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Susceptibility of aluminum alloys to corrosion in simulated fuel blends containing ethanol

J.K. Thomson *, S.J. Pawel, D.F. Wilson

Oak Ridge National Laboratory, One Bethel Valley Road, P.O. Box 2008, MS-6156, Oak Ridge, TN 37831-6156, USA

HIGHLIGHTS

- Aluminum is susceptible to rapid corrosion rates in dry ethanol blended fuels.
- Water concentration and temperature were found to be the principal drivers.
- Higher ethanol concentrations result in faster corrosion rates of aluminum alloys.
- Galvanic corrosion did not appear to play a factor in the corrosion mechanism.
- Pretreatment of the aluminum surface delayed the onset of rapid corrosion.

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ABSTRACT

The compatibility of aluminum and aluminum alloys with synthetic fuel blends comprised of ethanol and reference fuel C (a 50/50 mix of toluene and iso-octane) was examined as a function of water content and temperature. Temperatures examined ranged between 20 °C and 200 °C and water content ranged between sub 50 ppm and 10% by volume. Commercially pure wrought aluminum and several cast aluminum alloys were observed to be similarly susceptible to substantial corrosion in dry (<50 ppm water) ethanol. Corrosion rates of all the aluminum materials examined were accelerated by increased temperature and ethanol content in the fuel mixture, but inhibited by increased water content. Substantial corrosion was observed only at temperatures exceeding 78 °C, the boiling point of ethanol. Pretreatments designed to stabilize passive films on aluminum increased the incubation time for onset of corrosion, suggesting film stability is a significant factor in the mechanism of corrosion.

1. Introduction

The ever increasing rate of fossil fuel consumption coupled with the desire for energy independence has influenced the United States to enact legislation to integrate renewable biofuels such as ethanol into the nation's fuel supply [1]. As of 2012, over 95% of standard refueling stations distribute gasoline blended with up to 10% fuel-grade ethanol, often termed E10. Due to various national policy goals and initiatives to pursue energy independence, there is mounting pressure to increase the ethanol content of transportation fuels to levels of 15–20% ethanol (E15-E20) in the near future, and flex-fuel vehicles capable of utilizing E85 (85% ethanol) fuel blends are in production by many manufacturers.

The addition of ethanol to gasoline is expected to be a source of concern for increased corrosion in two primary ways. Firstly, compared to gasoline, ethanol has significant affinity for water. Thus, additions of ethanol to transportation fuel invite the possibility of aqueous corrosion of all materials in contact with the fuel, including vehicle fuel systems and engines as well as the infrastructure for distributing and dispensing the fuel. Due to the hygroscopic nature of ethanol, absorbed water can phase separate from the organic fuel phase leading to a number of potential issues with fuel and containment corrosion [2]. Secondly, ethanol is orders of magnitude more electrically conductive than gasoline [3], so even modest additions of ethanol can contribute to corrosion possibilities in ethanol fuel blends, such as galvanic attack, that are not observed in ethanol-free gasoline.

This investigation examined the potential impact of changing fuel compositions on fuel compatibility with materials of interest for lightweight engine materials. The focus of the effort has been on aluminum and its alloys, primarily because it is low density and is used extensively in automotive engines as a piston and head material for fuel-efficient vehicles. There are mixed results reported in the open literature suggesting varying degrees of corrosion susceptibility of aluminum in ethanol [4–11]. Yoo et al. reported that both oxygen and water enhance the corrosion resistance in aluminum by forming a protective hydrous oxide film [5].

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* Corresponding author. Tel.: +1 (865)576 3402.
E-mail address: thomsonjk@ornl.gov (J.K. Thomson).

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Kruger et al. found that aluminum corrosion in ethanol is predominantly a chemical mechanism dependent on temperature and water content, and that ethanol content and aluminum grain size are of secondary importance [7]. Nie et al. concluded that aluminum alloys Al6061/Al319 are compatible with ethanol containing fuels but would be susceptible to galvanic corrosion if coupled to ferrous materials [9]. Inconsistencies exist possibly as a result of variations (intended or not) in critical exposure variables and/or incomplete interpretation of the results. The present work represents an effort to systematically define the critical exposure variables that lead to accelerated rates of corrosion of aluminum in ethanol containing fuels.

2. Experimental

2.1. Galvanic corrosion assessment

Identically sized/shaped specimens (1.3 cm × 1.0 cm × 0.8 cm) of type 1100 aluminum, copper, cartridge brass, mild steel, and type 304 stainless steel were immersed individually or as couples between 1100 aluminum and one of the other materials in approximately 100 ml of anhydrous ethanol (E100) purchased as a reagent grade chemical (Aldrich). In the case of couples, specimens of aluminum were connected to the other metal via a short (~1 cm) section of threaded stainless steel rod, and the composite specimen was tightened until the ends of the different metals were in physical contact, and under slight tension. The resistance across the couple was measured with a Fluke 287 multimeter and if not found to be less than 0.1 ohms the contact was tightened and remeasured. The test vessel was a round-bottom glass flask fitted with a mantle-style heater and a water-cooled Allihn-style condenser. The opening at the top of the condenser incorporated a glass elbow filled with a molecular sieve material to prevent ingress of water vapor over the course of the experiment without actually sealing the heated vessel. The liquid temperature, which was initially at approximately 22 °C, was increased to 78 °C (solution boiling point) and maintained constant for 24 h. The water concentration of the E100 was measured before and after each experiment using a Karl Fischer titration. Assessment of corrosion included visual appearance as well as dimensional changes and mass changes.

