*Key Engineering Materials Vols. 189-191 (2001) pp 352-357*

*doi:10.4028/www.scientific.net/KEM.189-191.352*

# Corrosion of Spray Formed Al-Si-Cu Alloys in Ethanol Automobile Fuel

S.M. Traldi[1], I. Costa[1] and J.L. Rossi[2]

[1] IPEN, Instituto de Pesquisas Energéticas e Nucleares, Traverssa R. 400, Cidade Universitária, CEP 05508-900 São Paulo, Brazil

[2] Powder Processing Center CCP, Instituto de Pesquisas Energéticas e Nucleares, IPEN, CEP 05422-970 São Paulo, Brazil

**Keywords:** Al-Si Alloy, Corrosion, Ethanol Automobile Fuel, Spray Forming

**Abstract:** The use of aluminium alloys in the automotive industry has the weight saving attractiveness leading to improved engine efficiency and reduced vibration. The main restriction for the use of highly alloyed aluminium-silicon alloys is the casting difficulty. The spray forming technique allows the production of preforms of uniform microstructure, fine grains and low segregation effects. There are feasible commercial markets for spray formed Al-Si alloy for pistons, con-rod and cylinder liners. The use of these alloys in the automotive industry means that their corrosion performance in fuel environments needs to be evaluated. Lately, the interest in alcoholic fuels has been increasing due to pollutant emission restrictions. In this investigation, the corrosion behaviour of two Al-Si-Cu alloys produced by spray forming has been studied by means of weight loss measurements, electrochemical impedance measurements and potentiodynamic polarisation tests. The tests were carried out in ethanol automobile fuel. The corrosion of a grey cast iron has also been investigated, in the same solution for comparison reasons.

## Introduction

In the last decades, the automotive industry has been searching for new materials with increased performance. For this purpose, new technologies have been developed which resulted in the production of materials with improved properties such as low weight associated with low coefficient of thermal expansion and excellent mechanical properties - mainly wear resistance at high temperatures. The main types of alloys studied so far are Al-Li and Al-Si alloys [1,2].

Among the commercial Al-Si alloys, the hypereutectics have been found to be interesting, mainly because of their high wear resistance, a consequence of the high volume fraction of the primary-silicon phase. However, it was only after the technological development, represented by the introduction of the spray forming processes, the production of industrial components, such as cylinder liners, made possible. The spray forming process allows the production of Al-Si alloys with fine and homogeneously distributed primary-silicon phase[3- 6].

In recent years, there have been increasing concerns regarding environmental pollution, mainly that caused by fuel emissions from automobiles. This has renewed interest in ethanol automobile fuels as substitutes for petrol (gasoline) in internal combustion engines, since ethanol is considered more environment friendly compared to petrol. Several research programs were carried out in Brazil in the 70's and early 80's [7-10] on the corrosion behaviour of materials used in ethanol fuelled cars and trucks. Despite the decreasing number of automobiles using ethanol as fuel nowadays, the Brazilian Government is showing increasing interest in the use of ethanol as fuel and has already allowed the amount of ethanol in petrol to be increased.

Since one of the many applications of Al-Si alloys is in the automotive industry, as pistons, con-rods and cylinder liners, the knowledge of their corrosion behaviour in fuel environments is necessary. This investigation has been carried out to characterise the corrosion behaviour of two Al-Si-Cu alloys in ethanol automobile fuel. The corrosion behaviour of a grey cast iron was also studied in the same medium for comparison.

**Materials and Methods**

***Materials.*** The materials used in this investigation consisted of two hypereutectic Al-Si-Cu alloys, named alloy 1 and alloy 2. The chemical composition of these alloys is given in table 1. A grey cast iron was also used, since it is commonly used in some similar application as the Al-Si alloys. Alloy 2 is actually used in cylinder liners of internal combustion engines, and alloy 1 is being considered for similar applications. Both alloys have been produced by spray forming - Osprey Process.

