

Comparison of Corrosion Behavior of P110 And P110-3Cr Low-alloyed Steel in Supercritical CO₂-saturated Brine And Water-saturated Supercritical CO₂ Environments

Zezhou Wen, Yong Hua, Anne Neville
Institute of Functional Surfaces, School of Mechanical Engineering
University of Leeds, Leeds, LS2 9JT
United Kingdom

Shujie Liu, Xijin Xing, Dapeng Li
CNOOC Research Institute
China National Offshore Oil Corporation
25# North Street, Dongcheng District, Beijing, 100010
P. R. China

Jiong Qian, Yubin Zhou, Jianping Zhu
Corrosion and Integrity Center Zhejiang Jiuli Hi-Tech Metals Co.Ltd,
Hu zhou 313028, Zhejiang District, Zhejiang P. R. China

Xiaoqi Yue, Lei Zhang
Institute of Advanced Materials and Technology
University of Science and Technology Beijing
30# Xueyuan Road, Haidian District, Beijing, 100083
P. R. China

ABSTRACT

With the increasing production of oil and gas fields or in the carbon capture and storage application in recent years, the service environment of downhole casing is becoming increasingly harsh and complex. Downhole casings are faced with supercritical CO₂ environments in deep wells containing CO₂ at elevated temperatures and pressures. In this paper, we investigated the corrosion behavior of P110 and P110-3Cr steel, as well as the structure of the corrosion product scales, in both water-saturated supercritical CO₂ and supercritical CO₂-saturated water environments. P110 and P110-3Cr steel samples were exposed to the CO₂ phase and the water phase at 200°C with a 9 MPa CO₂ partial pressure using a high temperature and high pressure autoclave. The corrosion rates of samples were determined by weight loss measurements. The surface morphology and the composition of the corrosion product layers were analyzed by using surface analytical techniques (SEM, EDS, XRD, and Raman). The results show that P110 samples in supercritical CO₂-saturated water can reach a general corrosion rate of 0.15 mm/y and a localized corrosion rate of 0.78 mm/y was measured throughout a

168-hour immersion test, compared to 0.33 and 0.56 mm/year, respectively for P110-3Cr. Comparatively, general corrosion rates and localized corrosion rates of P110-3Cr in water-saturated supercritical CO₂ (0.07 and 0.70 mm/y separately) are both higher than those of P110 (0.05 and 0.37 mm/y separately).

Keywords: 3Cr low-alloyed steel; supercritical CO₂-saturated water; water-saturated supercritical CO₂; corrosion product scale

INTRODUCTION

Carbon capture and storage is one of the known methods to manage the significant reduction of CO₂ emission into the atmosphere. The large amounts of CO₂ are transported through pipelines to either inject for enhanced oil recovery purposes or storage of CO₂ in deep saline aquifers. The most economically-viable materials to construct pipelines from are carbon steel or low Cr-bearing steels (1-5Cr) [1,2]. The corrosion issues in CO₂ transportation have received significant attention for over 20 years. CO₂ corrosion imposes significant problems for steels due to CO₂ reacting with water to form carbonic acid. The pH can decrease to low levels (~3.1) under high pressure conditions and increase materials degradation. With regards to the transport and injection of CO₂, carbon steels and low Cr steels are susceptible to corrosion when an aqueous phase forms within the system. Previous research^[1] shows that a certain Cr concentration can improve the resistance to CO₂ corrosion and reduce the localized corrosion sensitivity of carbon steel under the condition of low CO₂ pressure partial pressures. However, research on corrosion mechanisms of Cr-containing steels in supercritical CO₂ environments is very limited. A review of the literature has revealed that the highest reported temperature for corrosion studies in supercritical CO₂ systems has been 150°C [3], but the temperature reaches 200°C is rare for deep well, the recent deep well was found in Bohai from China in 2019. Therefore, it is necessary to study the corrosion behavior of carbon steel and Cr-containing steel in the supercritical CO₂ (SC CO₂) environment at 200°C.

