

Environmentally-assisted cracking (SSC and SCC) of martensitic stainless steel OCTG material in sour environment in 5%NaCl and 20%NaCl solution.

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ABSTRACT

This paper mainly deals with the environmentally-assisted cracking (EAC) behavior of martensite-based stainless steel OCTG materials of (1) Modified-13CR-110 grade (13Cr-5Ni-2Mo), (2) 15CR-125 grade (15Cr-6Ni-3Mo-Cu: UNS S42625) and (3) 17CR-110 grade (17Cr-4.5Ni-3Mo-Cu-W: UNS S42825) in 5 mass% and 20 mass% NaCl solutions with 0.01 MPa H₂S - 5 MPa CO₂ at temperatures from 24 °C to 200 °C (75 °F to 392 °F) and pH from 3.0 to 4.0 by Four Point Bent Beam (FPBB) tests. Also, the corrosion rate was evaluated by the weight loss method. The experimental results demonstrated that the tested martensite-based stainless steels did not show a cracking-susceptible temperature region at around 80 °C to 100 °C (175 °F to 210 °F), unlike duplex stainless steels. In addition, the results revealed that the applicable conditions of the martensite-based stainless steels are limited by EAC in the lower temperature region and by the corrosion rate at higher temperatures. In order to judge whether EAC is based on a SCC-typical anodic reaction or SSC-typical a hydrogen-embrittlement caused by cathodic reaction, the fracture surfaces of the post-testing specimens were investigated by using Modified-13CR-110 under sour conditions of 20 mass% NaCl solution at 24 °C and 50 °C (75 °F and 122 °F). The fracture surface is brittle with intergranular cracking and quasi-cleavage. It indicates the crack is caused by SSC (hydrogen embrittlement), because quasi-cleavage can be observed only in SSC but not in SCC. At least, at tested corrosion environment, it can be concluded that the domain map in EAC for martensite-based stainless steel is limited by both SSC at low temperature and corrosion rate at high temperature.

Key words: environmentally-assisted cracking, EAC, sulfide stress cracking, SSC, stress corrosion cracking, SCC, martensitic stainless steel, OCTG, 13%Cr, 15%Cr, 17%Cr, duplex stainless steel

INTRODUCTION

Martensitic stainless steels for OCTG materials are widely used in sweet and mild sour conditions. Environmentally-assisted cracking (EAC) is a major corrosion-related issue when using stainless steels as OCTG materials. The EAC in specific oil/gas well conditions with sour environments is defined as sulfide stress cracking (SSC) and stress corrosion cracking (SCC). The SSC is a type of cracking caused by hydrogen embrittlement, which is attributed to a cathodic reaction under acidic conditions, while SCC is associated with an anodic reaction. SSC testing for martensitic stainless steels for OCTG material is often carried out at or near ambient temperature under conditions simulating condensed water, and SCC tests are conducted at higher temperatures under conditions simulating formation water and/or the brine availability test.

Duplex stainless steel is another choice of higher alloys for OCTG application. The previous paper by Ishiguro et al.¹ reviews several papers concerning the crack susceptibility of duplex stainless steels and summarizes the results as follows.

- (1) As for duplex stainless steel, the main concern is SCC including pitting at higher temperatures and the secondary concern is SSC at lower temperatures (near ambient temperatures).
- (2) As a major way of thinking, SCC in a specific temperature range of around 80 °C to 100 °C (175 °F to 210 °F) is still regarded as a concern for duplex stainless steel, even though some limited papers report that their duplex steel samples do not exhibit cracking under their experimental conditions.
- (3) The cracking phenomenon at around 80 °C to 100 °C (175 °F to 210 °F) is often treated as SCC, except in limited papers. Many papers do not show any detailed information to judge whether the cracking is SCC (anodic-dissolution-involving), and use the technical term of SCC to describe such cracking phenomena as though the cause is self-evident. It is often difficult to judge whether cracking is based on SCC caused by an anodic reaction or SSC which is attributed to cathodic reaction.

