

From pits to cracks: A review of 45-years of published research on surface trenches in low alloy steels exposed to H₂S-containing environments

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ABSTRACT

Surface trenches are described as elongated pits or blunt cracks with a large depth (d) to width (a) ratio that occur as the result of an environmentally and stress-assisted damage. Trenches may represent a transition from pits to cracks in stressed carbon and low alloy steels specimens when exposed to H₂S-containing solutions under certain experimental conditions. In the literature, surface trenches are also known as deep or sharp pits, small blunt cracks, stress-induced microgrooves, fissures, cracklets, or microcracks. Since these features were first presented in 1977 by Dunlop, many authors have typically reported their depth while others have included the shape aspect ratio (d/a) for a more consistent characterization. In 2000, Pargeter published a flowchart to distinguish pits from cracks based on the microscopy analysis of the cross-sections of tested samples. In the absence of detrimental phases such as hard microstructures, and for indications with a depth higher than 250 µm, Pargeter classified cracks as features that presented sharp tips and parallel sides. However, indications with depths below the 250 µm limit reported in the literature remain unclassified according to Pargeter's guidelines. In recent years, efforts have been made to clarify the limits between trenches with respect to pits and cracks. Nonetheless, there is still a lack of precise guidelines to characterize the appearance of surface trenches and what is more relevant, conducting only a dimensional analysis of these features could be insufficient to evaluate their influence in crack initiation. Additionally, the variables that control trench formation, such as the threshold stress for trench initiation, are not clearly defined or controlled in tests. This review compiles previous findings and explores the effect of the factors that control trench nucleation and growth, including chemical composition, thermomechanical history, microstructure, and mechanical properties of steels, surface preparation, chemical composition of the environment (e.g., H₂S concentration, pH, the presence of organic acids, and level of chlorides), temperature, electrochemical potential, time of exposure, and applied loads.

Key words: low alloy steel, H₂S, trenches, stress-induced grooves, elongated pits, cracks, sulfide stress cracking, NACE TM0177, sour service, environmental assisted cracking

INTRODUCTION

Carbon and low alloy steels (CS and LAS, respectively) used for exploration and production in the oil and gas (O&G) industry are normally exposed to environments that may contain H₂S in a wide range of concentrations. In aqueous solutions, H₂S acts as a cathodic poison.^{1,2} A cathodic poison inhibits the recombination of atomic hydrogen to H₂, and as a result, favors its absorption by the metal.^{1,2} In the presence of a susceptible microstructure and the simultaneous effect of applied or residual tensile stress, a crack can nucleate and propagate, when a critical concentration of hydrogen is reached in the metal.³ This environmentally assisted cracking (EAC) phenomenon is known as Sulfide Stress Cracking (SSC).² SSC is commonly addressed as a case of hydrogen embrittlement (HE) damage.² However, under certain experimental conditions, intermediate morphologies between pits and cracks, have been observed for CS and LAS in H₂S-containing environments, which grow by an anodically assisted and stress-level dependent mechanism.^{4–13,14–19} These features are described as elongated pits or small blunt cracks with a large depth (d) to width (a) ratio, that are perpendicular to the principal direction of the applied load, and in some cases can present ramifications.^{6,7,13} They have received different denominations across the literature: surface trenches^{7,13,19}, deep or sharp pits^{11,12,15}, small blunt cracks⁶, stress-induced microgrooves¹⁸, fissures^{9,10,14}, cracklets¹⁶ or microcracks⁸. Considering the characteristics mentioned above, “surface trenches” is a suitable term to avoid confusions between other morphologies, such as purely pits or cracks. In this review, proposed mechanisms and main factors that influence trench formation will be analyzed.

Materials selection processes for assets expected to last decades usually rely on short term tests (typically not longer than 30 days).²⁰ Except for fracture mechanics tests where a pre-existing crack is already present in the specimens to assess the material's crack propagation resistance, at a given stress level and testing solution composition, the outcome of a short term test is cracking (fail) or no-cracking (pass). For these cases surface trenching represents a grey zone between pits and cracks, and different approaches were proposed to evaluate if they constitute or not an incipient crack. If a trench evolves to a crack in service, the integrity of assets, people and the environment may be threatened. The aim of this review is to expose the complexity of this issue due to the interrelation between variables, and to foster the determination of clear criteria for surface damage classification required to ensure materials' integrity.

