Engine Materials Compatibility with Alternate Fuels

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Project ID # PM039

Project Overview

Timeline

- Start – December 2009
- End – December 2012
- Percent complete ~ 85%

Budget

- Total DOE funding = $900K ($300K/y for 3 years)
- Partners are matching funding with 1:1 in-kind contributions
- FY10 funding received = $300K
  FY11 funding received = $300K
  FY12 funding expected = $270K
  FY13 funding expected = $ 30K

Barriers Addressed

Propulsion Materials Technology

A. Changing internal combustion engine component regimes
   - Task 1 - examine impact of new fuels on light duty engine components
   - Task 2 - collaborate with industry partners to characterize materials-related life-limiting mechanisms

Fuels and Lubricant Technology

E. Inadequate data on long term impact of fuel composition on durability of engine components

USCAR Partners

This project is a Cooperative Research and Development Agreement (CRADA) between ORNL and USCAR, LLC [includes GM (lead), Ford, Chrysler]

A Potential Compatibility Concern with Utilization of Alternate Fuels

- Recent experience in the US and elsewhere with production and testing of flex-fuel vehicles (e.g., E85 fuel) has prompted concerns over the possibility of corrosion not previously encountered with low-ethanol or ethanol-free fuels

General Strategy

- Utilize laboratory exposures and forensic analysis of materials from field testing to assess aluminum corrosion rates/forms and mechanisms as a function of key fuel blend variables and alloy composition

Project Objective ➡ Conduct a systematic assessment of aluminum corrosion in ethanol fuel blends

Goals to reach this objective include:

- develop a mechanistic understanding of aluminum corrosion associated with increased ethanol content
- consistent with mechanism, identify potential mitigation techniques
- develop rapid test protocols to enable anticipation of potential problems in design stage

An Integrated Approach to Examine Compatibility Issues Has Been Developed

Task 1: Surface analysis of materials exposed in field and laboratory testing

Task 2: In-situ extraction of gas and/or fluid from operating engines

Task 3: Laboratory corrosion exposures of coupon materials

Task 4: Development of test protocols for rapid evaluation of material/fuel combinations

Milestones – shaped around results

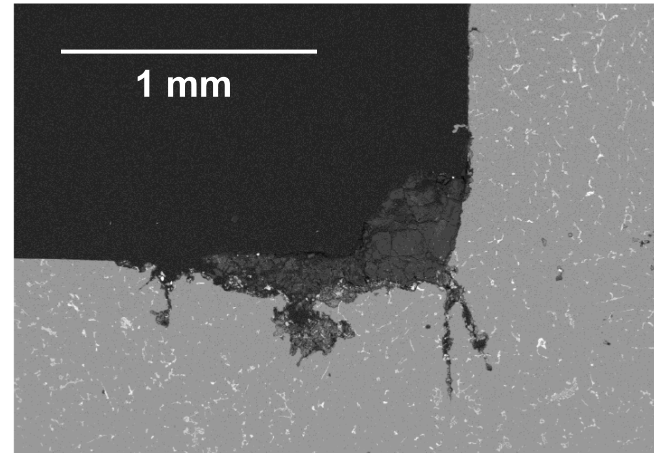
- Perform baseline forensic analyses of components exposed in field/engine tests — ~ COMPLETED RESULTS MAY 2012
- Demonstrate in-situ sampling of gas/liquid from operating engines — COMPLETED RESULTS MARCH 2012
- Design/construct system for high temperature corrosion tests in ethanol fuel blends — COMPLETED DATA GATHERING ON-GOING
- Assess relevance of electrochemical testing (go/no-go) — COMPLETED FEBRUARY 2011 DETERMINED UNSUITABLE
- Extend literature review on material performance in ethanol fuel blends — ON-GOING

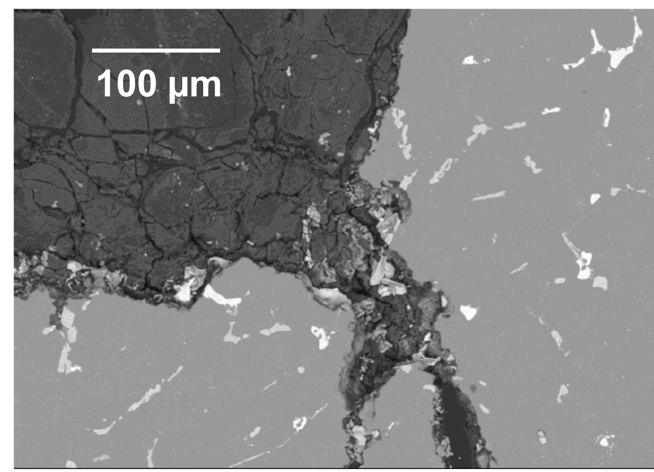
Accomplishments and Progress – Task 1

- Engines for destructive analysis provided by USCAR Partners

- When aluminum corrosion is detected
  - intensity varies
  - corrosion products obscured or contaminated by combustion products
  - aluminum and oxygen in variable stoichiometry