**Table 1.** Chemical composition of Al-Si-Cu hypereutectic alloys investigated

| Material | Element (wt. %) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Al | Si | Cu | Mg | Ni | Fe | Other |
| Alloy 1 | 67.8 | 26.64 | 5.2 | 0.02 | 0.006 | 0.19 | 0.144 |
| Alloy 2 | 71.9 | 23.16 | 2.7 | 1.00 | 0.960 | 0.19 | 0.090 |

***Test environments:*** Corrosion testing was performed in ethanol automobile fuel whose composition is given in table 2. Two solutions were used for the removal of the corrosion products formed during the immersion test: (i) a Clarke's solution and (ii) a solution of chromic and phosphoric acids, for the grey cast iron and the aluminium alloys, respectively. The solutions and the procedures used for the removal of corrosion products were according to ANSI/ASTM G1–72[11]. All the tests were carried out at room temperature, and the test medium was quiescent. The specimens were immersed in the ethanol automobile fuel and the potential allowed to stabilise for one day. After stabilisation, the electrochemical tests were performed.

**Table 2.** Results of chemical analysis of the ethanol fuel used.

| Chloride (ppm) | Sulphate (ppm) | Pb (ppm) | Fe (ppm) | Water (g/L) | Total acidity (mg KOH/g) |
|---|---|---|---|---|---|
| <10.0 | <10.0 | <0.21 | 1.20 | 15.28 | 0.01 |

***Weight loss test.*** The weight loss test was carried out according to ANSI/ASTM G1–72 [11]. Rectangular specimens of alloys 1 and 2, and of the grey cast iron, were cut to size with an area of approximately 4 $mm^2$. The surfaces were prepared by successive grinding with emery paper of grades 320, 400 and 600. Subsequently, the area of the specimens was measured. Prior to corrosion testing the exposed surfaces of the specimens were ultrasonically cleaned in methanol and dried in a hot air stream. After immersion in the ethanol automobile fuel for specified lengths of time the specimens were withdrawn, the corrosion products on their surfaces removed, rinsed, dried and weighed. The specimens were re-immersed in the test environment for a new immersion period. Initially, the specimens were weighed after 1 day of immersion and later on at 5 day intervals.

***Electrochemical impedance spectroscopy.*** The electrochemical impedance spectroscopy tests were carried out using a Solartron 1255 frequency response analyser coupled to EG&G 273A potentiostat, and controlled by a software PAR model 398. The perturbation amplitude of voltage for the EIS test was 10 mV and the frequency range was from 100 kHz to 10 mHz.

***Potentiodynamic polarisation tests.*** Potentiodynamic polarisation tests were performed with a potentiostat / galvanostat (EG&G PARC, model 273 A) interfaced with a microcomputer via a GPIB interface. A three-electrode system was employed, with an Ag/AgCl electrode as the reference electrode, and a graphite rod as the counter electrode. A salt bridge filled with agar-agar with 5 (wt. %) $Na_2SO_4$ was used to avoid contact of the working electrode with the test medium. The capillary tip was placed near the surface of the working electrode (approximately 2 mm). The polarisation of the specimens was carried out in a range from –1.0 V up to 1.5 V, at a sweep rate of 1.0 mV/s. Ohmic drop compensation was used by the current interruption method.

**Results and Discussion**

The results obtained from the gravimetric test are shown in figure 1. Both the Al-Si-Cu alloys presented much lower weight losses compared to the grey cast iron. The grey cast iron specimens showed increasing weight losses with immersion time, indicating that the corrosion product layer on its surface did not protect the underlying metal. The corrosion resistance of alloy 2 was slightly higher than that of alloy 1, although both alloys showed similar kinetics. A reason for the difference in the corrosion behaviour of the two Al-Si-Cu alloys could be attributed be their microstructures, which are shown

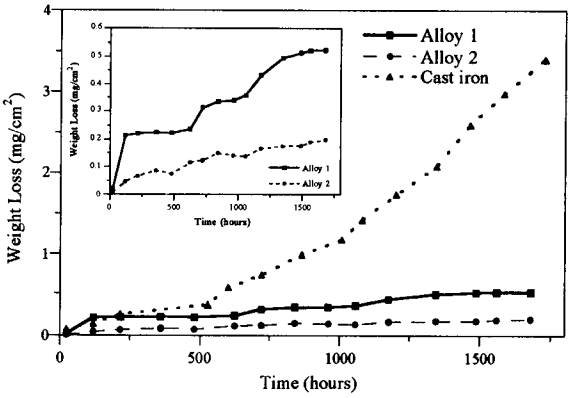


**Figure 1.** Weight losses of Al-Si alloys and grey cast iron in ethanol automobile fuel. The insert in the figure shows only the weight losses of the two Al-Si-Cu alloys.