2.2. Water content, temperature, and ethanol concentration studies

Tests were carried out in custom low volume (~100 ml) Teflon lined 316 stainless steel autoclaves. All test solutions were prepared from reagent grade chemicals and high-purity water (18 MΩ-cm). Test fuel mixtures were based on the test-fuel standard specified in SAE J1681 [12], which was developed as a simulated gasoline for laboratory testing. The composition of the test fuel, often termed fuel 'C' in the literature, is 50% iso-octane and 50% toluene. Synthetic purified ethanol, not bio-derived ethanol, was used to minimize variables which could be introduced based on the production and handling of fuel grade ethanol [13]. Aggressive formulations of the simulated fuel, containing upper limits of concentrations of potential contaminants such as acids and/or salts were also tested. Test solutions were mixed and loaded into the autoclaves along with the appropriate test specimen within an argon glove box to exclude unintentional additions of water and oxygen. Test specimens included type 1100 aluminum, as well as specimens of seven cast aluminum–silicon–magnesium–copper alloys representing a range of compositions. One specimen per vessel per experiment was mounted into the bottom of each reaction vessel via a Teflon screw, and each experiment incorporated a nominal test solution volume of about 50 ml. After filling the reaction vessel inside the glove box, the mixture was shaken vigorously for ~2 min to ensure complete mixing, and a ~1 ml aliquot was removed for water content analysis by Karl Fischer titration. The reaction vessel was then sealed under argon and transferred to the test station where it was attached to a manifold fitted with a pressure relief valve (500 psi). The entire vessel and manifold were then purged with argon for ~15 min at room temperature. An additional set of experiments were conducted with an oxygen purge of the manifold and autoclave chamber to test the contribution, if any, of oxygen alone to the corrosion/passivation mechanism. Subsequently, equilibration at the desired temperature was accomplished with heat tapes for each vessel, and temperature was maintained constant (±1 °C) for the duration of the experiment. Following the desired exposure, the vessels were allowed to quickly cool to room temperature, and a second aliquot (~1 ml) was removed for assessment of water content. Assessment of corrosion was again primarily a yes/no evaluation based on visual changes on the specimen as well as pressure and temperature changes within the autoclave as the general performance boundary of aluminum in ethanol as a function of critical variables was sought. Where appropriate, mass change of the before and after test sample was also recorded.

2.3. Pretreatment studies

A collection of seven commercial and experimental aluminum alloys was pretreated and tested for corrosion susceptibility in ethanol. The specimens underwent a pretreatment step based on the 'HFIR' surface treatment, named after a standard surface treatment given to aluminum fuel cladding at the High Flux Isotope Reactor at the Oak Ridge National Laboratory. This treatment includes immersion of the specimens in a room temperature solution of (by volume) 15% reagent grade nitric acid, 1% reagent grade hydrofluoric acid and 84% demineralized water for 3 min [14]. The specimens are then rinsed in pure demineralized water and the passive film is allowed to heal itself into a continuous film in an additional volume of demineralized water for 3 min at 70 °C. For each test an untreated specimen was attached to the treated specimen with a Teflon screw to assure subsequent identical environmental exposure. The specimens were then tested for corrosion susceptibility in an identical setup as outlined in the galvanic assessment section above with the exception that the specimens remained in the test solution for a period of 72 h rather than 24.

3. Results and discussion

3.1. Galvanic coupling

Karl Fischer titration showed that the water content pre- and post-test was less than 100 ppm in all cases. The corrosion results are summarized in Figs. 1a and 2a, which pictorially indicates that uncoupled (stand-alone) aluminum specimens corroded to an essentially identical degree to the aluminum exposed in each galvanic couple. Further, the end of the aluminum specimen physically in contact with each coupled material revealed no more or less corrosion than the rest of the specimen, again suggesting no effect of electrochemical potential for these exposure conditions. In all cases, whether exposed as part of a couple with aluminum or as individual specimens, the other materials – copper, cartridge brass, mild steel, and 304 stainless steel – were found to be completely immune to corrosion under these conditions. The mass loss of aluminum material in each case was approximately 20 ± 3%. The corrosive attack on aluminum appears to initiate at discrete locations as rather intense general corrosion. These areas of intense corrosion have some similarities to pitting, but the corroded area