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Corrosion of low alloy steel and stainless steel in supercritical $CO_2/H_2O/H_2S$ systems

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ABSTRACT

The corrosion of low alloy steel and stainless steel in the dynamic supercritical $CO_2/H_2O/H_2S$ system was studied. A Cr-containing scale, mainly consisted of $FeCO_3$, $Cr(OH)_3$ and iron sulfide (mackinawite), formed on low alloy steel. $FeCO_3$ formed via the solid state reaction and precipitation reaction, while mackinawite could only form via the solid state reaction. In the aqueous phase, low alloy steel suffered severe general and localized corrosion, but 316 L stainless steel suffered pitting corrosion. In the supercritical CO_2 phase, localized corrosion was dominant for low alloy steel, and 316 L stainless steel was highly resistant to corrosion.

1. Introduction

Carbon capture and storage (CCS) is recognized as an effective technology to reduce carbon emission [1]. CCS primarily involves three stages: CO_2 capture, CO_2 transport, and CO_2 injection into geological reservoirs [2]. Captured CO_2 can also be used in the oil and gas fields for enhanced oil/gas recovery (EOR/EGR) [3]. In addition, during the exploitation of high pressure gas fields with large quantities of CO_2, the CO_2 must be separated from the gas, captured and transported to the storage sites [4], which presents similar challenges as seen in the CO_2 transport related to CCS; while the inlet temperature of the transport pipeline (80 °C) is higher than that of CO_2 transport. An important risk that must be understood in CCS, EOR/EGR applications and the exploitation of high pressure gas fields is the supercritical CO_2 (SC CO_2) corrosion problem of the steel materials.

Whether in the SC CO_2 phase (SC CO_2-rich phase, which is normally present in the CO_2 transport and injection processes) or in the aqueous phase (water-rich phase, such as the saline aquifers, normally present in the CO_2 injection process and oil and gas production), SC CO_2 can dissolve in the aqueous phase, significantly decreasing the pH value. In these two phases, once the aqueous phase encounters steel, the steel undergoes severe corrosion [5]. Steel corrosion in SC CO_2/H_2O environments has been investigated by researchers over the past few years [5–10]. In addition to H_2O, other impurities may exist in the SC CO_2 system, such as O_2, SO_2, NO_2, and H_2S [11–13]. The current studies on the SC CO_2 corrosion mainly focus on impurities such as O_2, SO_2 and NO_2, while the effect of H_2S on the corrosion of steel in SC CO_2 systems has rarely been reported. Most investigations on the effect of H_2S on steel corrosion are under low CO_2 partial pressure conditions and with a high H_2S content [14–19].

The corrosion rates of carbon steels in the SC CO_2/H_2O environments (especially in the water-rich phase) are high [6–8,20]; thus, steel with a high corrosion resistance to SC CO_2 should be studied and developed. In addition, to enhance the corrosion resistance of steel, low alloy steels have been developed, and the effect of alloy elements (especially Cr) on the CO_2 corrosion behavior of steels under low CO_2 partial pressure conditions has been widely investigated [21–24]. However, there are few studies focusing on the SC CO_2 corrosion behavior of low alloy steel. As summarized in the previous study [25], the content of H_2S was almost less than 200 ppm, basing on health and safety considerations; while the researcher have found that the steel suffered severe corrosion in SC CO_2/H_2O environment containing 200 ppm [4]. Therefore, a lower H_2S content (50 ppm (mole)) was selected to investigate in this study. The objective of this work is to understand the corrosion mechanism of low alloy steel and stainless steel in the dynamic SC $CO_2/H_2O/H_2S$ system.