The weight loss curves of both the Al-Si-Cu alloys displayed successive periods of increasing weight loss followed by periods of stabilisation. This indicates the cyclic exposure of new areas of the metal/alloy to the corrosive environment. The exposure of new material lead to accelerated kinetics and consequently, rapid formation of corrosion products, which eventually covered the underlying material, causing the weight loss to stabilise until new areas were once again exposed. Figure 3 shows the surface morphologies of the corrosion products on the materials tested.

The corrosion layer formed on both Al-Si-Cu alloys show discontinuities. White particles of primary-silicon phase can be seen to detach from the surface. The material surrounding these particles appearss to have been attacked, and this could have caused them to detach. At these regions, new material would become exposed to further corrosion. The corrosion product formed on the grey cast iron was more voluminous and presented many cracks, accounting for the continuously weight loss during the whole test period.

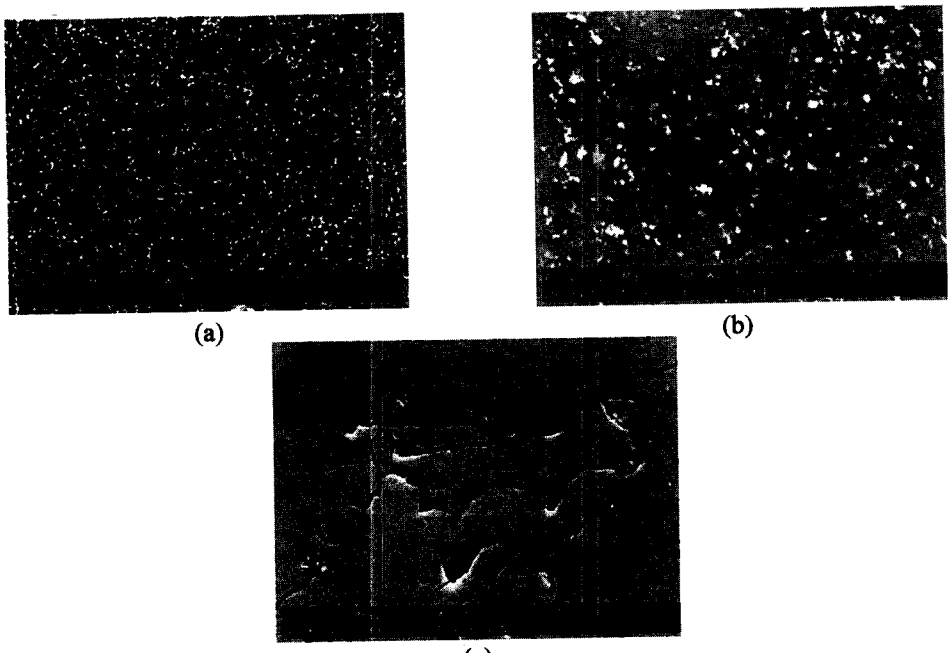


**Figure 2.** Scanning electron micrographs of (a) alloy 1 and (b) alloy 2, showing very fine and evenly distributed primary silicon phase and (c) grey cast iron, showing the graphite lamellae.

