

Effect of Aggressive Substance on the Nature of Corrosion Scales Formation on Super 13Cr Stainless Steel in Formate Completion Fluid

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ABSTRACT

The nature of corrosion scales formed on super 13Cr stainless steel surface after exposure in formate completion fluid in the presence of various aggressive substances was investigated by a combination of surface characterization techniques such as SEM/EDS, XRD, Raman, etc. The results indicated that the corrosion products mainly comprised Fe_3O_4 for super 13Cr exposed to KCOOH at 180°C under N_2 environments. However, the addition of CO_2 progressively increased the general corrosion rate, suggesting that the calculated high corrosion rates were attributed to the presence of CO_2 in the system tested. The formation of FeCr_2O_4 and $\text{Cr}(\text{OH})_3$ were detected in the inner corrosion product layers and the precipitation of blade-shaped iron carbonate (FeCO_3) was detected in the outer layer on the super 13Cr stainless steel surface. The results suggested that the outer corrosion product layer showed less corrosion protectiveness compared to the formation of nano-polycrystalline FeCr_2O_4 and $\text{Cr}(\text{OH})_3$ inner layers, based on its less compact and observed gaps between crystals from the SEM images. The presence of Sulfur on the metallic surfaces in both N_2 and CO_2 environments caused the increase in material degradation.

Keywords: Potassium formate, super 13Cr stainless steel, high temperature, CO_2 , sulfide

INTRODUCTION

The material such as super 13%Cr martensite stainless steel (SS) has been successfully used as tubing material for dowhole conditions based on its good corrosion resistance, low cost and excellent mechanical properties behaviour. The corrosion issues of high density brine-base completion fluids on tubing and casing materials in ultra-deep high-temperature wells have been a research hotspot in the course of oil and gas exploitation [1]. The considered completion fluids for the oil and gas industry are

mainly the bromine salt completion fluids (KBr, ZnBr₂, and CaBr₂) [2], [3] and/or formate brines (NaCOOH, KCOOH and CsCOOH) [4]–[6]. In the past decades, one of the major issues is the localised corrosion by using bromine salts due to the presence of Br⁻ [7], [8]. It has become apparent that formate brines with filtrate viscosity and low water activities are more potential to be safe option for the deep wells (the average depth >6000 m) and also the operating temperature can be over 150 °C [6], [9]. Clarke states that the formate brines have many advantages during drilling and completion processes at temperatures up to 160°C, such as preventing the thermal degradation for the conventional drilling and completion fluid polymers [10].

Among formate brines, KCOOH solution has been widely used as completion fluid under high temperature gas well based on its large solubility and low corrosivity [4]. However, control of tubing material corrosion during completion period remains an obstinate issue for corrosion engineers due to the intrinsically complicated corrosion processes, especially in the presence of CO₂ under high temperature and high pressure environments. The CO₂ influx in annulus protection fluids will react with formate brines and form trace amounts of formic acid, which is less stable than the formate ion and acts as catalyst in reactivity of formate [6]. Along with the growing understanding of the influence of aggressive substance on the corrosive of formate brines [6], [11], there has been a growing demand for understanding the nature and evolution of the corrosion scales during this period as well as their protective capabilities to the surface.

This article complements the literature conducted in this area by systematically quantifying the level of the general corrosion measurements and studying the influence of N₂ or CO₂ on the corrosion product kinetics. The weight loss method is implemented to review the extent of uniform corrosion in both N₂ and CO₂ environments. The nature and morphology of the corrosion products are identified using a combination of scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and Raman spectroscopy in order to identify the role CO₂ plays on the corrosion product film composition and morphology. This paper mainly discussed the relationship between the corrosion products and the extent of general corrosion of super 13Cr SS at 180°C.

EXPERIMENTAL PROCEDURE

Material Samples

The test material used was an API⁽¹⁾-P110 grade super 13Cr (UNS⁽²⁾ S41425) stainless steel with heat-treated through normalization and tempering at 980°C and 590°C, respectively. The chemical composition (wt%) for the material is given in Table 1.

