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Corrosion of Spray Formed Hypereutectic Al-Si-X Alloys in Alcoholic Fuel

PRODUÇÃO TECNICO CIENTÍFICA
DO IPEN
DEVOLVER NO BALCÃO DE
EMPRÉSTIMO

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ABSTRACT

In this study the corrosion behavior of two high silicon aluminum alloys produced by spray forming and a cast iron has been evaluated in alcoholic medium. The comparative results obtained by visual observation and electrochemical impedance spectroscopy are discussed. All tested materials showed extremely low corrosion rates in a commercial alcoholic fuel used as the corrosion test medium.

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INTRODUCTION

There is no general agreement in the literature as to many aspects of the corrosion behavior of metals in alcoholic media such as, type of corrosive attack, nature of corrosion products and aeration effects [1-7]. Although it is generally accepted that impurities in fuel media have a strong effect on the corrosion behavior of the materials exposed to these media, many authors disagree about the contents related to passive or active behavior. Therefore, investigations on this subject are necessary to clarify some conflicting aspects.

In Brazil, many studies were carried out in the 1970's and 1980's to investigate the corrosion behavior of many metals and alloys in alcoholic media to solve corrosion problems caused by ethanol fuel in the automotive industry [1-5]. As a consequence of the technological progress made, based on the research carried out during that period, the main corrosion problems in automotive parts were solved and afterward the number of researches on the subject decreased considerably.

Meantime, the use of aluminum in the automotive industry increased, due to better engine performance, reduction of vibration, weight, wear and pollutant emission. Development of production processes led to the incorporation of new materials of improved properties in the automotive industry. Spray forming permitted the use of hypereutectic Al-Si alloys in the fabrication of cylinder liners. This technique resulted in aluminum alloys with low segregation effects and finely distributed primary silicon particles. This microstructure allowed the mechanical forming of billets by hot extrusion and consequently the manufacture of cylinder liners. There is a growing market for these alloys for application in the so called "all aluminum blocks". However, corrosion studies are required to understand the behavior of the involved materials by fuel environments.

The aim of the present investigation was to evaluate the corrosion behavior of two hypereutectic Al-Si-X alloys, used as cylinder liners as alternative to cast iron and to compare their behavior in alcoholic fuel environment.

MATERIALS AND METHODS

Two hypereutectic Al-Si-X alloys (Alloy 1 and Alloy 2) were used in this investigation. Both alloys were spray formed (Osprey Process). Alloy 1 specimens were prepared from as fabricated preform, showed in figure 2. Alloy 2 is a commercial alloy used in cylinder liners of combustion engines, see figure 2. Specimens of Alloy 2 were prepared from a used cylinder liner.

The chemical composition of the hypereutectic alloys used is shown in table 1 and the composition of the cast iron, in weight percentage, is: Fe=92.7; C=3.1; P=0.1; Si=2.1; S= 0.09.

Table 1. Chemical composition of used Al-Si-X

hypereutectic alloys (wt %).

Alloy	Element						
	Al	Si	Cu	Mg	Ni	Fe	Others
1	67.8	26.6	5.2	0.02	0.006	0.19	0.144
2	71.9	23.2	2.7	1.00	0.960	0.19	0.090

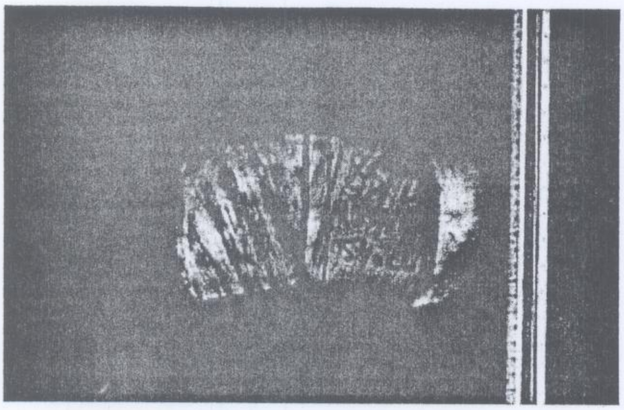


Figure1. Osprey preform of Alloy 1 in the as sprayed condition.

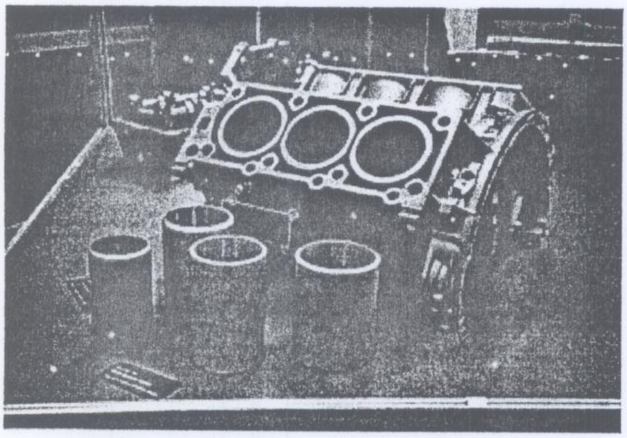


Figure 2. Spray formed aluminum cylinder liners used in combustion engine.