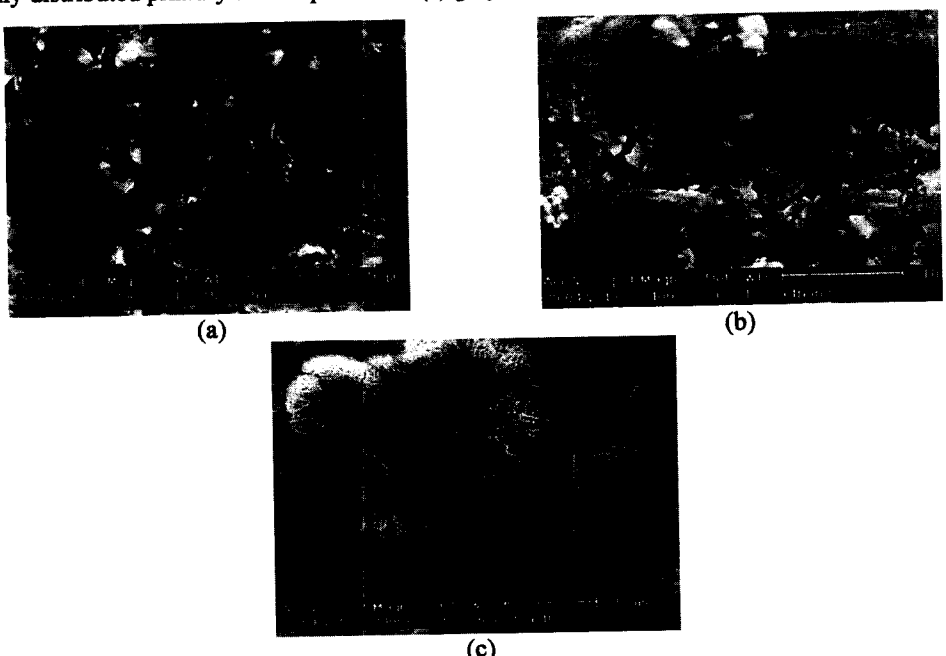


**Figure 3.** Morphologies of corrosion products on (a) alloy 1, (b) alloy 2 and (c) cast iron.

Based on the weight loss test, the tested materials in increasing order of corrosion resistance are: grey cast iron, alloy 1 and alloy 2. The results from the electrochemical impedance measurements are shown in figure 4.

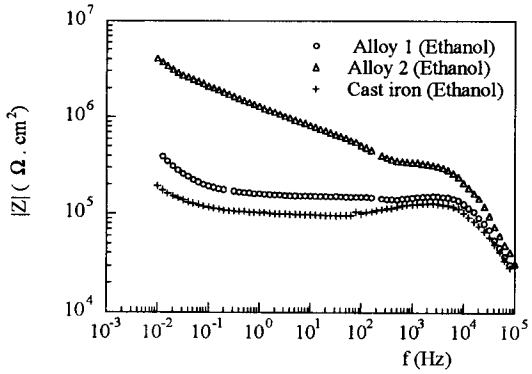


**Figure 4.** Bode diagrams (log |Z| vs. log f) of the materials tested in ethanol fuel.

The impedance response also indicated that alloy 2 had the highest corrosion resistance among the tested materials, followed by alloy 1, and finally the grey cast iron with the lowest corrosion resistance, supporting the results obtained from the weight loss test. The electrochemical impedance data also suggested that all the three materials tested had high corrosion resistance after one day of immersion in ethanol fuel. In fact, figure 1 showed that after one day of immersion all the materials tested had low weight losses. Tests are to be carried out after longer periods of immersion.

Potentiodynamic polarisation data of the materials, shown in figure 5, confirms the results of the electrochemical impedance and weight loss measurements The corrosion potential and corrosion rates estimated from the polarisation curves are shown in table 3. As can be seen, the corrosion rates of both the tested materials, after one day of immersion, were lower than 1 $\mu A/cm^2$, suggesting that all the tested materials were passive in the ethanol fuel used in the test. The corrosion rates increased in the following order, alloy 2, alloy 1 and grey cast iron. Figure 5 also shows that both reactions, the cathodic and the anodic reactions, were depolarised on the grey cast iron compared to those on both the Al-Si-Cu alloys, and despite its nobler corrosion potential, much higher corrosion rates were obtained for the grey cast iron. The presence of graphite in its microstructure must be partially responsible for this behaviour. Graphite is a conductor and the cathodic reaction can easily take place on its surface. The electrical contact of graphite with another more active phase (ferrite) depolarises the anodic reaction on the active phase.

The passive layer on alloy 2 showed a higher resistance to polarisation than that on the other materials. Transpassivity in alloy 2 only occurred at approximately 1000 mV (vs. Ag/AgCl). For the other two tested materials, small overpotentials caused significant increase in the corrosion currents, indicating, dissolution of the passive layer.

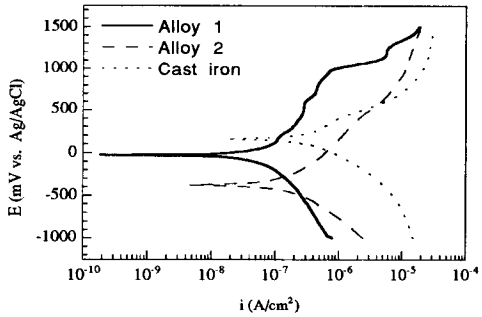


**Figure 5.** Potentiodynamic polarisation curves of materials studied in ethanol fuel

**Table 3.** Corrosion potential and corrosion rates from the polarisation curves.

| | $E_{corr}$ (mV vs. Ag/AgCl) | $i_{corr}$ ($nA/cm^2$) |
|---|---|---|
| Alloy 1 | -373 | 261.2 |
| Alloy 2 | -32 | 159.5 |
| Cast iron | 156 | 938.5 |