Table 1: Elemental composition of super 13Cr SS (wt.%)

C	Si	Mn	P	S	Cr	Mo	Ni	Fe
0.041	0.34	0.34	≤0.001	≤0.001	12.8	1.92	4.78	Balance

Coupon specimens for immersion tests were machined to dimension of 30 mm × 13 mm × 3 mm. Prior to each test, the specimens were ground to 1200 grit using silicon carbide paper, then rinsed with deionized water, acetone and dried.

Test solution

Test solutions to simulate the completion fluid from a gas field, were made from potassium formate (>97.1%) and deionized water. The chemical composition is shown in Table 2. The formate completion fluid usually uses CO purified from industrial tail gas as synthetic raw material, and its containing sulfide causes the existence of certain amount of K₂S in KCOOH. The solution was de-aerated by saturating the 1.5 g/ml solution with N₂/CO₂ in a separate container overnight prior to testing. All lines to the autoclave were purged with high pressure N₂/CO₂ and evacuated to ensure the O₂ content within the system was below 5 ppb. The prepared, de-aerated brine was carefully transferred from the sparging vessel into the closed autoclave containing the test specimens at ambient pressure and temperature using a shoe

⁽¹⁾ American Petroleum Institute (API), 1220 L St., N. W., Washington, DC 20005-4070.

⁽²⁾ Unified Numbering System for Metals and Alloys (UNS). UNS numbers are listed in Metals & Alloys in the Unified Numbering System, 10th ed. (Warrendale, PA: SAE International and West Conshohocken, PA: ASTM International, 2004).

suction pump. Then the autoclave was pressurized and stabilised at 10 bar N₂ or CO₂ at 25 °C, respectively. The solution was heated to the desired temperature, and the final pressure was 26 bar in N₂ condition and 34 bar in CO₂ condition.

Table 2. Chemical composition of the formation water

Composition	KCOOH	DI Water	K ₂ S
Content (g/100g)	54.60	45.36	0.04

Immersion tests

A 316L stainless steel static autoclave was utilized to conduct all the weight loss tests as schematically shown in Fig. 1. For mass loss experiments, three coupons were mounted on a designed PEEK holder, and fully immersed in the test solution. All tests were performed at 180°C with N₂ or CO₂ partial pressure of 10 bar at 25°C. And the volume to surface ratio was kept at approximately 30 ml/cm².

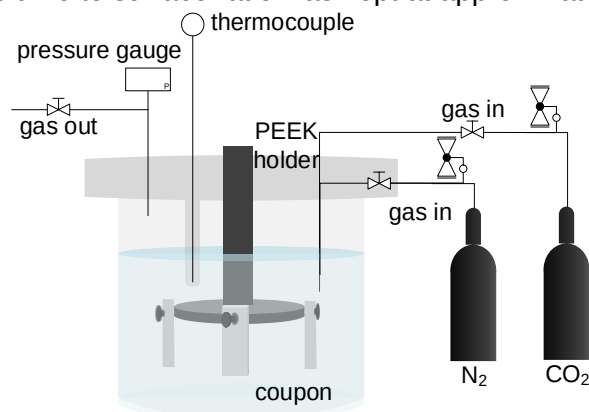


Figure 1: Schematic diagram of the high temperature and high pressure autoclave and the location of mass loss samples.

The original weight (m_0) of coupon was measured before the test, and final weight (m_1) was obtained after the removal of corrosion products (ASTM⁽¹⁾ G1-03 standard) [12]. The corrosion rate (C_R) was reported in mm/year according to the obtained weight loss via Eq. (1).

$$C_R = \frac{87600(m_0 - m_1)}{t\rho A} \quad (1)$$

Where t represents the immersion time, h; ρ is steel density, g/cm³; and A is exposed surface area in cm².