The purpose of the paper is to present results of a study to assess the susceptibility of P110 and P110-3Cr steels at 200°C and 9 MPa CO₂ partial pressure by determining the general and localized corrosion rates through the implementation of the weight loss method and detailed surface profilometry. A selection of SEM, Raman spectroscopy and XRD results are provided to show the morphology and composition of the corrosion products and how these are influenced when samples are exposed to both supercritical CO₂-saturated water phase and water-saturated supercritical CO₂ phase.

EXPERIMENTAL PROCEDURE

The chemical composition of P110 and P110-3Cr steels are provided in Table 1. Test specimens were machined with dimensions of 50×13×3 mm³. Surface preparation consisted of grinding the entire sample surface up to 800 grit silicon carbide abrasive paper, rinsing with distilled water, followed by acetone, high purity ethanol and drying gently with compressed air. Samples were then stored in a desiccator until needed and weighed immediately before use on an electronic balance to an accuracy of 0.01 mg before suspending inside the autoclave.

Table 1
The chemical composition of P110 and P110-3Cr steels (wt, %).

Element	C	Si	Mn	P	S	Cr	Mo	Ni	V	Ti
P110	0.26	0.25	1.29	0.010	0.006	0.012	≤0.010	0.014	≤0.010	0.018
P110-3Cr	0.19	0.28	0.48	0.008	0.003	3.01	0.403	0.027	0.021	0.017

The test samples were fixed in a specimen holder made of polytetrafluoroethylene (PTFE) to prevent galvanic effects, and 5 samples were placed in the autoclave for each test condition. Air in the autoclave was removed by introducing 3 times high pressure CO₂ gas (4MPa) before transferring the test solution. 2L prepared corrosion medium (saturated with CO₂) was introduced into the autoclave at ambient temperature and pressure via a booster pump. The starting point of the test was taken from the

time at which the autoclave reached the required temperature and pressure (200°C and 9 MPa CO₂ partial pressure in this study).

The entire matrix of the experimental conditions is provided in Table 2, the composition of the test solution is listed as follows (g/L): 13.000 NaCl, 2.589 CaCl₂, 0.014 KCl, 1.073 MgCl, and 0.527 NaHCO₃. The solution, which simulated oil field formation water, was prepared from analytical grade reagents and deionized water. They were deoxygenated before sequential transfer into the reactor by bubbling ultrapure CO₂ gas through them for 8 h.

Static immersion experiments were conducted in high temperature and high-pressure autoclave with a 6 L capacity and the schematic diagram of the experimental setup has been published in the previous paper [4]. There are two main corrosive systems within this study:

- The supercritical (SC) CO₂-saturated water system (water-rich phase) - samples completely exposed in water, and
- The water-saturated SC CO₂ system (SC CO₂ rich phase) - samples exposed in the SC CO₂ phase.

Table 2: Test matrix for corrosion experiments

Supercritical CO ₂ -saturated brine phase					
Temp (°C)	CO ₂ partial Pressure (MPa)	Total pressure (MPa)	Materials	H ₂ O	Immersion time (hours)
200	9	10.5	P110 P110-3Cr	2 L	168
Brine-saturated supercritical CO ₂ phase					
200	9	10.5	P110 P110-3Cr	200ml	168

After 168 h of immersion, the corroded specimens were extracted from the autoclave and immediately rinsed with absolute ethyl alcohol. The corrosion products were removed according to ASTM⁽¹⁾ G1-03 standard,^[5] then rinsed, dried, and reweighed to obtain the final weight of the specimen. The corrosion rate was calculated by the following equation.

$$R_{Corr} = \frac{8.76 \times 10^7 \times \Delta m}{S \times T \times \rho} \quad (1)$$

Where R_{Corr} is the general corrosion rate, mm/y; Δm is the weight loss, g; S is the exposed surface area, cm²; ρ is the density of the steel, g/cm³; and T is the immersion time, h.