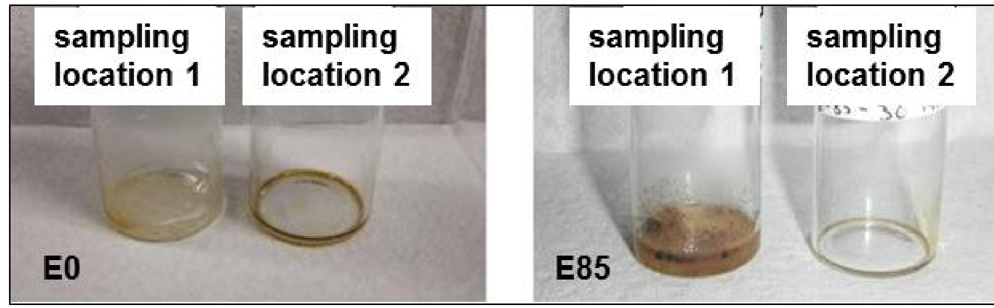
- Metallography indicates primarily pitting and some aggressive general attack; some hints that second phase is relatively resistant





Accomplishments and Progress – Task 2

- Samples collected from operating engine with support of USCAR Partners
  - E0 and E85
  - 30 min collection



- Two liquid phases collected

aqueous phase	organic phase
pH = 3 (E0) and pH = 3.5 (E85)	> 95% aromatic hydrocarbons
formic and acetic acid	E85 product has more aromatics

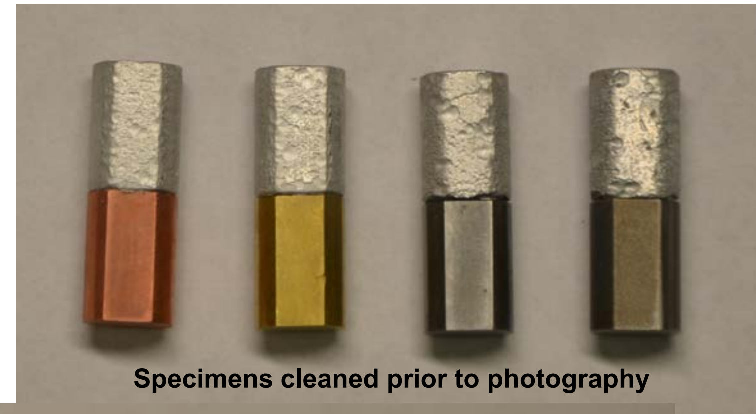
- Sampling location #1 produced more than twice the condensate of sampling location #2 in both experiments