Surface analyses

The coupons after immersion tests were scanned via a Scanning Electron Microscope equipped with an Energy Dispersive X-ray detector (SEM/EDS). And X-ray Diffraction (XRD) and Raman spectroscopy were performed on the surface to determine the morphology and chemical composition of the crystalline and amorphous corrosion products formed on the surface.

RESULTS

Experiments in N₂-deoxygenated formate fluid in the presence of sulfide as impurity

Fig. 2 shows the general corrosion rates of super 13Cr SS exposed to the formate fluid at 180°C under N₂ environments for various immersion times. It can be seen that the corrosion rates were high (1.177

⁽¹⁾ American Society for Testing and Materials (ASTM), 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959.

mm/year) at the temperature of 180°C for the first 5 hours. For longer tests, the corrosion rate reduced and maintained at 0.063 mm/year after 120 hours.

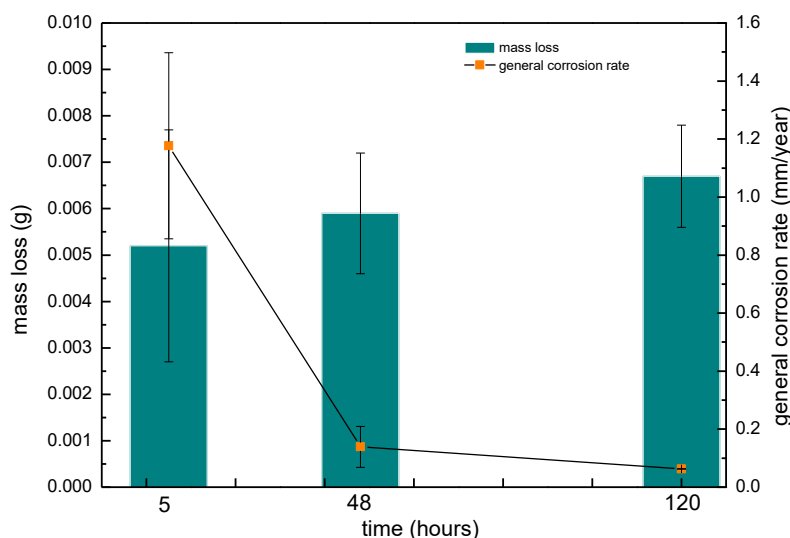


Figure 2: Total mass loss and corrosion rates of super 13Cr stainless steel in 180°C formate condition after 5, 48, and 120 hours.

Fig. 3 shows the macroscopic morphology of super 13Cr stainless steel exposed to 1.5 g/ml formate solution after various immersion times at 180°C. The specimens were shining in the first 5 hours and gradually covered by the corrosion products with the time prolonged. The SEM morphology of the corrosion product scales formed on the super 13Cr SS surface at various immersion times are given in Fig.4. After 5 hours exposure, the polishing marks were still visible on the surface as showed in Figure 4a. Only Fe, Cr and Ni signals were detected on the surface via EDS, which was identified as metal substrate. It is interesting to noting that the corrosion products with irregular shapes observed after 48 hours of exposure and increased in number after 120 hours. The EDS results in Fig. 4c indicate the scattered corrosion products are high concentration of sulphur compound.



Figure 3: Macroscopic morphology of super 13Cr stainless steel in 180°C formate condition (a) after 5 h, (b) after 48 h and (c) after 120 h immersion time.