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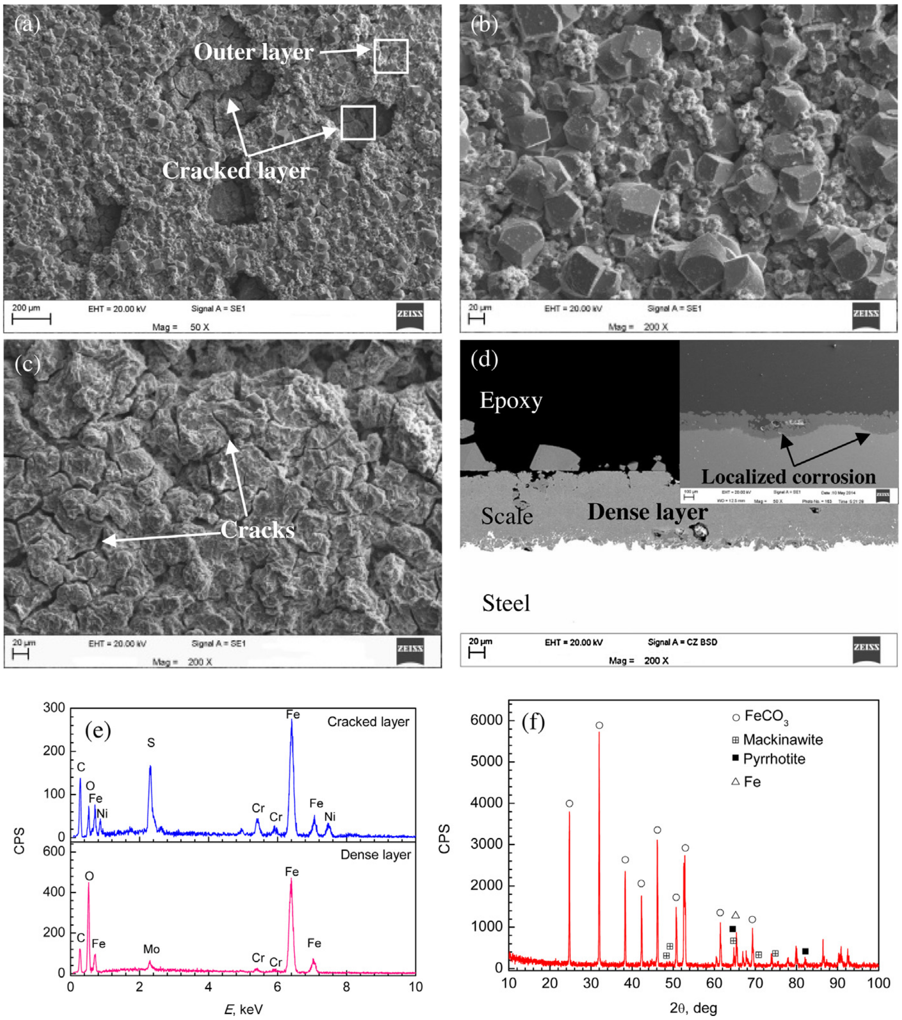

Fig. 1. (a, b, c) SEM surface morphology, (d) cross-section morphology, (e) EDS analysis and (f) XRD spectra of the corrosion product scale formed on P110 low alloy steel immersed in SC CO_2-saturated aqueous phase at 10 MPa and 80 °C with 1 m/s flow velocity for 240 h: (b) the magnified outer $FeCO_3$ layer in (a); (c) the magnified cracked layer in (a).

Table 1
Chemical compositions of the three different types of steels (wt.%).

Steels	C	Si	Mn	Mo	Cr	Ni	P	S	Fe
P110	0.27	0.26	0.60	0.60	0.50	0.25	≤0.009	≤0.003	Bal.
3Cr	0.14	0.28	0.50	0.16	2.68	0.17	≤0.009	≤0.003	Bal.
316L	0.02	0.50	1.01	2.64	17.30	12.00	0.016	0.002	Bal.

2. Experimental

2.1. Materials and solution

P110 and 3Cr low alloy steels and 316 L stainless steel were used in this study. The chemical compositions of the three steels are listed in Table 1. Specimens were machined with dimensions of 10 × 10 × 3 mm^3. The specimens were ground with 800-grit silicon carbide (SiC) paper and rinsed with deionized water followed by alcohol. After drying with cold air, the specimens were weighed using an electronic balance with a precision of 0.1 mg and then were stored in a desiccator until use.

Before the specimens were placed in an autoclave, they were fixed in a specimen holder composed of polytetrafluoroethene (PTFE) to prevent the galvanic effect, and six specimens were placed in the autoclave for each test. The corrosion medium was 3.5 wt% NaCl. Prior to each exposure experiment, the solution was deaerated by CO_2 bubbling for 12 h.

2.2. Corrosion experiments

Corrosion experiments were conducted in a high temperature and high pressure autoclave, and a schematic diagram was presented in detail in a previous study [25]. After the solution was placed in the autoclave, the autoclave was sealed and deoxygenated continuously by purging with CO_2 at ambient temperature and pressure for 2 h. Subsequently, a mixture of CO_2 and H_2S with a certain ratio was introduced into the autoclave that was adjusted to the required temperature (80 °C) and pressure (10 MPa). The flow velocity was 1 m/s, and the test duration was 240 h.

Two corrosion systems were considered in this study: the CO_2-saturated aqueous phase and the water-saturated SC CO_2 phase. During the experiment in the aqueous phase, 1000 mL of solution was introduced into the autoclave. Based on the model of Spycher et al. [26], the saturation limit of H_2O in the SC CO_2 phase at 80 °C and 10 MPa is approximately 10,000 ppm. Therefore, to ensure the water-saturated SC CO_2 state during the test, 100 mL of solution was introduced into the autoclave.