Corrosion Science 75 (2013) 415–425

Contents lists available at SciVerse ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

The influence of simulated fuel-grade ethanol on fatigue crack propagation in pipeline and storage-tank steels ☆

J.W. Sowards *, T.S. Weeks, J.D. McColskey

Applied Chemicals and Materials Division, National Institute of Standards and Technology, Boulder, CO, USA

ARTICLE INFO

Article history:
Received 24 January 2013
Accepted 18 June 2013
Available online 27 June 2013

Keywords:

C. Corrosion fatigue
B. Modelling studies
B. SEM
A. Steel
C. Stress corrosion

ABSTRACT

This study presents an evaluation of fatigue crack propagation in three steels (A36, X52, and X70) in a simulated fuel-grade ethanol environment. A fracture mechanics testing approach was used to determine crack propagation rates as a function of the stress-intensity-factor amplitude (ΔK). Results of this testing and the fracture analysis indicate that all three materials are susceptible to enhanced fatigue damage in fuel-grade ethanol environments. We show that the damage mechanism is attributed to susceptibility of each material to ethanol stress-corrosion cracking under fatigue loading conditions and propose a model for determining crack growth rates in ethanol fuel.

Published by Elsevier Ltd.

1. Introduction

Demand for renewable, alternative fuels such as fuel-grade ethanol (FGE) will increase over the next decade as energy security, environmental concerns, and rural socioeconomic issues continue to rise in importance on a global scale [1]. Ethanol fuel is a particularly attractive alternative fuel, because it can be blended with gasoline fuels already in use and since it is oxygenated, which reduces particulate emissions from combustion engines [2]. Biomass sources and production facilities generating FGE are typically located in rural areas (e.g., corn sources and producers in the Midwestern United States) requiring transportation by railroad, truck, and barge tankers to major consumer markets [3]. The distribution chain would be capable of significantly higher productivity and greater safety if dedicated pipelines were constructed or if existing pipelines were repurposed for FGE transport. However, there are concerns with batching FGE in multiproduct pipelines that are related to fuel cleanliness requirements, because ethanol is a solvent and readily absorbs water. Ethanol stress-corrosion cracking (ethanol-SCC) has become a widely recognized problem in the storage tank and piping infrastructure associated with FGE usage [4]. Ethanol corrosion and ethanol-SCC have been the topics of numerous recent evaluations [5–14]. However, more data are required to improve the safety of ethanol transport, particularly with respect to reliability assessment with fracture mechanics.

The significant electrochemical influences on corrosion and ethanol-SCC have been thoroughly evaluated for several pipeline and storage-tank steels. The presence of oxygen has the most significant influence on increasing pipeline steel ethanol-SCC susceptibility [6] and was also shown to increase the corrosion potential of steel in ethanol fuel. Applied cathodic potential has been shown to completely eliminate ethanol-SCC [8,13]. A decrease in dissolved oxygen levels reduces the pitting susceptibility [15]. The presence of chloride increases oxygen solubility in ethanol by a significant amount relative to aerated ethanol; however, oxygen solubility decreases with added chloride. Chloride promotes SCC initiation and growth and is required for SCC [7,16], but does not appear to influence crack growth rates [13]. Increasing the water content (>4.5–5.0%) in ethanol may inhibit SCC altogether [7,10]. Increasing the ethanol pH (pHe) can also inhibit ethanol-SCC [7]. A systematic study of ethanol corrosion and pitting showed that increasing water concentration increases the pitting and corrosion rates and increased chloride and acidity induce the initiation and growth of pits by destabilizing the passive films [15]. The influence of pitting on crack growth in FGE is not clear at this point, but it is generally considered that pitting enhances corrosion fatigue propagation [17].

Mechanical and metallurgical variables have been shown to influence ethanol-SCC. Cracking of pipeline steel (X65) in ethanol fuel has shown strain-rate dependency where crack velocity decreases and crack density increases with decreasing strain rate [7]. The mechanical breakdown (induced by plastic deformation)

☆ Contribution of NIST, an agency of the US government. Not subject to copyright.

* Corresponding author. Address: 325 Broadway, Boulder, CO 80305, USA. Tel.: +1 303 497 7960.
E-mail address: jeffrey.sowards@nist.gov (J.W. Sowards).

0010-938X/$ - see front matter Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.corsci.2013.06.026

of surface films produced in ethanol fuel leads to ethanol-SCC initiation [8] and the growth of the cracks is controlled by the competition between anodic dissolution and repassivation of the crack tips [8,10]. Plastic deformation exposes fresh metal at the crack tip, which consumes oxygen. Then fresh metal at the crack tip coupled with the adjacent passivated metal in oxygenated ethanol creates anodic polarization to allow crack tip advance by dissolution. Scratch testing has shown that repassivation is difficult when oxygen is removed from the ethanol fuel [11]. At least two studies have evaluated the cracking phenomena with fracture mechanics testing [10,18]. Values of K_{ISCC} (plane strain stress-intensity factor that will produce crack propagation by stress-corrosion cracking) were reported in the range of 33–36.8 MPa $m^{1/2}$ for pipeline steels of grades X42 through X60 [10]. Crack growth rates under cyclic loading conditions have also been reportedly influenced by batching with a variety of gasoline-ethanol blends [10], inhibitor additions and deaeration with N_2 [10], and have been shown to significantly increase in the presence of increasing amounts of water [18]. Metallurgical inclusions have been shown to promote initiation of ethanol-SCC in X65 due to strain mismatch between the inclusion and the steel matrix [7]. The laboratory ethanol-SCC tests have produced transgranular and intergranular fracture [8,10] although industrial failures have tended more towards intergranular fracture [4].