Localized corrosion measurement

Profilometry measurements were performed on samples after the removal of the corrosion products by using Clarke's solution. The sample surface was scanned using a Confocal Laser Scanning Microscope. The pit depth analysis was conducted in alignment with ASTM Standard G46- 94.^[6] The standard stipulates that an average of the 10 deepest pits should be used for pit damage characterization of each sample area.

¹ ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959.

RESULTS

Figure 1 shows the general corrosion rate and the profilometry measurements (in the form of a localized corrosion rate) extracted from the P110 and 3Cr samples exposed to the SC CO₂-saturated water environment at 200°C and CO₂ partial pressure of 9 MPa. It is obvious that the general corrosion rate of P110-3Cr (0.33 mm/y) in water phase was nearly twice greater than that of P110 (0.15 mm/y). For both materials, the localized corrosion rates after 7 days of exposure are higher than the general corrosion rates.

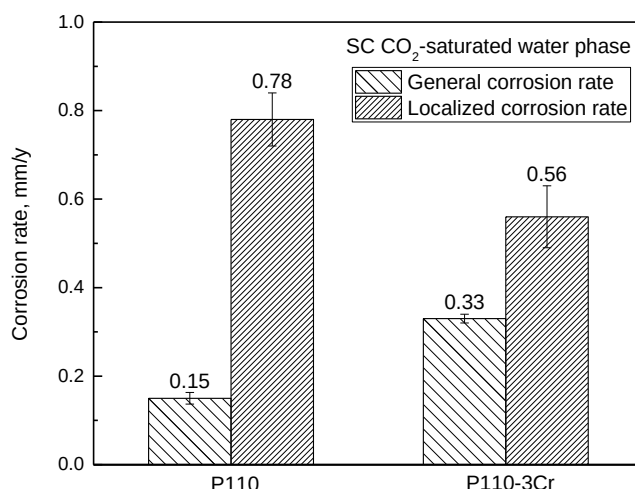


Figure 1: Corrosion rates of P110 and 3Cr in SC CO₂-saturated water phase.

In terms of the localized corrosion rates, Figure 2 shows examples of the 3D surface characteristics of P110 and P110-3Cr steel surfaces after removal of the corrosion product scales. The results confirm that the localized corrosion rates are significantly larger than the general corrosion rates in both conditions. It is interesting to note that P110-3Cr steel shows better-localized corrosion resistance than P110 steel when the samples are exposed to SC CO₂-saturated brine. The results show that the most severe localized attack was on P110. This produced a penetration rate of 0.78 mm/year compared to 0.56 mm/year for P110-3Cr steel.

