

Corrosion and Stress Corrosion Cracking Behavior of Super 13Cr Martensitic Stainless Steel in CO₂-saturated High Temperature and High Pressure (HTHP) Downhole Environment

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

Richard Barker
Institute of Functional Surfaces
School of Mechanical Engineering
University of Leeds
Leeds, LS2 9JT
United Kingdom

Jiong Qian
Jiuli Corrosion and Integrity Centre, Zhejiang
JIULI Hi-Tech Metals Co. Ltd
1899# Zhongxing Road
Hu Zhou, Zhejiang, 313028
China

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

Qiang Zhong
Jiuli Corrosion and Integrity Centre, Zhejiang
JIULI Hi-Tech Metals Co. Ltd
1899# Zhongxing Road
Hu Zhou, Zhejiang, 313028
China

Yong Hua
Jiuli Corrosion and Integrity Centre, Zhejiang
JIULI Hi-Tech Metals Co. Ltd
1899# Zhongxing Road
Hu Zhou, Zhejiang, 313028
China

Chun Wang
Institute of Functional Surfaces
School of Mechanical Engineering
University of Leeds
Leeds, LS2 9JT
United Kingdom

ABSTRACT

The service environments in deep/ultra-deep oilfields are particularly corrosive due to the high temperatures, chloride contents and CO₂ partial pressures, which pose significant challenges to the integrity of tubing materials. In this research, we investigate the corrosion and stress corrosion cracking behavior of Super 13Cr martensitic stainless steel (S13Cr MSS) exposed to formation brine at 200°C with a 5.2 MPa CO₂ partial pressure through immersion tests and slow strain rate (SSR) tests. The corrosion products composed of amorphous Cr(OH)₃ and Cr₂O₃ were identified, which acted as a barrier

© 2022 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP. Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

to slow down the corrosion process at the material interface. The general corrosion rate of S13Cr MSS in a simulated downhole environment was 1.70 mm/y in the first 5 hours then decreased to 1.37 mm/y after 20 hours immersion and the general corrosion rate of 1.04 mm/year was recorded over 7 days exposure. Meanwhile, the pitting rate was high (2.27 mm/year) and the corresponding pit depth was 1.30 μm after 5 hours of exposure. After 7 days, the pitting rate was reduced to 0.37 mm/y. The results of SSR tests indicate that the fractures of S13Cr MSS initiated from the pits and were characteristic of ductile behavior at 200°C. Moreover, the stress corrosion cracking susceptibility of S13Cr MSS increased for the pre-corroded sample, suggesting that the increase in the level of stress concentration is due to the decrease in radius to depth ratio of pits during the corrosion progress.

Key words: Super 13Cr martensitic stainless steel; CO₂ corrosion; SCC; high temperature and high pressure; SSR tests

INTRODUCTION

Corrosion is one of the major issues in oil and gas production, as well as geothermal energy due to the aggressive environments, such as high temperatures and pressures.^{1, 2} Material selection for downhole tubing is therefore paramount importance to ensure well integrity. Thus, the selected materials must be corrosion resistant, cost-effective, reliable, and have the required strength for such arduous conditions.

A number of modified 13Cr MSS such as 13Cr-2Ni-0.5Mo, 13Cr-4Ni-1Mo, 13Cr-5Ni-2Mo etc. has been proposed to improve the corrosion resistance and mechanical properties of UNS S42000.³ One alloy, known as super 13Cr martensitic stainless (S13Cr MSS, UNS S41426) containing approximately 5% Ni and 2% Mo has shown its great corrosion resistance compared to conventional 13Cr MSS under arduous environments with cost-effective performance.^{4, 5} It was reported that in a simplified formation brine (containing 29503 mg/L Cl⁻), S13Cr MSS maintained a passive state at 90°C and 0.13 MPa CO₂ partial pressure, while an active state existed at 200°C with 0.27 MPa CO₂ partial pressure.⁶ Further research in this simplified formation brine at 200°C revealed that flow rate can promote the general corrosion but reduce the localized corrosion risk through the formation of the uniform corrosion scales under various CO₂ partial pressure.⁷ The current studies in HTHP CO₂-containing environments were mainly focused on the formation and evolution of the corrosion scales and corrosion behaviors of S13Cr MSS.^{7, 8} However, the fracture behavior of S13Cr MSS in high-temperature CO₂ containing downhole environments need to be further clarified. Therefore, in this research, we investigate S13Cr MSS exposed to the simulated downhole environments from the Traim field in China, the materials exposed to high temperature, high CO₂ partial pressure and high salinity conditions. A combination of immersion test, slow strain rate (SSR) tensile test and surface analysis CO₂-containing to systematically investigate the corrosion and fracture behaviors.

