

Oxidation of Welded Materials in High Temperature Supercritical Carbon Dioxide

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ABSTRACT

Martensitic stainless steel (UNS S41000), austenitic stainless steel (UNS S31000), and nickel-based alloys (UNS N06625) specimens were exposed at 450°C and 7.6 MPa in pure supercritical CO₂ (sCO₂) for a total of seven months. The exposure was performed in order to assess the effect of various parameters on the oxidation of materials that may be used in oxy-combustion gas turbine systems using sCO₂. Materials and environment parameters such as composition, pressure and temperature have been covered in the literature. However, engineering design will result in atypical conditions, usually localized, that are well known to affect environmental performance of materials (such as crevices, welds, stresses, or galvanic coupling). As a result of those atypical conditions, other types of failure that have not been studied in those conditions may occur, such as stress corrosion cracking, or crevice corrosion. Some of those failures resulting from engineering design are being presented in this paper.

All martensitic stainless steel specimens (plain, welded, or coupled) had a matt black surface finish after the two months exposure. The austenitic stainless steel and the nickel alloy were both discolored after the exposure. Mass gain density inspection of the specimen was performed before and after exposure. The highest mass gain density was found for the martensitic stainless steel (0.5 mg/cm²), while it was close to the minimum measurable for the austenitic stainless steel and nickel alloy. The mass gain rate density decreased significantly after the first 2 months exposure from 0.35 to less than 0.1 µg/(hr·cm²) from the fourth months onward. The welded specimens of martensitic and austenitic stainless steels showed mass gain densities up to 50% higher than for the non-welded specimens. The mass gain densities of the coupled materials (galvanic coupling or similar crevice coupling) were not different from that of the single specimens but significant corrosion bonding was observed in all couples.

Keywords: Supercritical CO₂, Oxidation, High temperature, High pressure, Oxycombustion

INTRODUCTION

Supercritical CO₂ is being considered for a wide range of energy production-related application. The foreseen benefits are a significant increase in cycle efficiency, a reduction in size, and the opportunity to use CO₂. Energy production currently relies heavily on water and steam to produce energy, which limits its efficiency to a maximum of 40%. The sCO₂ Brayton cycle can theoretically result in a cycle efficiency of over 50%.¹ Higher efficiency not only can be used to improve existing electricity producing designs, it can also make new designs, such as concentrated solar power, economically viable. In addition to an increase in cycle efficiency, the Brayton cycle will result in a significant reduction in size of hardware. For a similar power output, a sCO₂ turbine can be as ten times smaller than a steam turbine.² Finally, Brayton cycle will rely on using sCO₂ and therefore reduces the CO₂ gas emissions.

However, sCO₂ turbines operate at very high pressure and high temperature unlike conventional steam turbines. This creates new material requirement that are currently being investigated. Exposure of materials to high pressure and temperature sCO₂ result in two main form of environmental interaction: carburization and oxidation. Carburization may result in spallation of the oxide.³

Three type of alloys have been investigated in the literature to use with high temperature sCO₂: martensitic and ferritic stainless steel, austenitic stainless steel and chromium nickel alloys. The temperature limits are shown in Table 1. Those limits are based on their oxidation properties and on the maximum temperature criteria in the ASME Boil & Pressure Vessel Code, Sec. VIII Div 1 and Div II. Oxidation has been assessed by measuring mass gain density after exposure of test coupons to sCO₂. The effect of parameters such as pressure, sCO₂ contamination, and coatings have been studied in the literature.

Table 1: Temperature range of different type of alloys considered for use in high-temperature sCO₂.