As mentioned above, duplex stainless steel is often susceptible to SCC at 80 °C to 100 °C (175 °F to 210 °F). This gives rise to a concern as to whether martensite-based stainless steels also have the same tendency or not. In a previous paper¹, we have investigated the EAC resistance of martensite-based stainless steels such as Modified-13CR-110 grade, 15CR-125 grade and 17CR-110 grade by the Four-Point Bent Beam (FPBB) test in 20 mass% NaCl solutions. The conclusion of the report was that the martensite-based stainless steels did not exhibit a cracking-susceptible temperature region at around 80 °C to 100 °C (175 °F to 210 °F), thereby answering the concern stated above. However, the classification of the cracking behavior is based on cross-sectional observation. The way of judgment is that cracking of “near straight” line is due to SSC, and that of “lightning pattern with a lot of branches (wormhole-like)” is attributed to SCC. The way empirically makes sense, but differentiation of them is sometimes difficult or it still remains ambiguous.

The main body of this paper is the fractographic investigation of post-testing specimen to make clear whether cracking is caused by cathodic HE-based SSC or anodic corrosion-based SCC. In addition, EAC domain maps in 20 mass% NaCl conditions are upgraded by using newly-added data at some pH-temperature conditions in order to define the applicable limit of each material clearly and to reconfirm the conclusion in the previous report. Also, EAC resistance data in 5 mass% NaCl are newly introduced in this paper.

EXPERIMENTAL PROCEDURE

Table 1 shows the information concerning the materials used in this paper. Modified-13CR is a martensitic stainless steel with small amount of retained austenite and is categorized as 13-5-2 in ISO⁽¹⁾ 13680².

⁽¹⁾ The International Organization for Standardization, Chemin de Blandonnet 8 CP 401-1214 Vernier, Geneva, Switzerland.

15CR is also a martensitic stainless steel with some amount of retained austenite and has the UNS⁽²⁾ S42625. 17CR has a martensite phase of around 60 to 70 % as the main phase, a ferrite phase of around 20 and 30 % as a secondary phase and an austenite content of around less than 10%, and is registered as UNS S42825. In this paper, “martensite-based materials” refers to these three materials.

Table 1: Information of materials used in this paper

Martensite-based stainless steel sample				Chemistry (mass%)						Yield Strength at room temp
Name in this paper	UNS No.	Cr-Ni-Mo	YS grade	C	Cr	Ni	Mo	N	Others	
Modified-13CR-110	-	13-5-2	110ksi	0.03	13	5	2	0.06	-	124ksi (858MPa)
15CR-125	S42625	15-6-3	125ksi	0.03	15	6	2	0.05	Cu	142ksi (976MPa)
17CR-110	S42825	17-4.5-3	110ksi	0.03	17	4.5	3	0.05	Cu, W	126ksi (872MPa)

The base materials were seamless tubes manufactured in the mill. The sizes of the tubes are OD188.0 mm x WT25.4 mm (7.40 inches x 1 inch) for Modified-13CR, OD188.6 x WT18.3 mm (7.43 inches x 0.72 inches) for 15CR-125 and OD198.8mm x WT24.3 mm (7.83 inches x 0.96 inches) for 17CR-110. Specimens for FPBB testing were machined from the center part of wall thickness of tubes. FPBB specimens are 110 mm-long x 15 mm-wide x 5 mm-thick (4.3 in-long x 0.59 in-wide x 0.20 in-thick). The surface was polished to Ra of less than 0.25 μm as per NACE-TM0316³, which can be reached by SiC paper of #800 in JIS⁽³⁾, which roughly corresponds to polishing with #400 to #500 in ANSI⁽⁴⁾ and P1000 in FEPA⁽⁵⁾.

Table 2 shows the details of the test conditions. All tests were carried out in an autoclave in accordance with NACE-TM0316³. A load of 100 % actual yield stress at the testing temperature was applied to each FPBB specimen by adding strain using a strain gauge attached on the middle position on the tensile side of the specimen. The test conditions in the autoclave were as follows: (1) The NaCl solution with acetic acid and sodium acetate was prepared in an ambient environment to achieve an intended pH at testing temperature and pressure. (2) In the ambient condition, the solution was blended and then saturated with pre-mixed gas. (3) The detailed condition in the ambient environment was calculated by an OLI Studio Stream Analyzer[†]. (4) After the solution was prepared in the ambient condition, the temperature was elevated to the test condition, and CO₂ gas was added to achieve the testing condition.