EXPERIMENTAL PROCEDURE

Material

The material used in this work was cut from an API-P110 grade S13Cr MSS industrial tubing (72 J of Charpy absorbed energy) that was hot rolled, homogenized at 1020°C for 30min followed by quenching, then tempered at 620°C for 60 min followed by air cooling, the chemical compositions of S13Cr MSS are provided in Table 1. The chemical compositions were consistent with that specified for UNS S41426.

Table 1
The chemical composition of S13Cr MSS (wt%)

Element	C	Cr	Ni	Mo	Mn	Si	S	P	Fe
S13Cr	0.01	12.6	5.1	1.6	0.4	0.3	0.002	0.01	Bal.

Immersion Test

The immersion tests were carried out in a high-temperature-high-pressure autoclave system, and the schematic is shown in Figure 1. Samples with a dimension of 30 mm × 13 mm × 3 mm (1.18 in × 0.51 in × 0.12 in) were fixed to a polytetrafluoroethylene (PTFE) holder. The sample surface was ground to a 1200 grit finish using silicon carbide paper, then rinsed with acetone, ethanol, and deionized water, respectively, followed by cold-air drying. Samples were then stored in a desiccator until needed and weighed on an electronic balance to an accuracy of 0.01 mg before suspending inside the autoclave.

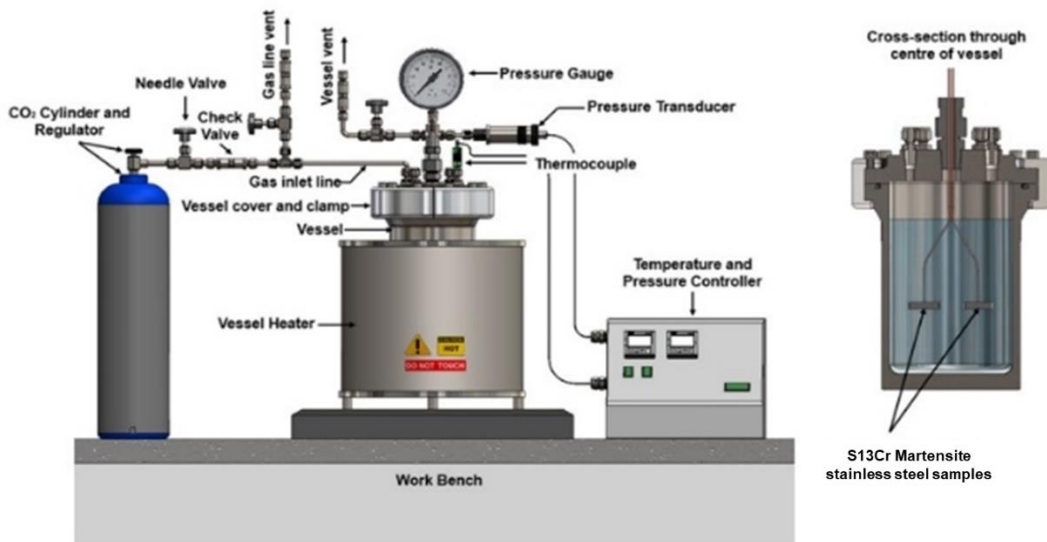


Figure 1: A schematic diagram of the experimental setup for the immersion tests.

The immersion tests were carried out according to the test matrix as shown in Table 2, the ratio of the exposure area of samples to solution volume was 33 mL/cm². The operating procedures (solution preparation and deoxygenation, deoxygenation of autoclave and pipeline, solution transfer) can be found in our previous publication.⁹ The formation brine was made by the analytical grade reagents and deionized water, the composition of formation brine is provided in Table 3. The starting point of the test was taken from the time at which the autoclave reached the required temperature.

Table 2
Test matrix for immersion tests

Temperature (°C)	CO ₂ partial Pressure at 200°C (MPa)	Calculated pH	Immersion time (hours)
200	5.2	5.15	5
			20
			48
			168

Table 3
The chemical composition of formation brine

Composition	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	SO ₄ ²⁻	Cl ⁻	HCO ₃ ⁻
Content (mg/L)	68850	5960	505	7479	387	115200	170

After immersion tests, the corroded specimens were extracted from the autoclave and immediately rinsed with ethyl alcohol and deionized water. The corrosion products were removed according to ASTM⁽¹⁾ G1-03 standard¹⁰ using Clarke's solution, then rinsed, dried, and reweighed to obtain the final weight of the specimen. The corrosion rate was calculated by the following equation.

