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Effect of MnS inclusion dissolution on carbon steel stress corrosion cracking in fuel-grade ethanol

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ABSTRACT

The intrinsic dissolution rate of manganese sulfide (MnS) was measured in water with hydrochloric acid and in fuel-grade ethanol (FGE) with acetic acid and hydrochloric acid using static disk system. The intrinsic dissolution rate of MnS is used to evaluate conditions inside the intergranular stress corrosion cracks (SCC) by studying partially dissolved MnS inclusions on intergranular SCC fracture surfaces of failed carbon steel piping handling FGE. The penetration rate of MnS inclusion dissolution front was measured to vary from 11 μm/year up to 127 μm/year inside the cracks. According to the results the conditions inside intergranular SCC crack are not acidified.

1. Introduction

Recently many countries have started to promote the use of biofuels or other renewable fuels to reduce greenhouse gas emissions and to diversify fuel sources. Due to this reason the ethanol content in ethanol–gasoline blends has increased lately. The material used for handling gasoline or fuel-grade ethanol (FGE) is mainly carbon steel, which is susceptible to stress corrosion cracking (SCC) in FGE or ethanol–gasoline blends with sufficient amount of ethanol. There have already been some failures in the industry due to this phenomenon mainly in storage tanks and piping handling FGE [1].

Vast majority of the information available on SCC of carbon steels in ethanol is from laboratory studies made using commercial or simulated FGE (SFGE) as the environment. Most common method to study SCC of carbon steel in FGE has been slow strain rate testing (SSRT). The SCC fracture mode in majority of the laboratory studies has been transgranular or a mixed transgranular and intergranular mode of cracking, while in the industrial cases the SCC fracture mode is mainly intergranular [1]. This is because small amounts of chlorides cause transition in the SCC fracture mode from intergranular to cleavage-like transgranular [2,3]. Only 2 mg/L of chlorides leaked from a commonly used silver/silver chloride/ethanol (Ag/AgCl/EtOH) reference electrode was found to cause transition from intergranular to transgranular SCC in a ethanol–gasoline blend [3]. Most of the laboratory studies have been made using SFGE with added chlorides and the electrochemical measurements by using the same Ag/AgCl/EtOH reference electrode with buffer solution of ethanol containing lithium chloride (LiCl) [2–10]. Intergranular SCC has been successfully produced in two studies using the Ag/AgCl/EtOH reference electrode, but the electrochemical measurements are difficult due to the low conductivity of the test solution [2,4,8]. Fully intergranular SCC has also been produced in ethanol–gasoline blends without chlorides, when no electrochemical measurements were used [3].

The roles of different environmental parameters on the ethanol SCC are well known [2,4–16], but the conditions within the ethanol SCC crack are still not known very well. One way to get information of the conditions within the SCC crack is to study the dissolution of the manganese sulfide inclusions. Manganese sulfide inclusions are known to act as pitting corrosion nucleation sites for stainless steels and therefore the dissolution process of the manganese sulfide inclusions in aqueous conditions has been studied extensively [17–24]. Manganese sulfide inclusions have also been found to affect the environmentally assisted cracking of pressure vessel steels in high-temperature water [25–34]. Dissolution rate of MnS has not yet been directly measured but the chemical dissolution rate of MnS inclusions of stainless steels in acidic conditions containing NaCl has been estimated between 0.01 and 0.19 μm^3/min by using in situ atomic force microscopy [17]. It has not been studied whether the sulfur species released during the dissolution of the MnS inclusions can affect the ethanol SCC mechanism or to what extent the MnS inclusions dissolve in FGE. Partially dissolved MnS inclusions were observed on the ethanol SCC fracture surface of ST35 carbon steel notched SSR test specimens, which does indicate that some dissolution occurs within the ethanol SCC cracks [10].

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In this article the intrinsic dissolution rate of MnS was measured in FGE with various concentrations of acetic acid and hydrochloric acid. The intrinsic dissolution rate was measured using rotating disk system (USP Wood apparatus), which is commonly used in the pharmaceutical industry [35]. This method was selected because there are lots of reference values available in the literature and the dissolution tests are easy to reproduce as identical test equipment is readily available. The intrinsic dissolution rate of MnS is used for evaluation of the conditions inside the intergranular SCC cracks by examining partially dissolved MnS inclusions on the fracture surface of failed carbon steel piping handling FGE. The failure case is also presented as a background for the study.