Fuel-transport pipelines contain flaws and are subjected to regular cyclic pressure fluctuations. This operation scenario sets up a situation where integrity must be monitored, and useful engineering life can be predicted based on the pressure fluctuations, flaw size, and growth rate of the flaws [19]. The objectives of the current study are to investigate the effects of cyclic loading of a storage tank steel and two pipeline steels exposed to simulated ethanol fuel environments. A fracture mechanics testing approach is employed here so that data may be used for predictive modeling of pipeline and storage tank structural integrity. The crack growth rates are discussed in relation to the theory of corrosion and SCC in the previous studies.

2. Experimental procedures

2.1. Materials

Two grades of pipeline steel (API 5L X52 and X70) and a steel (ASTM A36) used for fabricating storage tanks were obtained for this study. The pipeline steels were donated by an oil & gas transmission company and the storage tank steel was donated by a steel tank fabricator. The X52 pipe was 324 mm diameter with 9.53 mm wall thickness and the X70 pipe was 508 mm diameter with 6.60 mm wall thickness. The A36 plate was 6.35 mm in thickness. Chemical compositions (reported by the suppliers) of the three alloys are shown in Table 1. Metallographic specimens were sectioned from the pipeline materials and prepared with standard polishing methods for optical microscopy (1 μm final polish and 2% nital etch). Representative microstructures of the two pipeline materials are shown in Fig. 1. The A36 and X52 materials are very similar and contain a mixture of polygonal ferrite and pearlite, and the X70 material contains a finer-grained polygonal ferrite and bainitic structure. The finer grain size in the X70 material relative to the other materials is a result of the higher microalloying content (Ti and Nb) which aids in grain refinement during a controlled rolling process.

2.2. Mechanical properties

Tensile tests were performed in air according to ASTM E8/E8M Standard Test Methods for Tension Testing of Metallic Materials [20] using a 250 kN servohydraulic test frame. Three uniaxial tension tests were performed for each steel. Average properties and corresponding standard deviations are shown in Table 2. Tensile properties were evaluated prior to fatigue propagation studies to determine the precracking conditions and for calculation of the plastic zone size ahead of the fatigue crack tip.

2.3. Fatigue crack growth testing

Compact tension C(T) specimens were machined from the three steel materials (in the LT orientation) in accordance with ASTM E647 Standard Test Method for Measurement of Fatigue Crack Growth Rates [21]. The configuration and relevant dimensions of the C(T) specimens are shown in Fig. 2. Note that both pipeline materials were machined from curved pipe, i.e., the pipes were not flattened prior to machining. The X70 pipe had the thinnest wall section (6.60 mm) which limited the B dimension (specimen thickness) to 5.715 mm due to pipe curvature. Specimens sectioned from each material were limited to this thickness so that the stress state of the crack would be consistent among the tests. Specimens were precracked and crack propagation rates were calculated with the compliance technique according to ASTM E647. Crack mouth opening displacements (CMOD) were measured along the load line with a displacement gauge (6.35 mm gauge length) that was attached to integral knife edges machined at the crack mouth (shown in Fig. 2). Precracking force was shed incrementally so that initial forces during propagation studies were greater than final forces during precracking. Tests were performed in a 100 kN closed loop servohydraulic test frame with a constant force (P) ratio $R = P_{min}/P_{max} = 0.1$. The cycling frequency (f) of baseline tests performed in air was 10 Hz, and the cyclic frequency of tests in simulated fuel grade ethanol (SFGE) was typically 0.1 Hz. Sinusoidal loading was used resulting in a variation in the stress-intensity factor during a loading cycle. The stress-intensity-factor amplitude (ΔK) is determined with Eq. (1) for the C(T) specimen geometry:

$$\Delta K = \frac{\Delta P}{B\sqrt{W}} \frac{\left(2+\frac{a}{W}\right)}{\left(1-\frac{a}{W}\right)^{3/2}} \left(0.886 + 4.64\left(\frac{a}{W}\right) - 13.32\left(\frac{a}{W}\right)^2 + 14.72\left(\frac{a}{W}\right)^3 - 5.6\left(\frac{a}{W}\right)^4\right). \quad (1)$$

where ΔP is the force range (kN), B is the specimen thickness (mm), W is the width (mm), and a is the crack length (mm). The stress-intensity-factor amplitudes were continually increased during testing with a normalized K-gradient (C) of 0.15 mm^{-1}, which describes the rate of change of K with increasing crack size according to Eq. (2), where ΔK_0 and a_0 are the initial stress-intensity-factor amplitude and crack length, respectively:

$$\Delta K = \Delta K_0 e^{C(a-a_0)}. \quad (2)$$

Table 1
Chemical compositions (wt.%) of the steels.

Alloys	C	Si	Cr	Ni	Mn	Cu	Mo	Nb	Ti	Al	V	S	P
A36	0.22	0.04	0.08	0.08	0.9	0.23	0.02	<0.01	<0.01	0.03	<0.01	0.01	0.01
X52	0.070	0.195	0.030	0.020	1.050	0.050	0.004	0.021	0.001	0.029	0.003	0.008	0.008
X70	0.050	0.185	0.043	0.017	1.505	0.030	0.01	0.084	0.015	0.032	0.01	0.006	0.012