The methods used in the corrosion evaluation were: gravimetric tests after increasing times of immersion, to estimate corrosion rate and pitting density; electrochemical impedance spectroscopy (EIS); and surface observation at increasing times of test.

Rectangular specimens with area of approximately 0.4 cm^2 were used in the immersion test. Electrodes were prepared for EIS tests by epoxy cold resin mounting. Electric contact was provided between the material studied and a copper wire, previous to resin mount. The surface of specimens was prepared by mechanical grinding up to #600 finishing.

The corrosion behavior of two hypereutectic Al-Si-X alloys and a cast iron was evaluated in commercial ethanolic fuel, of following properties: water content (5.7±0.2) %; specific mass at 20 °C (0.8086 g/mL); alcoholic content (83.4 ° INPM). Ethanol of analytical grade and ethanol (analytical grade) with chloride and/or acid additions were also used as test media in this study. Tests were carried out at room temperature and the alcoholic media were naturally aerated.

RESULTS

Results of the gravimetric test showed extremely low corrosion rates (order of 10^{-6} mdd) associated to the two hypereutectic alloys and the cast iron tested. The three tested materials showed a bright metallic surface, with no signs of corrosion, after 60 days immersion in commercial alcoholic fuel. This result indicates passivation of the hypereutectic aluminum and the cast iron in the fuel used for immersion tests. The mass variation obtained from the gravimetric tests showed that the alcoholic fuel used was less corrosive towards the tested materials than ethanol (analytical grade). These results suggested the addition of corrosion inhibiting substances to the commercial ethanolic fuel used in the corrosion tests.

The addition of small chloride contents (1 mM) to ethanol caused pitting of the hypereutectic Al alloys. The simultaneous addition of acid (1 mM) and chloride (1 mM), also resulted in pitting corrosion of these alloys, but pitting density (number of pits per cm^2) was larger (45 after 45 days) than that of the alloys immersed in ethanol with addition of chloride only (approximately 10 after 45 days). The immersion tests showed that chloride and increase in acidity are detrimental factors to the corrosion resistance of the Al hypereutectic alloys in alcoholic media, chloride being the cause of pitting corrosion, even at very low amounts.

Surface observation of the two hypereutectic alloys at increasing times of immersion allowed the comparison of the corrosion performance of the two hypereutectic alloys in the alcoholic media used. The results are shown in figure 3.

Ethanol with addition of chloride and acid was the most corrosive medium for both hypereutectic alloys. Pitting corrosion was observed in the two hypereutectic alloys since the first days of immersion in this medium, for all specimens used. On the other hand, all specimens showed extremely high corrosion resistance in the commercial alcoholic fuel used, presenting a behavior typical of passive materials in this medium. No visible signs of corrosion were seen on the specimens of Alloy 2 immersed in this medium during the 60 days of test, and only one of the specimens of Alloy 1 showed signs of corrosion after 30 days of test in alcoholic fuel.

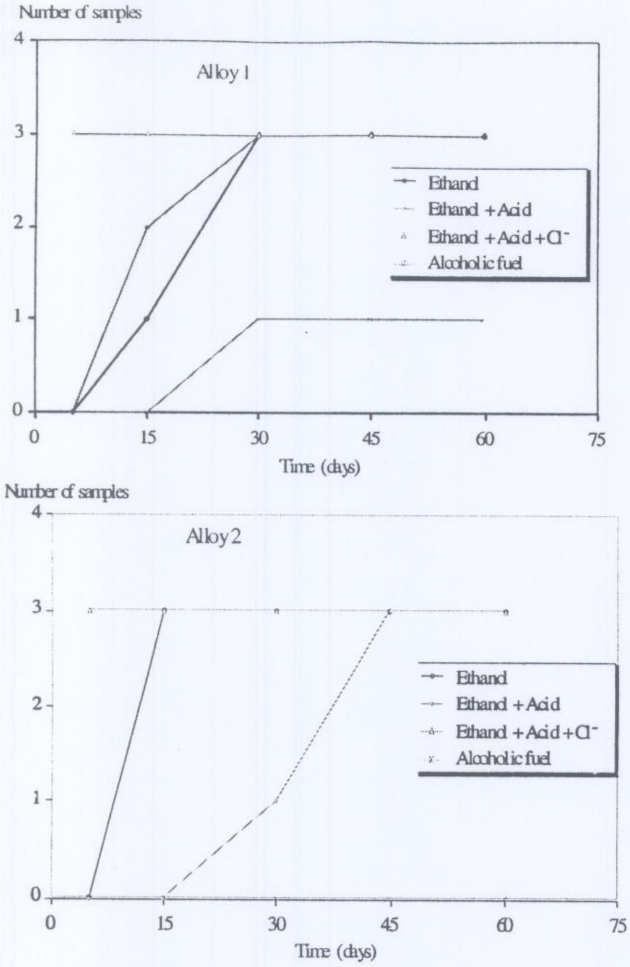
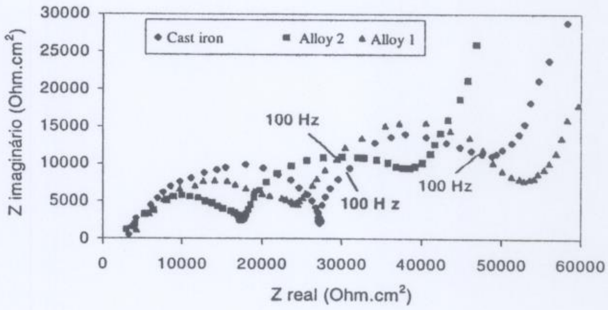


Figure 3. Number of specimens tested (Alloy 1 and Alloy 2) with visible signs of corrosion at increasing times.