2. Experimental method

The intrinsic dissolution rate was measured using rotating disk system (USP Wood apparatus) in Sotax AT7 dissolution tester (Sotax Group, Switzerland). For the intrinsic dissolution test 200 mg of MnS with purity of 99.9% (Product number: 400947, CAS: 18820-29-6, Sigma–Aldrich, USA) was pressed within the test apparatus using a hydraulic pressure of 2000 kg force (Pye Unicam, United Kingdom). The surface roughness parameters were measured using surface profilometer (Mahr Perthen Perthometer, Göttingen, Germany). No rotation was used in the tests as the purpose was to measure the intrinsic dissolution rate in stagnant conditions. Nine hundred milliliters of FGE or purified water (Milli-Q, Merck Millipore, Darmstadt, Germany) was used as the medium and maintained at 25 °C during the dissolution tests. The chemical analysis of the commercial FGE used is given in Table 1. The pH or pHe was controlled by either glacial acetic acid (CAS: 64-19-7, J.T. Baker, Holland) or 4.61 M hydrochloric acid diluted from 37% hydrochloric acid (Product number: 258148, CAS: 7647-01-0, Sigma–Aldrich, Germany). The pH was measured using pH glass electrode (ScienceLine pH combination electrode, Schott, Mainz, Germany) and the pHe was measured according to ASTM Standard Test Method D6423-08 using the same pH glass electrode. At appropriate time intervals samples were taken from the medium and Mn concentration was analyzed. The Mn concentrations of the FGE samples were measured from the residue left after evaporation by a colorimetric method developed by Willard and Greathouse [36]. This method uses periodate in acidic conditions to oxidize the manganese to permanganate, which was then analyzed at 526 nm using a spectrophotometer (UV-1600PC spectrophotometer, VWR, Radnor, Pennsylvania, USA). When the amount of dissolved MnS is plotted as a function of time, the slope of the curve represents the intrinsic dissolution rate of MnS.

Table 1
Chemical analysis of the FGE used in the tests.

Component	Method	Value	Unit
Density	ENISO12185	788.1	kg/m^3
Water	EN15489	0.299	wt%
Conductivity	EN15938	1.59	µS/cm
Acetic acid	ASTM D1613	0.0021	wt%
Chloride	EN15492	<1	mg/l
Sulfate	EN15492	<1	mg/l
Sodium	NM122	0.69	mg/kg
Copper	NM122	<0.02	mg/kg
Iron	NM122	<0.03	mg/kg
Methanol	NM40	0.05	vol%
Ethanol	NM40	92.4	vol%
MTBE	NM40	<0.01	vol%
ETBE	NM40	0.13	vol%
TAEE	NM40	0.32	vol%
Gasoline		7.1	vol%

3. Results and discussion

The acid strength of ethanol as measured according to standard test method ASTM D6423 is defined as pHe. The pHe of the FGE used was measured vs. the acetic acid and hydrochloric acid concentrations. The results are shown in Fig. 1.

Total acidity of ethanol gives an accurate estimate of the acid concentration in the ethanol while pHe is a good predicator of the corrosion potential. A pHe value of ethanol is not comparable to pH values of water solutions as seen from Fig. 1. The pH of water would be significantly higher than the pHe of ethanol with identical hydrochloric acid concentrations. On the other hand, pH of water would be lower than the pHe of ethanol with identical acetic acid concentrations. This is why the contribution of weak acids can be overestimated and the contribution of strong acids underestimated in ethanol. The pHe depends somewhat on the fuel blend used. The results in Fig. 1 describe well the acid strength of the FGE solutions used in this experiment. The water content of the FGE was found to affect the pHe measured.

The intrinsic dissolution rates of MnS were measured using a rotating disk system without any rotation and the MnS surface facing downwards. In this case the dissolution process is controlled either by diffusion or reaction kinetics. Free convection can cause a systematic error to the results. The intrinsic dissolution rate measurement is standard method used in the pharmaceutics to measure dissolution rate of pure solid substances having null porosity, which is defined as intrinsic dissolution rate [37]. The principle is that compacting the MnS powder removes all porosity restricting the surface area to the visible sample surface. Because very small amount of MnS is dissolved during the dissolution rate measurement the conditions of surface area are considered as constant. The surface roughness of the sample depends on the surface plate used while compressing the MnS powder. The same surface plate was used for all samples and can cause systematic error to the results. The average surface roughness parameters R_a and R_z were measured as 0.29 µm and 1.61 µm. The solid state properties like grain size of the MnS used can affect the results, which needs to be taken into account while comparing the results to the dissolution rate of the MnS inclusions. The average grain size of the MnS powder used was from 1 to 2 µm. The nominal surface area of the MnS was 0.5 cm^2 and taking into account the surface roughness the true surface area can be somewhat higher. The compacting of the MnS appeared to be successful so there should be no porosity left in the samples. All dissolution mediums were naturally aerated. The dissolution rate in FGE was very slow and each dissolution rate measurement lasted for approx. one week. The

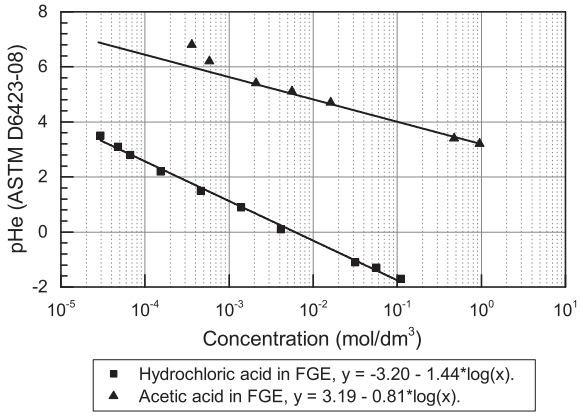

Fig. 1. The pHe of the FGE vs. acid concentration. Notice how the hydrochloric acid has stronger and acetic acid weaker effect on the pHe than what would be expected for pH in water.