Another observation is that the cathodic and anodic reactions on alloy 1 were depolarised compared to those on alloy 2. This could be partially due to the higher silicon content in alloy 1 and consequently, of primary silicon in the microstructure, as shown in figure 2. The primary silicon particles, which are smaller and more homogeneously distributed in alloy 1, compared to those in alloy 2, could be facilitating the cathodic reaction on the surface of the former, besides providing sites for galvanic cells, resulting thereby in the lower corrosion rate of alloy 2 compared to alloy 1.

**Conclusions**

The Al-Si-Cu alloys showed high corrosion resistance in the ethanol fuel used as a test medium, and were far superior to the corrosion resistance of the grey cast iron. The Al-Si-Cu alloy with higher Si and Cu contents had lower corrosion resistance, and this is probably due to the larger percentage of primary silicon phase in that alloy. Further investigation is needed and is in progress.

**Acknowledgements**

The authors acknowledge the support received from FAPESP in the provision of a scholarship to S. M. Traldi, to the Powder Processing Centre - CPP and to Osprey Metals - UK for material supply.

**References**

[1] STOCKER, P.; RÜCKERT, F. and HUMMERT, K. The new aluminum - silicon cylinder barrel technology for die-cast aluminum crankcases. MTZ Motortechnische Zeitschrift, v. 58, n. 9, 1997, p.16-19.

[2] STALEY, J. T. and LEGE, D. J. Advances in aluminum alloy products for structural applications in transportation. Journal de Physique IV, Colloque C7, supplément au Journal de Physique III, v. 3, November 1993, p. 179-190.

[3] REDDY, A. S.; PRAMILA BAI, B. N.; MURTHY, K. S. S. and BISWAS, S. K. Wear and seizure of binary Al-Si alloys. Wear, v. 171, January 1994, p. 115-127.

[4] ESTRADA, J. L. and DUSZCZYK, J. Characteristics of rapidly solidified Al-Si-X preforms produced by the Osprey process. Journal of Materials Science, v. 25, 1990, p. 1381-1391.

[5] ANAND, S.; SRIVATSAN, T. S.; WU, Y. and LAVERNIA, E. J. Processing, microstructure and fracture behaviour of a spray atomized and deposited aluminum-silicon alloy. Journal of Materials Science, v.32, 1997, p. 2835-2848.

[6] ESTRADA, J. L.; JUAREZ, F.; LAVERNIA, E. J. Microstructure analysis of the alloy A-390 and the Al-Si (308) MMC processed by atomization and deposition. Advances in Powder Metallurgy and Particulate Materials , v. 1, Conf. Paper, Chicago, 1997, p. 2-61 and 2-70.

[7] WANDERLEY, V. G.; BASTOS, S. M. ; WEXLER, S. and ULLER, L. The corrosivity of some metallic materials in alcohol motor fuel and type C petrol - the inhibitor effect of C in the corrosion. 9º Seminário Nacional de Corrosão, 1982, p.369-382. (In Portuguese)

[8] PERSIANTSEVA, V. P.; ROZENFELD, I. L.; ZORINA, V. E.; ENIKEEV, É. K H. and CHURAEVA, M. I. Corrosion of aluminium, copper and steel in aqueous ethanol. Protection of Metals, v. 15, n. 3, May-June 1979, p.245-248.

[9] WOLYNEC, S. Corrosion in alcohol powered vehicles, problems and solutions. Anais do 10º Senacor, 16-20 May 1983, Rio de Janeiro, p.17-31. (In Portuguese)

[10] TANAKA, D. K. and WOLYNEC, S. Corrosion in metals by alcohol: literature survey. 3º Simpósio Nacional de Corrosão na Produção e Utilização do Álcool, 7-9 December 1983, Annex 52, p. 1-38. (In Portuguese)

[11] ANSI/ASTM G1–72 - Standard recommended practice for preparing, cleaning and evaluating corrosion test specimens. American National Standards, 1979, p. 781-786.

**Advanced Powder Technology II**
doi:10.4028/www.scientific.net/KEM.189-191

**Corrosion of Spray Formed Al-Si-Cu Alloys in Ethanol Automobile Fuel**
doi:10.4028/www.scientific.net/KEM.189-191.352