Accomplishments and Progress – Task 3

- **No galvanic corrosion of Al observed:**

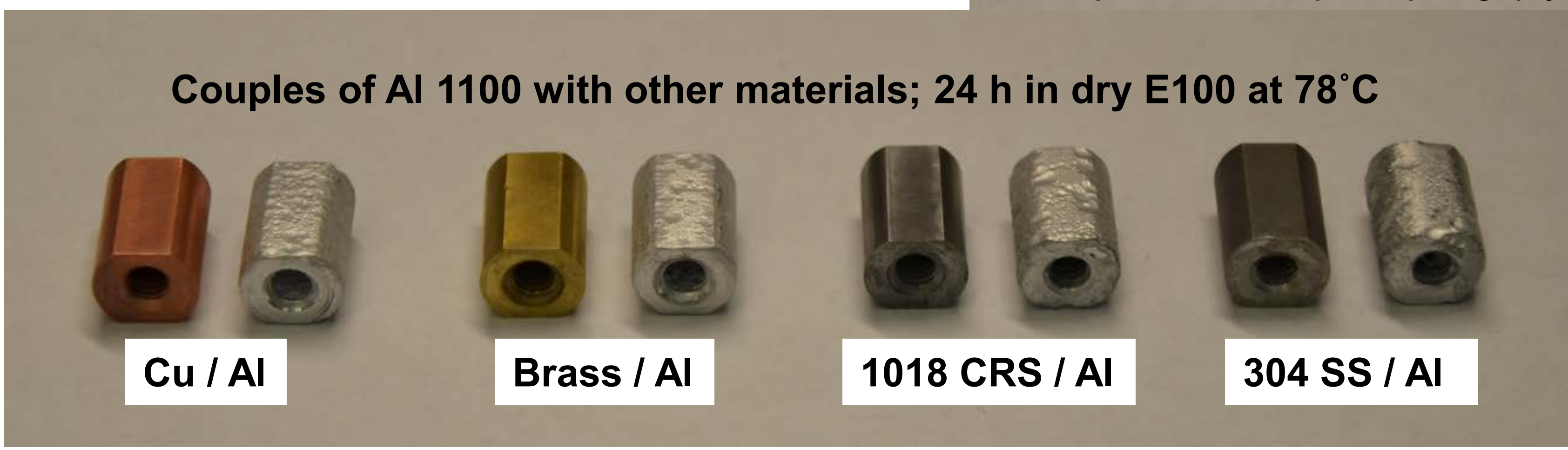
  - direct coupling of dissimilar metal specimens does not accelerate aluminum corrosion

  - metallographic observations suggest second phase does not accelerate attack in cast alloys