In this study, FPBB testing was performed in the Solution-A-modified 20 mass% NaCl-0.5 mass% CH₃COOH with a CH₃COONa buffer solution, and not in the Solution-C specified in NACE-TM0177⁴, because, according to Y. Ishiguro's papers^{5,6}, the Solution-A-modified buffer solution has a stronger pH buffer capacity than Solution-C, and the Solution-C has a much weaker pH buffer capacity than the estimated buffer stability in real oil/gas wells. The ratio of the test solution to the surface area was around 10 mL/cm², and the test duration was 336 h (14 d).

After a 336 h autoclave test, the post-testing samples were evaluated to clarify the “pass” and “fail” regions in domain maps. The post-testing specimens were pickled with a nitric acid-based solution (conc.HNO₃ : water = 1 : 10 in volume ratio) at 50 °C to 70 °C (122 °F to 158 °F) in order to remove

⁽²⁾ Unified Numbering System for Metals and Alloys (UNS).

⁽³⁾ Japan Industrial Standard (JIS), 3-13-12 Mita, Minato-ku, Tokyo 108-0073, JAPAN.

⁽⁴⁾ American National Standards Institute (ANSI), 1899 L Street, NW, Washington, DC 20036, USA.

⁽⁵⁾ Fédération Européenne des Fabricants de Produits Abrasifs (FEPA), 20 avenue Reille, 75014 Paris, France.

[†]Trade name.

corrosion products. In order to determine whether the specimens are “crack-free”, “pit-free” or not, the surface on the tensile side of the specimens after pickling was examined at 10X magnification to detect cracks, and if a crack was detected, the test result was regarded as “fail.” If a crack was not found by 10X examination, the longitudinal cross-section of the specimen was investigated at 200X magnification. If a crack was found, the test result was judged as “fail”. As will be mentioned in detail far below in Fig. 3, a few specimens judged as “no-cracking” had pits as shallow as 6 to 6.5 μm , but any cracks were not observed at the bottom of pits. Therefore, the test results are determined by either no-cracking (pass) or cracking (fail).

In addition to the evaluation of cracking and pitting, corrosion phenomena was also analyzed in terms of corrosion rate (general corrosion), because the corrosion rate is also a factor that limits the applicable region of stainless steels. The corrosion rate is calculated by the weight loss method. If the corrosion rate exceeds the criterion of 5 mpy (0.127 mm/year)⁷, the test result is regarded as “fail” in terms of the corrosion rate.

Table 2: Test conditions in autoclave test by using FPBB specimens

Test parameter		Condition
Solution	NaCl	5 and 20 mass%
	CH ₃ COOH	0.5 mass%
	CH ₃ COONa	(pH adjuster)
Gas	partial pressure of CO ₂	5 MPa (725 psi)
	partial pressure of H ₂ S	0.01 MPa (1.45 psi)
pH		3.0, 3.25, 3.5 and 4.0
Temperature		24°C (75°F) to 200°C (392°F)
Test solution to surface area ratio		around 10 ml/cm ²
Test duration		336 hours (14 days)
Applied Stress		100%AYS at testing temperature

In addition, as for the cracked samples, both a longitudinal cross-section and a fracture surface for the same crack in a cracked specimen were analyzed to investigate whether cracking was caused by cathodic HE-based SSC or anodic Fe-dissolution-based SCC. Table 3 shows possible fracture category for cracking in SSC and SCC. Generally, intergranular surface can be observed in both SSC and SCC. However, quasi-cleavage is observed only in SSC (hydrogen embrittlement)⁸. Therefore, when quasi-cleavage is observed, the crack is caused by SSC (hydrogen embrittlement). In terms of cross-sectional micrograph, “near straight”-like crack propagates in SSC, and “lightning pattern with a lot of branches (wormhole)”-like one appears in SCC. Figure 1 shows an explanation of the sample preparation for fractograph analysis and cross-sectional micrograph. First, the sample was cut in the length direction, and a half sample was used for observation of the longitudinal cross-section. The sample was embedded in resin, and the cross-section was polished and then observed with an optical microscope. The other half sample was used for observation of the fracture surface. This sample was immersed in liquid nitrogen then broken mechanically to expose a fracture surface. The fracture surface was observed with a scanning electron microscope.