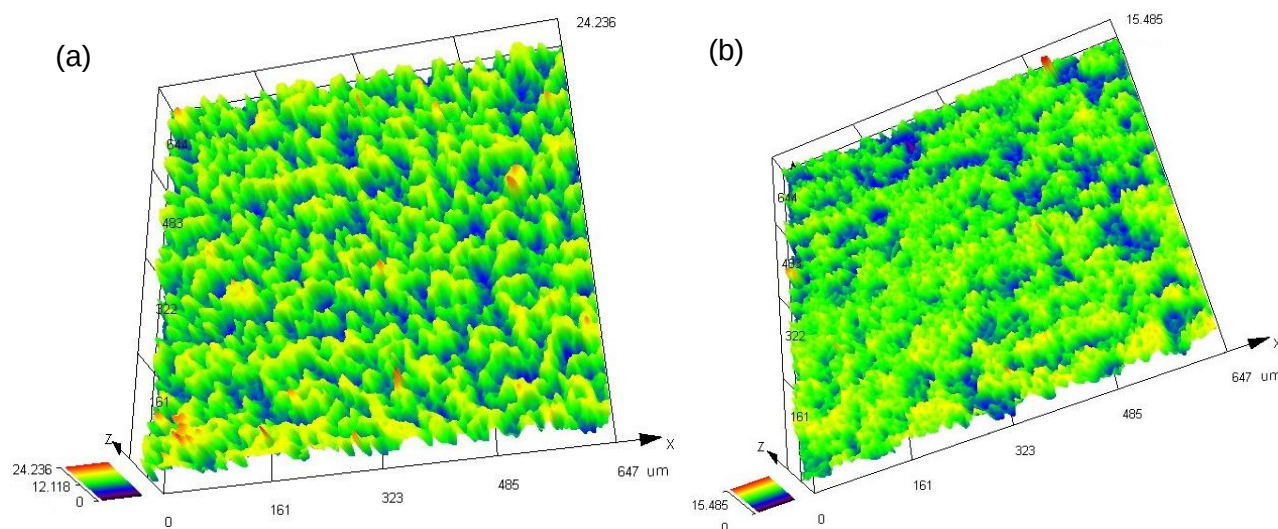


Figure 2: 2D profilometry images of (a) P110 and (b) P110-3Cr steels exposed to SC CO₂-saturated water phase.

Figure 3 shows the top-view SEM images for the surface morphologies of P110 and P110-3Cr steels after the samples were exposed to SC CO₂-saturated brine for 168 h. Figure 3 (a) shows that the cubic crystals did not cover the entire surface and some prominent gaps between crystals are observed on the P110 steel surface (Figure 3 (a)). The corrosion products are randomly distributed on the P110-3Cr steel surface, as shown in Figure 3 (b).

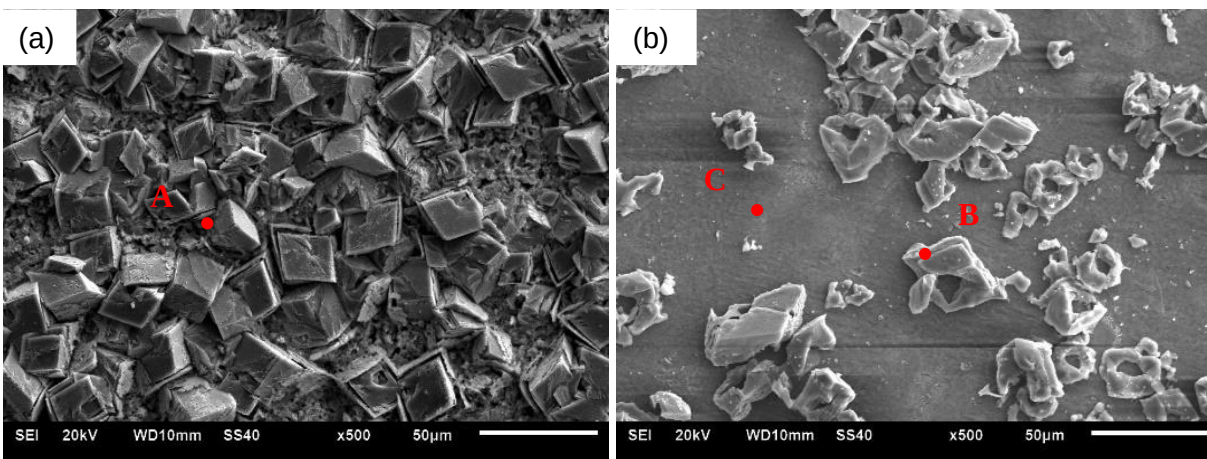


Figure 3: Surface morphologies of corrosion product scale on P110 (a) and 3Cr (b) exposed to SC CO₂-saturated water phase.

EDS analysis of the corrosion products was performed at different locations as marked in Figure 3 and the corresponding elemental contents are listed in Figure 4. The observed cubic crystals on the surface of P110 and P110-3Cr steels consist of Fe, Ca, Mg, C, and O elements as shown in Figure 4 (a) and Figure 4 (b). It is interesting to note that the outer cubic crystals are precipitated on the inner corrosion product layer, which consists a higher content of Cr element than the matrix which means an inner Cr-rich product layer formed on the surface of P110-3Cr steel (Figure 4(c)).