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

Where $R_{G_{corr}}$ 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.

Slow Strain Rate Test

Tensile specimens were cut parallel to the rolling direction from the industrial tubing, samples are 3.81 ± 0.05 mm (0.150 ± 0.002 in) in diameter and 25.4 mm (1.00 in) in length according to NACE⁽²⁾ TM0198-2018 standard¹¹. Prior to the test, all the surfaces were ground with grit SiC paper to a 1200 grit finish sequentially and the final grinding was performed perpendicular to the tensile axis of the specimen. Samples were then cleaned with alcohol, and dried in cold air.

The specimen was wrapped with PTFE tape on the thread to ensure the insulation between the specimen and the holder. The solution preparation and transfer, deoxygenation operation of the solution and the test system, CO₂ injection, and heating steps were consistent with immersion tests. Then the tests were carried out according to the test matrix as shown in Table 4.

Table 4
Test matrix for the SSR tests.

Temperature (°C)	Gas	Solution	Strain rate (s ⁻¹)	Exposure time in SSR test environments (without load) before tensile (hours)
200	N ₂	/	4*10 ⁻⁶	0
				168
	5.2 MPa CO ₂	Formation brine		0
				168

The plastic strain to failure ratio (E_pR) and reduction in area ratio (RAR) were used to determine the index of relative susceptibilities to the SCC of the specimens in different test conditions. E_pR and RAR can be expressed as follows:

$$E_pR (\%) = \left(\frac{E_{pE}}{E_{pA}} \right) \times 100 \quad (2)$$

$$RAR (\%) = \left(\frac{RA_E}{RA_A} \right) \times 100 \quad (3)$$

Where E_{pE} and RA_E are the plastic strain to failure and reduction in area in different test conditions; E_{pA} and RA_A are the plastic strain to failure and reduction in area in N₂ without pre-heating for 7 days.

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

² NACE International, 15835 Park Ten Place, Houston, Texas 77084-5145.

© 2022 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.

Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

Surface Analysis

Scanning electron microscopy (SEM) was carried out on samples using a Carl Zeiss EVO MA15 SEM[†] to assess the morphology of the fracture and corrosion product film of S13Cr MSS. The X-ray diffraction (XRD) analysis was carried out to analyse the composition of the corrosion product using a Bruker D8 multipurpose diffractometer[†]. A combination of Raman spectroscopy (488 nm radiation) was used to further identify the nature of the corrosion products at specific positions on the surface.

Profilometry measurements were performed on samples after the removal of the corrosion products. The sample surface was scanned using an NPFLEX 3D Surface Metrology System[†]. The pit size analysis was conducted using Vision64 software[†], the 10 deepest pits were used for pit damage characterization of each scanned area. The pitting rate was calculated by the following equation.

$$R_{\text{Pitting}} = \frac{D \times 8.76}{T} \quad (4)$$

Where R_{Pitting} is the pitting rate, mm/y; D is pit depth, μm ; and T is the immersion time, h.

Finite Element Analysis

Finite element (FE) analysis was carried out by using ANSYS V19.2[†]. A bar with 3.81 mm (0.150 in) in diameter and 25.4 mm (1.00 in) in length was modelled to simulate the tensile specimen. Pits with a half-ellipse section were created at the middle of the sample surface, the size of pits was set according to the measured radius to depth ratio (R/D ratio) and depth of the pit. Tensile stress (90% yield strength of API-P110 grade S13Cr MSS) was applied at both ends of the bar to obtain the distribution of stress within the pit.

RESULTS

Corrosion Behavior of S13Cr MSS in Formation Brine at 200°C

Figure 2 shows the general and pitting rates of S13Cr MSS at different immersion times in the formation brine at 200°C. It can be seen from Figure 2(a) that the general corrosion rates were recorded as 1.70 mm/year and 1.37 mm/year after 5 hours and 20 hours respectively, then dropped to a rate of 1.04 mm/year over 7 days of exposure. The slight reduction in corrosion rates can be contributed to the formation of the corrosion scales on the surface, suggesting that the corrosion scales can inhibit the mass transfer during the corrosion process and thereby slow the corrosion rate. As illustrated in Figure 2(b), the pit depth continually increased with increasing immersion time, however, the growth rate of the pit slowed down with immersion time, which corresponds to a decrease in pitting rate from 2.27 mm/y after 5 hours to 0.37 mm/y after 168 hours.

[†] Trade name

© 2022 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.

Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).