SURFACE TRENCHES

The presence of surface trenches was first reported by Dunlop after three point bending tests (TPBT) of Ni bearing LAS samples at H₂S partial pressures (pH₂S) between 0.015 and 0.045 psi in acidic solutions.^{6,21} In his pioneer work, Dunlop argued that the sulfide stress cracks of low and medium strength steels could be initiated by an anodic localized attack.⁶ Dunlop suggested that due to sidewall corrosion, those initiated cracks evidenced the tendency to blunt, which retarded its propagation rate.⁶ Many authors reported similar corrosion patterns for propagating and non-propagating secondary cracks of steels with varying strength levels and microstructures, and also after different testing methods. In all cases, cathodic polarization seemed to suppress the formation of trenches.^{6,7,18,19} Although some authors have proposed a co-operative mechanism between an initial anodically-driven stage due to Active Path Corrosion (APC) and a HE-assisted crack propagation process for SSC when trenches and cracks are present,^{5–8} trench to crack transition is still not fully understood. A brief discussion of the proposed mechanism is included in the following section.

Proposed mechanism for trench-to-crack transition

Yamane *et al.* proposed a mechanism based on an initial APC stage, responsible for transgranular trench initiation and growth, followed by an intergranular crack propagating from its bottom controlled by HE.⁸ At open circuit potential (OCP) APC and HE can compete. APC seems to govern at lower H₂S

concentrations, since it is responsible for trench formation which occur by local dissolution of the metal.^{6,7} Scanning electron microscopy (SEM) observation of C-110 steel after interrupted constant load tests under 90%SMYS (specified minimum yield strength) during 2, 7, 15, and 30 days have demonstrated that the sidewalls of a trench are consistent with an anodic dissolution pattern where no cleavage or intergranular attack features were found.¹⁸

While APC also presents transgranular branched crack/s that initiate at the bottom of the trench⁷ (coarse forking, Figure 1), for high strength steels HE can generally result in an intergranular crack that nucleates from the trench's bottom.⁸ It is generally accepted that if the cracking process is controlled by APC, an increase in anodic potential increases crack propagation rate. However, the reverse is not necessarily true, because an increase in anodic potential could favor localized corrosion, with a concomitant increase in hydrogen production rate due to metallic cation hydrolysis at the bottom of the trenches, as suggested by Wilde and Doyle.²² Indeed, Yoshino verified that a slight increase in the hydrogen permeation current was obtained for anodically polarized specimens vs. specimens tested at OCP.^{7,8} An increase in the hydrogen flux could result as a promotion of local hydrogen entry into the steel at the bottom of a pit/trench, since the solution there can experiment acidification and higher corrosion rates.⁷ On the bulk of the exposed surface, the effect of iron sulfides, as well as of other corrosion products containing nickel and chromium can hinder hydrogen absorption into the steel.^{14,23} On the other hand, with an increase in anodic potential trench-to-crack transition can be retarded, or even inhibited, due to crack tip blunting of CS and LAS with high anodic reaction rates.^{19,24} Summing up, the cracking mechanism cannot be solely determined from crack propagation rate dependence with electrochemical potential.

Using stress level, defect depth and fracture toughness as inputs, fracture mechanics can predict if a crack propagates or not from the tip of the defect. In a recent blog article, Iannuzzi calculated the depth of the critical defect (d_{crit}) that would result in brittle SSC crack propagation for an acceptable LAS operating under Region 3 of the pH₂S-pH diagram. Using Equation 1, based on linear elastic fracture mechanics considerations, a value of 675 μm was obtained for a quench and tempered (Q&T) LAS with a yield strength (YS) of 760 MPa and an acceptable conservative value of the Stress Corrosion Cracking (SCC) Critical Stress Intensity Factor (K_{ISSC}) of 35 MPa.m^{1/2}, under an applied stress (σ_{app}) equivalent to 100%YS.²⁵

$$d_{crit} = \left(\frac{K_{ISSC}}{\sigma_{app}} \right)^2 \frac{1000}{\pi} \quad \text{(Equation 1)}$$

The critical defect depth for pit-to-crack transition increases with SSC fracture toughness, which in turn increases by improving the microstructure of the steels or by decreasing the YS. In the latter case, lower values of d_{crit} would be expected for high strength steels. As suggested by Colwell, trenches can act as precursors to cracks in components tested in environments containing H₂S at low partial pressures.¹⁰ Experimentally, for steels with YS between 600 MPa and 1083 MPa it has been observed that for a stress level between 90% and 100%YS, the density of surface trenching is higher in less aggressive conditions, while in more severe environments the density of surface trenches decreases. Additionally, for those steels where a relatively low density of surface trenches was observed, crack initiation normally occurred at their bottom.¹⁰ Furthermore, the exposure time, the level of the applied loads, and the microstructure of the steels control both trench initiation and trench-to-crack transition.¹⁰

