

Effect of Impurity on The High-temperature Corrosion Performance of Alloys in Supercritical CO₂

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ABSTRACT

In advanced power generation systems, the supercritical CO₂ (s-CO₂) Brayton cycle has been developed as a promising technology because of its high efficiency, compactness, and potential to complete carbon capture. Selecting appropriate alloys as the constructional materials is one of the crucial steps to the successful deployment and long-term safe operation of the s-CO₂ Brayton cycle. Current work investigates the corrosion behavior of candidate alloys in s-CO₂ environments with impurities. The corrosion products are characterized and the possible corrosion mechanism in the high-temperature s-CO₂ environment is discussed. Besides, the effect of impurity on the corrosion behavior of alloys is discussed.

Key words: supercritical carbon dioxide, O₂, H₂O, steel, chromium.

INTRODUCTION

Over the years, the supercritical carbon dioxide (s-CO₂) Brayton cycle has been developed as a promising working fluid to replace supercritical water (s-H₂O) Rankine cycle. It could be used in various energy systems, including Generation IV nuclear reactors, concentrated solar power plants, fossil fuel thermal power plants, waste heat recovery, etc. due to its merits of high thermal efficiency, simple physical footprint, compact equipment size, high flexibility on operation, simple layout, compact turbomachinery.¹ By far, several s-CO₂ based power plants are being built at the demonstration level,² and more research is being conducted worldwide to remove the technical barriers concerning characterization on the behavior of s-CO₂, design and operation, material selection, turbomachinery, and so on.³ Among these issues, materials knowledge gaps regarding the selection of appropriate constructional alloys greatly hinder the successful deployment of this attractive technology. The Brayton cycle is operated at high temperatures and pressures, yet the available information is limited to support the selection of appropriate alloys with acceptable long-term compatibility in s-CO₂.

The s-CO₂ Brayton cycles are designed with the operating pressure up to 30 MPa and the working temperature up to 800 °C.⁴ From corrosion aspects, s-CO₂ streams in such conditions arouse not only oxidation, but also carburization on alloys. Up to now, a lot of Fe- and Ni-based alloys as high-temperature structural components have been studied with wide temperature and pressure ranges, and several crucial aspects that may affect the corrosion process have been investigated.⁵⁻⁷ The effect of s-CO₂ pressure has been studied by some researchers, and it is generally believed that pressure didn't play a decisive role in the corrosion process. For example, the variation on s-CO₂ pressure from 0.1 to 30 MPa only shows a minimal effect on the corrosion performance of several Fe- and Ni-based alloys after 500 hours of exposure at 750 °C.⁸ It was found that the alloy type and working temperature greatly affect the corrosion process. In one study, stainless steel (AL-6XN) and Ni-based alloys (PE-16, 230 and 625) were exposed to 20 MPa s-CO₂ at 650 °C for up to 3000 h. The results show that stainless steel had much higher corrosion rates than Ni-based alloys.⁷ In another study, ferritic steels (GR91, VM12), austenitic stainless steels (Corfer 22H, 304H, HR3C) and Ni-based alloys (617, 740H) were exposed to 20 MPa s-CO₂ environments, and the corrosion resistance followed the sequence of ferritic steels < austenitic stainless steels < Ni-based alloys.⁹ In addition, an increase of 50 °C on temperature increased the thickness of the formed oxide scale by a coefficient up to 4.⁹

Despite these studies, the effect of impurities on the corrosion performance of materials in s-CO₂ Brayton cycle still needs investigation. The level of impurities may vary from ppm level to % level, depending on the working environment and the type of Brayton cycle.¹⁰ Their effects on corrosion performance of alloys are not fully studied, and sometimes the results are even contradictory. For instance, Mahaffey et al.¹¹ found that Alloy 800H and AFA-OC6 showed higher corrosion rates in research grade s-CO₂ (99.999%) than in industrial grade s-CO₂ (99.95%) during a 1000 hours' test in 550 °C s-CO₂, and such difference was explained by the higher contents of impurities in the industrial grade CO₂ that affects the oxidation process. Yet in another study, several high-temperature structural alloys (F22, F91, 304H, 316H, 347H, 800H, HR120, and 617) were exposed to industrial/research grade CO₂ at 350 and 600 °C for 1000 h. At 350 °C, steels generally showed higher mass change values in industrial grade CO₂ while at 600 °C, the results were on the contrary.¹² It is tentatively proposed that the effect of CO₂ grade is affected by temperature, yet more studies are still needed to prove it. Some researchers found that O₂ plays a negative role in the high-temperature corrosion performance of alloys in s-CO₂. Mahaffey et al.¹³ found that O₂ impurity in 20 MPa s-CO₂ would enhance the formation of Ni- and Fe-based nodules on Alloy 625. They later confirmed the deleterious effect of O₂ impurity when exposing Alloy 230 to 650 and 750 °C s-CO₂ with 10 and 100 ppm O₂.¹⁴ Other researchers, however, found that low level (50 ppm) impurities (O₂ and H₂O) in 30 MPa s-CO₂ didn't obviously affect either the corrosion rates or corrosion products of several alloys (Alloy 282, Alloy 740, Alloy 625 and 25 SS) after 2500 hours of exposure.¹⁵ Until now, the effect of H₂O and O₂ on the corrosion behavior of Fe- and Ni-based alloys in high temperature s-CO₂ has not been fully studied and more research is still highly desired.