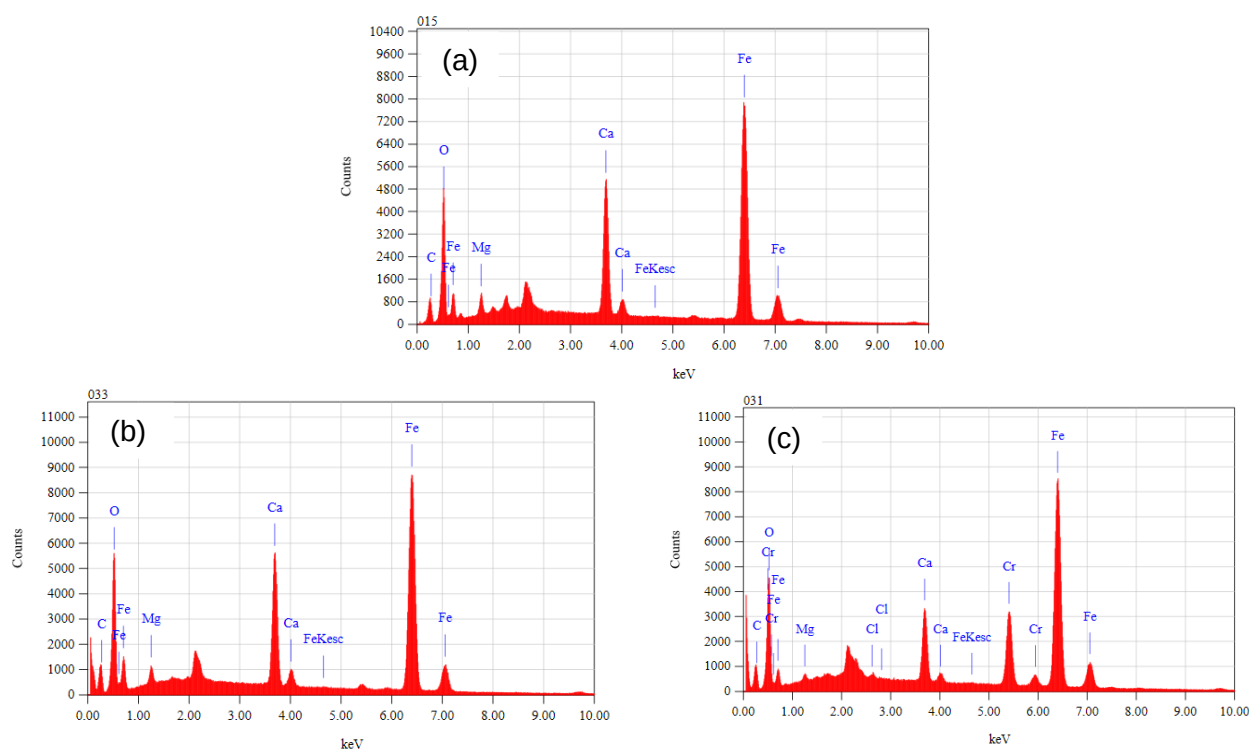


Figure 4: EDS of corrosion product on P110 and 3Cr exposed to SC CO₂-saturated water phase. (a) P110 region A; (b) P110-3Cr region B; (c) P110-3Cr region C in Figure 3.

Figure 5 presents the cross-sectional SEM images of corrosion product scales on P110 and P110-3Cr steels. The results show that the corrosion product layer formed on P110 steel surface after 168 h is 20 μm thick, which is around twice the thickness of that on P110-3Cr steel. Our previous work identified the inner layer formed on the P110-3Cr steel surface to be amorphous Cr(OH)₃,^[13]. However, the general corrosion rate was high, suggesting that the corrosion product layers formed on P110-3Cr indicate poor corrosion resistance compared to that of P110 steel under the test conditions here.