Temperature (°C)	300	350	400	450	500	550	600	650	700	750	800
Type of alloy											
Martensitic and ferritic stainless steel											
Austenitic stainless steel											
Chromium nickel alloys											

Temperature has been found to be the primary parameters on oxidation rate and can change significantly from location to location in a gas turbine. Consequently, various materials will be needed at various location in a sCO₂ system. Martensitic stainless steel can be used in locations where the temperature is below 450°C, while CrNi alloys will be required when temperatures reach 750°C. Although they have been found to suffer inter-granular oxidation at higher temperature, as was observed on Inconel 718 and 738 at 700°C / 25 MPa.¹ Temperature affects the thickness and composition of oxide film layer. The duplex layer found on austenitic can be detrimental to thermal conductivity.⁴ Steels containing less than 9-12% Cr form a duplex scale comprising an outer layer of iron-rich oxide and an inner layer of Cr-Fe spinel.⁵

Carburization has also been observed on alloys exposed to high temperature sCO₂. Chromium in martensitic stainless steels react with carbon to form chromium carbide during this process. The carbon is thought to be the result of the carbon diffusing through the oxide film layer to react with the chromium. Oxide spallation has been observed to be the most detrimental consequence of carburization, this has been observed in stainless steel 316 at 650°C/200 bar.³ Carburization is quantified by performing micro-hardness testing across the thickness of the oxide layer and the matrix underneath. Greater carburization resistance can be observed in austenitic stainless steels with high

Cr+Ni content.⁶ Carburization may also be measured as mass gain density as a result of the carbon intake. However, it can be difficult to differentiate carburization from oxide film growth as the cause of mass gain density.⁶

In the field, sCO₂ will not be pure and will contain contaminants, wanted or not. A lot of the studies of contaminants have been performed at pressures as low as 0.1 MPa based on the assumption that pressure does not affect oxidation in sCO₂.^{7,8} Oxidation has been found to increase when water contamination is present and oxidation rate increase with the amount of water.^{9,10} It is unclear if the presence of O₂ has a beneficial or detrimental role. Adding 100 ppm of O₂ (650-750°C at 200 bar) increased the oxide thickness independently from temperature (650-750°C).¹¹ Addition of 10 and 100 ppm oxygen in sCO₂ accelerated oxidation with a thicker oxide layer developing on the surface and evidence of spallation (650-750°C /20 MPa). For nickel alloys tested in environments containing oxygen impurity, thicker oxide layers were observed suggesting accelerated chromium diffusion.¹² This also led to void formation beneath the oxide layer, which was dependent on both test temperature and oxygen impurity concentration. The void regions were found to contain a larger concentration of chromia, which could lead to better adherence of the oxide.¹² Other work hypothesized that the presence of O₂ may promote more protective oxide scales (700°C / 200 bar).¹³ High water vapor content may increase the probability of breakaway oxidation.¹⁴

During this study, three type of materials have been considered of interest based on Table 1: martensitic and austenitic stainless steels, and one nickel alloy. It was decided to perform the exposure in non-contaminated sCO₂ in order to focus on the engineering variables: welding, and crevices between similar and different materials. Plain samples were also exposed to use as baseline.

Crevices or welding have not been studied in sCO₂, and were considered of interest for this study. Crevices were considered because it is well known that crevices result in an occluded chemistry that can have a strong impact on localized corrosion. Dissimilar material crevices were chosen not because a galvanic effect was expected, but because the oxidation of the lesser material may result in a local chemistry change that would affect the oxidation of the more noble material. Welding changes the local microstructure due to the high temperature in the vicinity of the weld. The chromium may diffuse to the grain boundaries and the chromium concentration in the matrix drop significantly. Consequently, the corrosion resistance near the weld will drop. Since welding will likely be used in the manufacturing process, it is of interest to test coupons containing the heat-affected zone near a weld.

EXPERIMENTAL PROCEDURE

Three different alloys were exposed to 100% sCO₂: martensitic stainless steel (UNS S41000), austenitic stainless steel (UNS S31000), and nickel alloy (UNS N06625). All specimens were machined as washers, which were 1/8" thick and 1" diameter with a 0.25" diameter hole. The effects of welding, and dissimilar and similar material couplings were studied. The details of the specimens are shown in the experimental matrix presented in Table 2.