Characterization of surface trenches

Cross-sections of tested specimens indicate that trenches evidence signs of anodic dissolution, that are mostly transgranular, and their morphology is consistent with an elongated pit with a blunted tip.^{6-8,13} The tip can be rounded, or present a triangular shape, or even a branched pattern can arise from it. For this last case, coarse and fine branching at the tip has been observed.⁶⁻⁸ Coarse branching appears as a fork that diverges from the tip. Fine branching usually looks like a funnel, where a necking is observed at the trench's tip showing thinner forking. Nonetheless, in some cases, an intergranular crack can nucleate from the trench's tip.⁸⁻¹⁰ Craig and Dunlop have also reported tertiary cracks that nucleated on the

sidewalls of the trench, parallel to the direction of principal stress on highly segregated areas of microstructure with hardness values higher than 22 HRC.^{6,13} Usually, a combination of two or more of these patterns are present in the cross-sectional cuts. A summary of the described trenches' morphologies and typical characterization parameters is detailed in Figure 1.

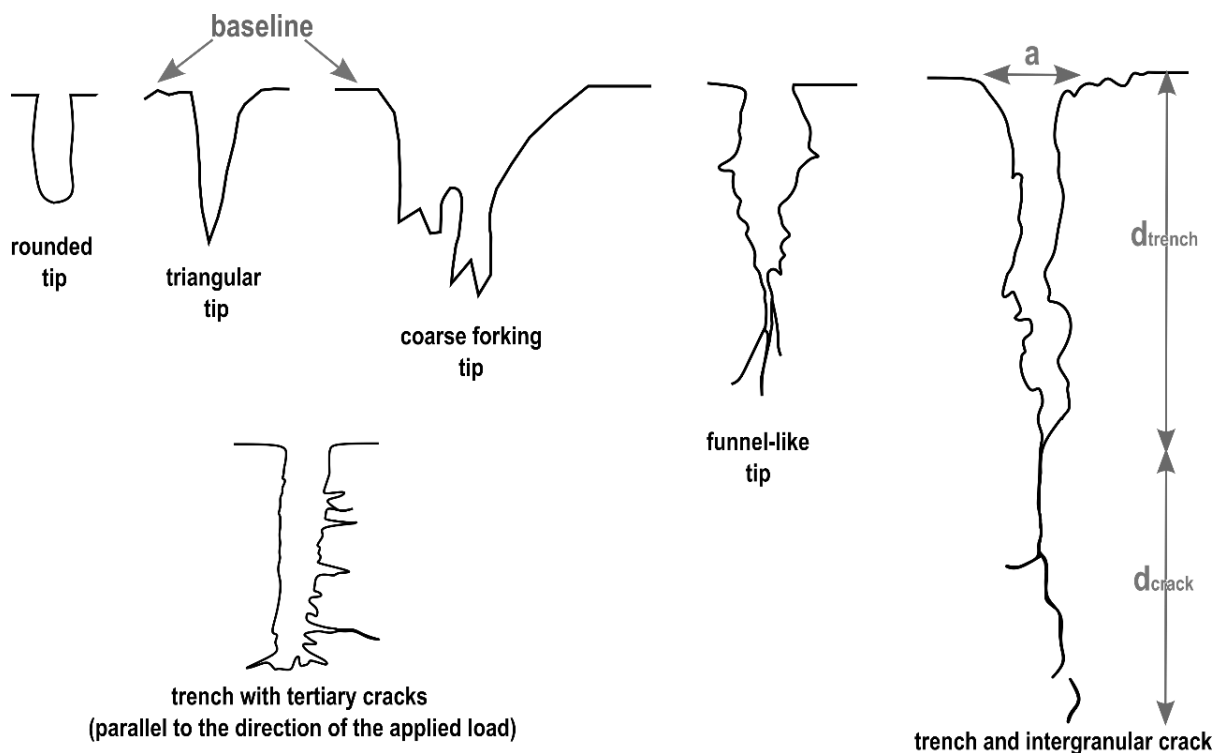


Figure 1. Different surface trenches' morphologies reported in the literature.^{6–9,13,16,18,19}