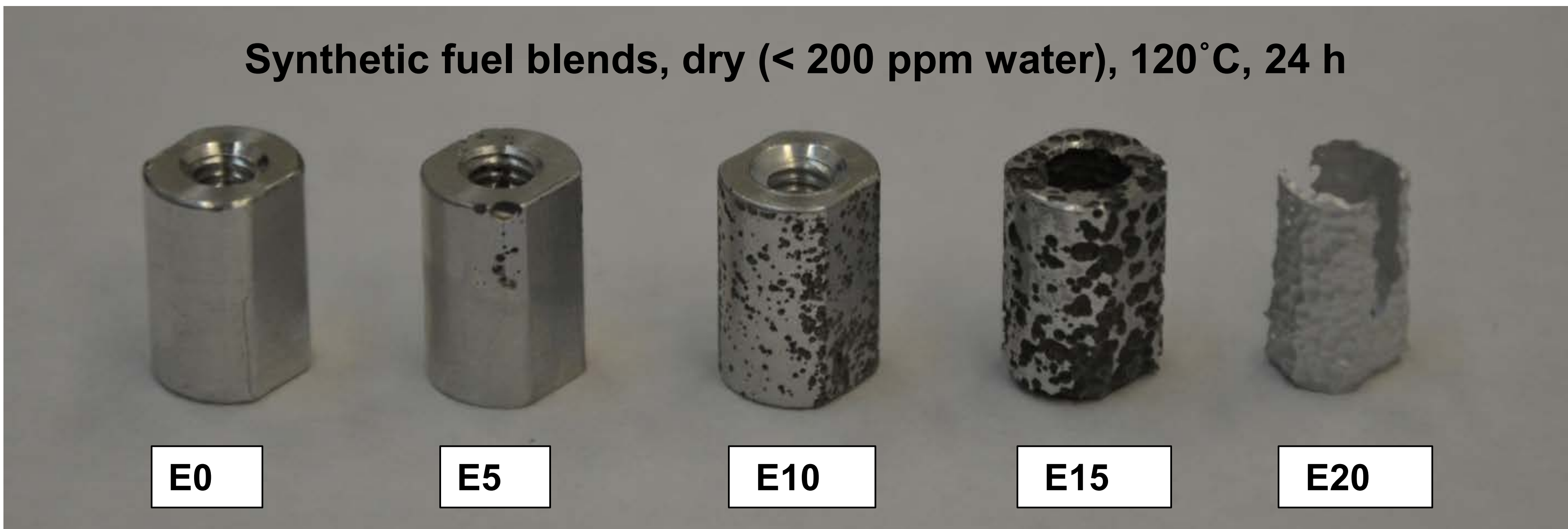
Specimens cleaned prior to photography

Couples of Al 1100 with other materials; 24 h in dry E100 at 78˚C

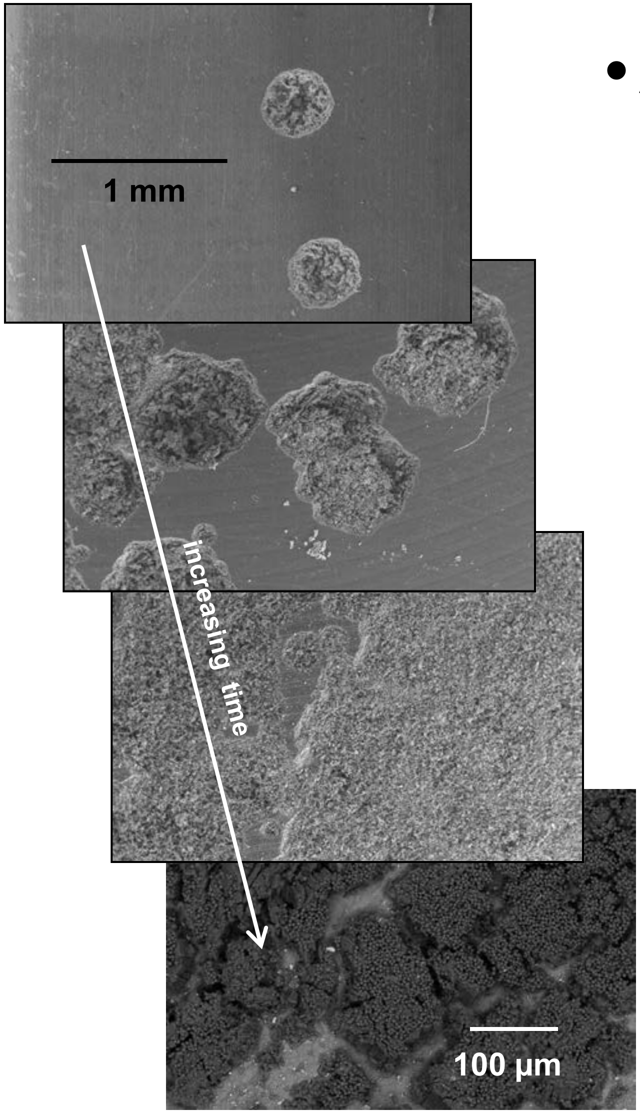


Accomplishments and Progress – Task 3

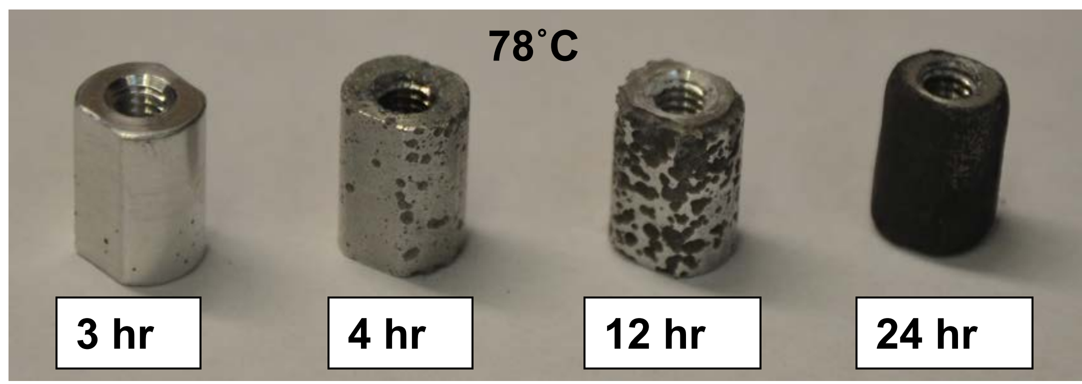
- **Aluminum 1100 exhibited corrosion rates that increased with dry ethanol concentration**
  - **similar trends for other aluminum alloys and fluid temperatures**
  - **increasing %ethanol decreases reaction incubation time**



Accomplishments and Progress – Task 3



- **Aluminum corrosion in dry ethanol fuel blends is highly dependent on time of exposure**
  - **Incubation time observed**
    - **-- prior to pit formation**
    - **-- prior to rapid increase in corrosion (active area)**
    - **-- at saturation, dissolved corrosion products (aluminum ethylate ions) precipitate (decrease active area)**



Accomplishments and Progress – Task 3

- **Temperature and water concentration significantly impacts aluminum corrosion in E100**