Table 2. Experimental matrix.

	Specimen A	Specimen B	Test design	Quantity A	Quantity B
1	UNS S41000	n/a	Washer	5	0
2	UNS S31000	n/a	Washer	5	0
3	UNS N06625	n/a	Washer	5	0
4	UNS S41000	n/a	Welded washer	5	0
5	UNS S31000	n/a	Welded washer	5	0
6	UNS S41000	UNS N06625	Coupled dissimilar washer	5	5
7	UNS S41000	UNS S41000	Coupled similar washer	5	5

The exposure was performed in a 3 feet long stainless steel 316 autoclave with a 1 ½" ID. A photo of the test autoclave is shown in Figure 1.



Figure 1. Test autoclave.

The welded specimens were made from original washers cut in half and then welded along the diameter using TIG welding as shown in Figure 2.

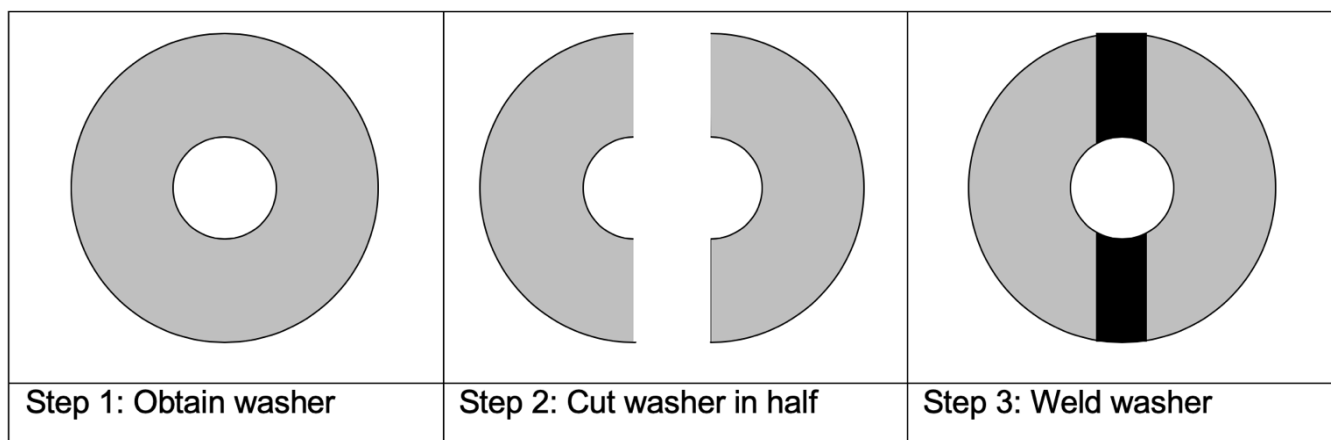


Figure 2: Preparation of welded washers.

All the specimens were polished down to 800 grit on one side and stamped with an individual number and on the other side. The specimens were photographed and weighed down to 0.1 mg before exposure.

The specimens were placed on a heat treated zirconium all thread separated in 3 sections. The specimens were separated using 1/8" thick heat treated zirconium spacers. The coupled specimens were placed against one another and a spring Belleville washer was added at the end of the all thread to keep the couples tightened. The three sections were connected together using threaded stainless steel couplers that allow to keep the all thread centered. The specimen holder was inserted in the autoclave, which was then sealed. The autoclave was pressure tested at 10.342 MPa at room temperature with nitrogen before being filled with CO₂. The temperature was increased to 450°C/842°F and the pressure was adjusted to reach 1100 psig. The exposure lasted a total of seven months broken down in three periods of two months and one period of one month. The autoclave was cooled down to ambient temperature and depressurized at the end of each period before being opened. The specimens were removed from the autoclave, weighed, photographed. In addition, some specimens were cross sectioned, mounted and polished, before being observed in a SEM.