root of time²⁷. Figure 2 is an Arrhenius plot with the measured RG sCO₂ rates in this study (large open symbols) compared to previous values (small open symbols)^{11,21}. The change from 8.6% to 11.5% Cr in the FM steels had little effect on the measured rates, presumably because the Cr mobility is slow in this temperature range²⁸. Without impurities, the rates were very low for both austenitic steels at 450° and 550°C and consistent with values measured for Ni-based alloys^{21,29}. As noted previously²⁶, accelerated oxidation of S31609 specimens was observed at 650°C in RG sCO₂ but not for the S31025

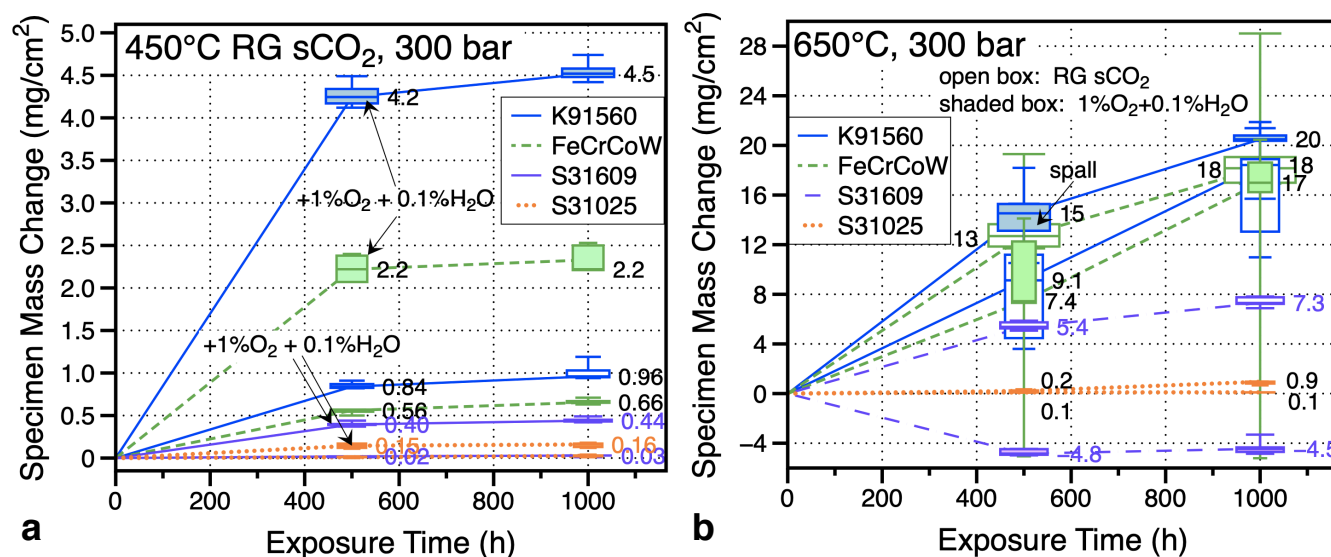


Figure 1. Specimen mass gain during 500-h cycles in 300 bar RG sCO₂ (a) 450° and (b) 650°C. Box and whisker plots show data for 5-6 specimens exposed and the median values are shown.