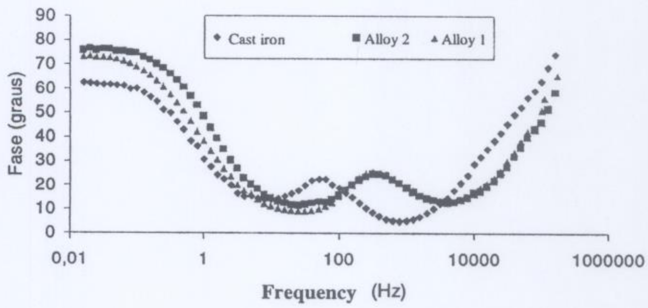
The addition of acid to ethanol apparently increased the corrosivity of the alcohol to Alloy 1 but it did not occur with Alloy 2, indicating that the effect of acid addition on the corrosion behavior of the hypereutectic alloys needs further investigation. The results of surface observation were supported by those obtained by EIS.

Figure 4 shows EIS results of the three materials tested (Alloy 1, Alloy 2 and cast iron) in alcoholic fuel. This figure allows a comparison of the corrosion behavior of the three materials. The Bode diagrams suggest three time constants, indicating the relaxation of three distinct processes. Nyquist diagrams show two flattened capacitive arcs at high and medium frequencies and the initial part of a third process is indicated in the response at low frequencies.

The capacitance values associated to each of the two arcs indicate the process to which they are associated. Bode diagrams show that at low frequencies constant phase angles are obtained for the three tested materials. At low frequencies, Bode diagrams show a highly capacitive behavior suggesting high corrosion resistance of the tested materials, and this capacitive response increases in the following order, cast iron, Alloy 1 and Alloy 2.



(a)



(b)

Figure 4. EIS results of Al-Si-X hypereutectic alloys and cast iron in alcoholic fuel. Nyquist diagrams (a) and Bode diagrams (b).

The capacitance values associated to the first arc (table 2) are typical of organic coatings (paints and lacquers), but in this study, they might be related to the highly resistive medium (alcohol) used. Low conductivity media act as barriers to ionic conduction, similarly to organic coatings. The differences in the values of capacitance are likely due to the experimental set up. Small variations in the distance between the working electrode and the reference electrode would cause significant differences in these values.

The capacitance values associated to the second arc (medium frequencies) are typical of oxides, and must be related to the air formed passive oxide that apparently continues to grown during immersion in the alcoholic fuel medium. The larger capacitance values associated to cast iron might be caused by an increased porosity of the oxide formed on this material comparatively to the porosity of the oxides on the hypereutectic alloys. The graphite phase must affect negatively the uniformity and continuity of the oxide formed on the cast iron. Alternatively, the homogeneous distribution of second phase particles of small sizes associated to the hypereutectic alloys must result in more uniform and continuous oxide films, an consequently, of lower porosity.

Table 2. Capacitance values associated to the two arcs in Nyquist diagrams.

First arc	
Capacitance (F/cm^2)	
Alloy 1	1.38×10^{-10}
Alloy 2	2.11×10^{-10}
Cast iron	5.26×10^{-10}

Second arc	
Capacitance (F/cm^2)	
Alloy 1	1.80×10^{-8}
Alloy 2	5.68×10^{-8}
Cast iron	1.24×10^{-7}

CONCLUSIONS

All tested materials, which were two hypereutectic aluminum alloys produced by spray forming and a cast iron, showed extremely low corrosion rates in a commercial alcoholic ethanol fuel used as the corrosion test medium. Surface observation at increasing times of test, supported the indication of a passive state for the three studied materials in the commercial alcoholic fuel used. Results of electrochemical impedance spectroscopy also indicated high corrosion resistances for all materials tested in the ethanolic fuel. It also suggested that the corrosion resistance of the tested materials increased in the following order: cast iron, Alloy 1 and Alloy 2.

The results indicated that care must be taken as to the contamination of alcohol with chlorides. Chlorides are very harmful to the corrosion resistance of aluminum alloys, causing pitting corrosion even when at very low contents in the medium. The effect of acidification of alcoholic media on the corrosion behavior of the hypereutectic alloys needs further investigation. The combined effects of chloride addition and increase in acidity are even more detrimental to the corrosion resistance, increasing pitting corrosion.

ACKNOWLEDGEMENTS

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