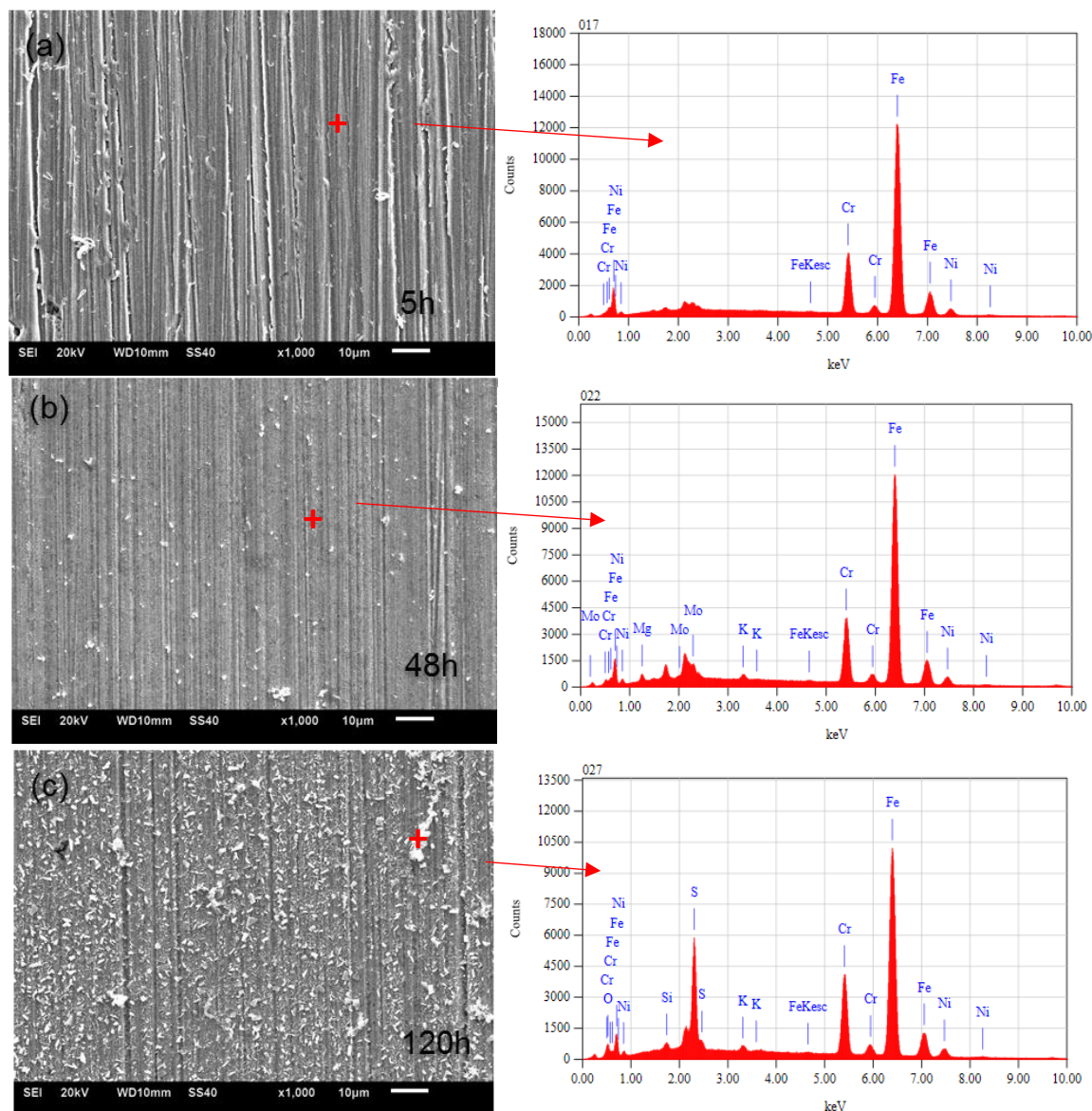


Figure 4: Top surface morphology (SEM, EDS) of the corrosion scale formed on super 13Cr stainless steel exposed to formate fluid after (a) 5h, (b) 48h and (c) 120 h at 180°C

Fig. 5 illustrates the XRD patterns of the corrosion product scales formed on the surface of super 13Cr SS at various immersion times. No crystalline corrosion products were detected after 5 hours of immersion time at 180°C. However, the peak of FeS (Mackinawite) was detected for the samples immersed in the solution after 48 hours, which is in agreement with the results observed through SEM/EDS. In order to identify the inner corrosion product layer, the Raman spectroscopy was used to supplement XRD measurements.