Although best practices are in place for examining a tested specimen in an H₂S-containing environment, there is a lack of uniformity in the guidelines to conduct a consistent characterization of pits, trenches, and cracks (Table 1). For example, specimens tested under constant load as in method A of the NACE⁽¹⁾ TM0177 standard, pass the test in the presence of cracks that were not originated as the result of an EAC process.²⁰ For testing methods B and C of the standard, a mention is made to “small cracks obscured by corrosion products” that require more careful examination.²⁰ For the case of four-point bend testing (FPBT), the NACE TM0316 standard requires that in the absence of cracking, the maximum depth of corrosion pits should be determined since they can propagate and transform to cracks upon more prolonged exposure times.²⁶ These tests are based on a pass/fail criteria for material's selection where failure is considered if complete separation of the specimens occurs due to cracking or if the visual examination at 10X, after 720 h of exposure, evidences the presence of cracks.²⁰ However, specimens that present trenches fall in a grey zone between the pass/fail range and can lead to deficient material's selection according to NACE standards. Additionally, the standards rarely include quantitative criteria for assessing trenches, with the exception of the Annex A of the EFC⁽²⁾ 16 document where a maximum depth of 100 µm for “stress corrosion cracks” is stated in the acceptance criteria for FPBT and C-ring tests.²⁷ Consequently, as also suggested by Anderson *et al.*, flowcharts or guidance based on objective

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⁽²⁾ European Federation of Corrosion (EFC)

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and quantitative and uniform criteria to characterize trenches must be discussed and considered in the standards.¹⁶

Table 1. Summary of failure criteria according to different SSC testing methods.^{20,26,28}

Standard	Failure Criteria
NACE TM 0177 Method A	Failure is considered as the complete separation of the specimen, or as the presence of cracks due to EAC in the gauge section (GS) of the specimen after cleaning and visual observation at 10X after 720 h exposure. Use of microscopy (optical or SEM) or mechanical testing is optional to determine if the cracks are evidence of EAC. If they are not related to EAC, the test specimen passes the test.
NACE TM 0177 Method B	Failed tests are those where cracking of the test specimen occurs or if it contains cracks. After 720 h exposure or after failure due to cracking, corrosion products that may obscure cracks must be removed and the specimens' surface must be cleaned followed by a 20 degree bending by hand. Crack examination by visual inspection using a low-power binocular microscope (10X) is mandatory and metallographic sectioning of the specimen is optional.
NACE TM 0177 Method C	Specimen's failure is considered when a crack propagates through the entire section. The user is warned that small cracks might be obscured by corrosion products. Criterion of failure is based on reporting the "first crack" observed at 10X magnification. Stressing the specimen beyond the test stress level is accepted to reveal cracks after 720 h exposure. Mechanically induced cracks can be discriminated from EAC since they are not expected to have a corroded crack surface.
NACE TM 0316 FPBT	Evaluation of the area of the center of the specimen (exposed to tensile stress) must be conducted for any evidence of surface or sub-surface cracking (crack type, size and location must be reported). In absence of cracks, the maximum depth of corrosion pits or other "notable feature" has to be determined since they could continue propagating and transition into cracks at longer test duration. In both cases, visual inspection, NDT's, and metallography are recommended. A blank specimen of reference (unstressed and unexposed) may be used to compare the obtained results. Care should be taken to avoid confusing EAC cracks from those originated during processing or welding.
NACE TM 0198 SSRT	This test guarantees complete fracture. A classification based on the visual inspection of the test specimen, i.e., presence of "fissures" in the necked region of the GS adjacent to the primary crack and secondary cracks in the GS, and the measurement of the loss of ductility (compared to specimens tested in air) must be conducted, which include: 1. Normal ductile behavior, 2. Ductile behavior with only slight loss of ductility (<20%), 3. Substantial loss of ductility (>20%), and 4. Evidence of SCC in the GS by observation of SCC on the primary surface or secondary cracking in the GS (or both).

A flowchart that presents a semi-quantitative criteria to classify pits and cracks based on the presence of hard zones in the microstructure, the depth of the defect, and the sharpness of its tip was developed by Pargeter after conducting metallographic observation of the cross-sections of tested samples.¹⁵ Anderson *et al.* have proposed a quantitative method and a micrography library to assess them, especially when different features are present in a single defect, such as a trench with a nascent or a propagating crack at its tip.¹⁶ Additionally, Yamane reported the trench density on cross-sections, i.e. by counting the number of trenches per unit length.⁸ Trench density varied from zero (no indications along the cross-section of the tested specimen) to saturation of defects on the studied extension. Saturation of defects can be defined as the point where mean interspacing of defects is on the order of the mean width of the defects. Yamane also conducted a detailed analysis of trenches' dimensions, which included the average depth ($\bar{d}$), the average width ($\bar{a}$) and the shape aspect ratio ($\bar{d} / \bar{a}$).⁸ In Yamane's work, it was observed that trench density increased when the average width decreased, for an almost constant defect average depth.⁸ The depth of the trenches was measured in this review using a cross-section's micrograph corresponding to Figure 11 in Yamane's work, and values between 71.5 and 11 μm were obtained. Reporting average values for trenches' characterization should be used with care if trench depth distribution is not uniform. Considering the fracture mechanics model presented before, more important