Therefore, the objectives of this paper are to examine the effect of H₂O and O₂ on the corrosion performance of alloys in high-temperature s-CO₂ environments. Besides, since Cr is a crucial element, the effect of Cr content on corrosion performance is further investigated by controlling the Cr content in tested alloys. It is anticipated to identify the influence of impurity (H₂O and O₂) on corrosion in high-temperature s-CO₂, and provide useful information on alloy design, both of which will eventually support the development of applicable materials selection strategy for the deployment of s-CO₂ Brayton cycle in advanced power production systems.

EXPERIMENTAL PROCEDURE

Sample Preparation

For alloy plates, S31600, S31000, N08120 and R20033, were purchased from commercial manufacturers and machined into metal coupons with a size of 20 mm long × 10 mm wide × 2 mm thick. A hole with a diameter of 4 mm was drilled near the top edge for the ease of suspension on the sample holder during the test. The chemical compositions of the alloys are shown in Table 1. It should be noted that the Cr contents are controlled as an increasing trend from 16.6 to 33.0 wt.%. Prior to autoclave tests, all the samples were well polished by SiC papers with the grits of #120, #240, #360, #480 and #600. Then, the samples were cleaned with distilled water and ethanol in an ultrasonic bath, and finally dried by compressed air. Then, the samples were weighted by a microbalance with a precision of 0.001 mg and dimensioned by a caliper with a precision of 10 µm. All the samples were kept in a vacuum container before corrosion tests.

Table 1
Chemical composition of four tested alloys (wt.%).

	Cr	Ni	Fe	Mo	Co	Mn	Si	C
SS31600	16.6	10.0	Bal.	2.0	0.3	1.2	0.32	0.022
SS31000	24.2	19.2	Bal.	0.2	0.1	1.7	0.54	0.043
N08120	25.2	37.3	Bal.	0.2	0.16	0.73	0.45	0.052
R20033	33.0	30.9	Bal.	1.49	-	0.61	0.24	0.015

Experimental Setup and Procedures

In this study, the effect of impurities O₂ and H₂O on the corrosion performance of steels in high-temperature s-CO₂ was studied. Three testing environments were set as (1) s-CO₂, (2) s-CO₂ + 100 ppm H₂O, and (3) s-CO₂ + 100 ppm O₂. The experiments were conducted in an autoclave with a controlled temperature of 600 °C and total pressure of 30 MPa.

In each environment, the corrosion tests were composed of six cycles. Freshly prepared coupons were accommodated on a sample holder, then placed in the autoclave. Once the autoclave is sealed, CO₂ was purged several times to remove the air inside the chamber of the autoclave. Then, the autoclave was heated to 60 °C for charging. At 60 °C, different gases were charged based on the testing environments: (1) For pure s-CO₂, research grade CO₂ (99.995%) was charged into the autoclave to 7.44 MPa with the help of a booster pump. (2) For s-CO₂ + 100 ppm H₂O, 141 ppm H₂O + bal.% CO₂ was charged to 7.23 MPa, and then research grade CO₂ was added to make the total pressure as 7.44 MPa. (3) For s-CO₂ + 100 ppm O₂, 856 ppm O₂ + bal.% CO₂ was charged to 0.86 MPa, and then research grade CO₂ was added to make the total pressure as 7.44 MPa. Since the impurity (H₂O/O₂) in s-CO₂ is as low as 100 ppm, pre-mixed gases (141 ppm H₂O + bal.% CO₂ or 856 ppm O₂ + bal.% CO₂) were used to increase the accuracy.

After charging, the autoclave was sealed and heated to 600 °C and the total pressure of the autoclave reached 30 MPa, which was treated as the starting point. After 170 h, the autoclave was powered off and cooled down to room temperature. Then, the samples were taken out for weight change measurement and further characterization of corrosion products and corrosion rates. In each environment, sixth cycles were employed and the last one was reduced to 150 h to make the total testing time as 1000 h.