Corrosion Science 90 (2015) 266–275

Contents lists available at ScienceDirect

Corrosion Science

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

Influence and role of ethanol minor constituents of fuel grade ethanol on corrosion behavior of carbon steel

Itaru Samusawa *, Kazuhiko Shiotani

Steel Research Laboratory, JFE Steel Corporation, Kawasakidori 1-chome, Mizushima, Kurashiki 712-8511, Japan

ARTICLE INFO

Article history:
Received 4 August 2014
Accepted 20 October 2014
Available online 28 October 2014

Keywords:
A. Carbon steel
B. AES
B. XPS
C. Anodic dissolution
C. Pitting corrosion

ABSTRACT

The influences of organic acids, chloride and water on the corrosion behavior of carbon steel in fuel grade ethanol (FGE) environments were investigated by immersion testing in simulated FGE. The roles of acetic acid, chloride and water in pitting corrosion were studied by using X-ray photoelectron spectroscopy (XPS), auger electron spectroscopy (AES) and electrochemical experiments. The results indicated that iron acetate is generated on oxide film. Iron(II) acetate shows high solubility in FGE environments. The sites where iron(II) acetate is existed become preferential anodic sites, and chloride promotes anodic dissolution at such sites.

1. Introduction

Fuel grade ethanol (FGE), which contains H_2O, methanol, chloride ion and organic compounds (e.g. acetic acid) as impurities, can be produced from a variety of feedstocks such as corn and sugar cane. FGE is widely used in mixture with gasoline in the United States and other countries. The production volume of FGE in the U.S. increased until 2011, but the growth of production has slowed recently. One of the barriers to using FGE is high transportation cost. Although there are plans to construct pipelines as an inexpensive transportation method, those plans are not readily realized due to corrosion issues such as pitting corrosion and stress corrosion cracking (SCC) of carbon steel in FGE [1]. Corrosion in alcoholic environments has been investigated since the 1980s [2–8]. Especially, in recent years, intensive laboratory research on SCC has been reported in response to the exteriorization of SCC issues in carbon steel tanks and piping in contact with FGE in user terminals. Since SCC leads to serious incidents in service, the development of new technology to prevent SCC in carbon steels under FGE environments has been expected [9].

Kane et al. showed that SCC occurred in slow strain rate tests (SSRT) in ethanol that met the ASTM D4806 specification [10,11]. Since then, SSRT have been widely used as the evaluation method for FGE–SCC in laboratory studies. Sridhar et al. conducted SSRT using carbon steel in FGE and simulated-FGE (SFGE) including various amount of H_2O, acetic acid, corrosion inhibitor, dissolved oxygen and sodium chloride, etc., and showed that the most important factor for SCC in FGE is dissolved oxygen [12]. Cao et al. reported that chloride is required for ethanol SCC, but it is not the controlling factor of crack growth for an existing crack [13]. Furthermore, Lou et al. investigated the effects of chloride ions, H_2O and the pH value on SCC in ethanolic environments by SSRT and showed that chloride ions and low pH promoted SCC. It is interesting to note that H_2O in SFGE affects corrosion behavior. The sample tested in the SFGE containing 2.5% of H_2O showed pit-initiated cracks, whereas the sample tested in the SFGE containing 5% of H_2O did not show any signs of SCC, but showed significant pitting attack on the surface. Additionally, it has been reported that high plastic deformation was necessary to initiate SCC [14,15]. The proposed SCC mechanism based on SSRT and electrochemical data by Lou et al. is as follows:

(1) The onset of film breakdown under local plastic deformation initiates micro-cracks on the surface.
(2) Competition between active anodic dissolution and repassivation ahead of the crack tip controls the propagation of SCC.

Other studies also support the conclusion that active path corrosion acts as the dominant factor in SCC in FGE [12,16–19].

However, the total mechanism of SCC is not clear, as understanding of the corrosion mechanism in FGE is not sufficient. The corrosion of carbon steel in FGE is pitting [1]. Pitting is closely related to active path corrosion type SCC from the viewpoint of local corrosion. Further, pits are likely sites for the initiation of SCC.

---

* Corresponding author. Tel.: +81 86 447 3883; fax: +81 86 447 3936.
E-mail addresses: i-samusawa@jfe-steel.co.jp (I. Samusawa), k-shiotani@jfe-steel.co.jp (K. Shiotani).