Temperature (˚C)	Water Content						
	≤ 50 ppm	≤200 ppm	≤ 0.1%	≤ 0.5%	≤ 1%	≤ 5%	≤ 10%
20	No	No	No	No	No	No	No
40	No	No	No	No	No	No	No
60							
80	Yes	Yes	No	No	No	No	No
100							
120	Yes	Yes	Yes	No	No	No	No
140							
160	Yes	Yes	Yes	Yes	Yes	No	No
180							
200	Yes	Yes	Yes	Yes	Yes	No	No

* YES = corrosion occurred in ≤ 24 h

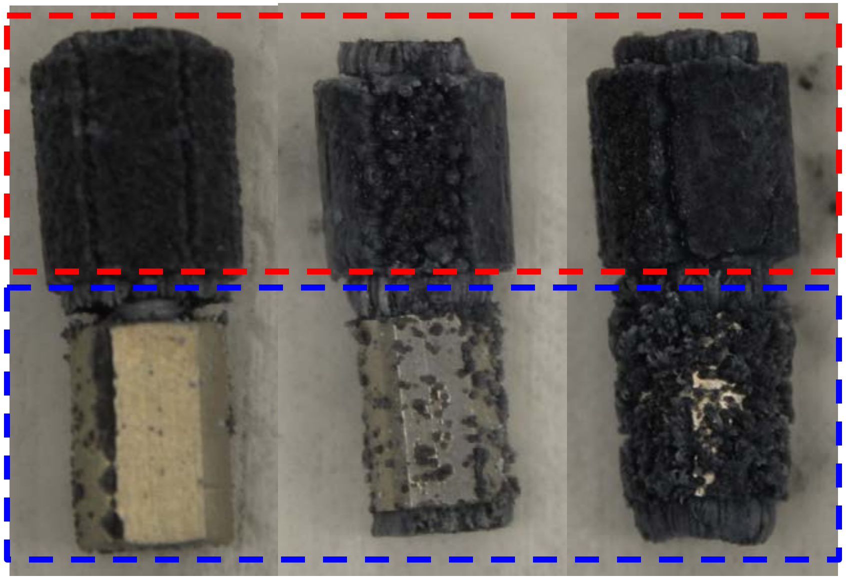
Evaluation time ≤ 24 hrs

Accomplishments and Progress – Task 3

- Modified surface film on aluminum alloys impacted corrosion susceptibility
  - incubation time generally increased
  - extent of corrosion decreased somewhat

Untreated aluminum alloys

Treated aluminum alloys



72 hours, E100, 80°C, $[H_2O]<200$ppm

Accomplishments and Progress – Task 4

- **Observed reactions preclude stable reference measurements at temperatures of interest**
- **Determined galvanic corrosion not a factor**
- **As a result, electrochemical testing is not appropriate**

Future Work

- **Continue laboratory testing**
  - **Expand blend variables to identify corrosive combinations of fuel and materials**
    - **performance boundaries**
- **Continue to explore various mitigation strategies including:**
  - **Fuel additives that would suppress corrosion reaction**
  - **Surface modification strategies to protect underlying aluminum**
  - **Alloy development to address aluminum corrosion susceptibility**

SUMMARY

In Collaboration With Industry Partners, Corrosion Of Aluminum As A Function Of Fuel Blend Exposure Conditions Was Characterized

- Aluminum is fundamentally susceptible to corrosion in ethanol under certain conditions
  - increasing temperature and ethanol concentration accelerate corrosion reactions
  - water in ethanol has an inhibiting effect

- Aluminum corrosion occurs (only) if liquid phase with an aggressive combination of
  - ethanol concentration
  - temperature
  - water content
  - surface condition of metal

  persists for a sufficient duration (incubation time) to initiate reactions

Technical Back-Up Slide 1

proposed corrosion mechanism for aluminum in ethanol with and without water

Excess air, water

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

$$Al_2O_3 + nH_2O \longrightarrow xAlO(OH) + yAl(OH)_3$$

$$Al + 3H_2O \longrightarrow Al(OH)_3 + 3/2\ H_2$$

Limited air, water

$$Al + 3C_2H_5OH \longrightarrow Al^{3+} + 3C_2H_5O^- + 3/2\ H_2$$

$$Al^{3+} + 3C_2H_5O^- \rightleftharpoons Al(C_2H_5O)_3$$

$$Al(C_2H_5O)_3 + 3\ H_2O \longrightarrow Al(OH)_3 + 3C_2H_5OH$$