http://dx.doi.org/10.1016/j.corsci.2014.10.020
0010-938X/

In order to understand the mechanism of SCC in greater detail, it is important to research the mechanism of pitting corrosion of carbon steel exposed to FGE. An early study of FGE corrosion suggested that the factors which increase the corrosivity of FGE appear to be increased H_2O content and decreased pHe [20]. Subsequently, some laboratory studies regarding corrosion factors in FGE or FGE-blended gasoline were reported [16,21–28]. For instance, Gui et al. reported that, as the dissolved oxygen concentration in simulated FGE is increased, the localized corrosion tendency decreases. This result suggested that a surface layer formed by oxygen protects steel from corrosion factors. Gui et al. also showed that chloride promotes the corrosion of carbon steel in FGE [16]. Moreover, Singh et al. investigated the influence of H_2O and acetic acid on localized corrosion in FGE. H_2O concentration affects surface passivation and localized corrosion. On the other hand, addition of 5.6 mg/L of acetic acid to simulated FGE containing 5 vol.% of H_2O caused very little change [21]. In subsequent research, the same researchers reported that addition of up to 560 ppm of acetic acid to simulated FGE inhibits steel repassivation in an ethanol environment [22]. Moreover, microbiologically influenced corrosion of carbon steel in ethanolic environments has been reported recently [29,30]. In those reports, existence of acetic acid producing bacteria lead to increase in pitting corrosion and crack growth rate. As indicated above, involvement of acetic acid, H_2O, oxygen and chloride ions in corrosion has been suggested. However, the role of those impurities in the pitting corrosion mechanism has not been clarified sufficiently. For example, it is unclear whether the effect of acetic acid on corrosion is largely a result of decreasing pHe or not. The aim of this study is to investigate the corrosion behavior and pitting corrosion mechanism of carbon steel for pipelines in FGE environments.

2. Experimental

2.1. Preparation of solution

Experimental solutions of simulated FGE (SFGE) were prepared with 200-proof regent ethanol and other reagent-grade constituents to control the solution chemistry and mimic the ASTM-regulated components of FGE outlined in ASTM D4806 [10]. In order to clarify the influence of minor constituents of FGE on the corrosion behavior of carbon steels, SFGE solutions were prepared with various contents of H_2O, chloride, acetic acid and formic acid as shown in Table 1. Formic acid was added to confirm the difference in the influence of organic acid species. pHe was measured for all tested environments before the tests. Electrical conductivities, for some SFGE tested in this work, were measured using DKK-TOA electrical conductivity meter model WM-22EP.

2.2. Sample preparation

API-5L X52 grade steel with the composition shown in Table 2 was used for the investigation. Specimens of two different sizes were machined for immersion tests (3.5 mm × 10 mm × 25 mm) and electrochemical experiments (5 mm × 30 mm × 50 mm), respectively. The tested specimens were dry-polished up to 2000 grit, degreased with acetone, and then dried in blowing air.

2.3. Immersion test

Specimens were immersed for 30 days in SFGE in a sealed test tube at room temperature. The specimens were then removed and photographed to evaluate their corrosion behavior. Some specimens were observed with a 3D laser scanning microscope (KEYENCE VK-8700) and scanning electron microscope (HITACHI-S4300) to observe the detailed surface morphology. Under some SFGE conditions, an additional test was performed for 30 days in order to investigate the surface characterization by auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS).

2.4. Electrochemical experiment

In this study, a silver/silver chloride/ethanol electrode with a 1 M LiCl supporting electrolyte [12,14,15,31] was used as a reference electrode, and a platinum wire was used as a counter electrode. Tests were conducted in an 80-mL glass cell fitted with ports for the specimen, reference electrode and counter electrode. All tests were performed in static air at room temperature. In performing various electrochemical experiments, an EG&G potentiostat model 263 was used. The open circuit potential (OCP) values in the various SFGE solutions were monitored over time during an immersion period of up to 24 h. Soon afterward, cyclic potentiodynamic polarization (CPP) scans were conducted from OCP to 0.5 V Ag/AgCl reference at a rate of 0.167 mV/s.

2.5. Analysis of auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS)

Characterization of the oxide surface film in the depth direction was performed by using an auger electron spectroscope (AES) from PHYSICAL ELECTONICS PHI Model 660, with a sample inclination angle of 30°, a sample current of 0.1 μA and a measurement region of 5 μm square. The acceleration voltage of the electron gun and

Table 1
Composition and pHe of simulated fuel grade ethanol (SFGE) solutions used in this study.

Solution ID	Ethanol (vol.%)	Methanol (vol.%)	H_2O (vol.%)	Inorganic chloride (mg/L)	Acetic acid (mg/L)	Formic acid (mg/L)	pHe
a (Baseline)	Bal.	0.5	1.0	8	56		5.4
b	Bal.	0.5	0.2	8	56		5.6
c	Bal.	0.5	4.0	8	56		5.6
d	Bal.	0.5	1.0	80	56		5.2
e	Bal.	0.5	1.0	160	56		5.2
f	Bal.	0.5	1.0	8	560		4.7
g	Bal.	0.5	1.0	8	1120		4.3
h	Bal.	0.5	1.0	8		43	4.3
i	Bal.	0.5	1.0	8		430	3.5
j	Bal.	0.5	1.0	80	560		4.4
k	Bal.	0.5	0.2	80	560		4.2
l	Bal.	0.5	4.0	80	560		4.6
m	Bal.	0.5	1.0	160	560		4.6
n	Bal.	0.5	1.0	80	1120		4.1
o	Bal.	0.5	1.0	32	56		5.5