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ABSTRACT

In this study, the corrosion resistance of four Al-Si hypereutectic alloys has been investigated in a solution of chemical composition typical of the condensed solution from automotive fuel combustion products - here named automotive synthetic condensed solution. The significance of the undertaken study was in the evaluation of materials used for cylinder liners fabrication in relation to the Brazilian motor fuel. Three commercial Al-Si alloys that have been used for cylinder liners and a laboratory made alloy (Osprey Process) were evaluated by electrochemical impedance spectroscopy measurements at increasing times of immersion in this solution. The surfaces of the alloys were evaluated before and after corrosion test by scanning electron microscopy and. Although the corrosion mechanisms present similarities for all the commercial alloys investigated, the results also indicated different corrosion resistances for these alloys, and these were related to their microstructure characteristics. The laboratory prepared alloy showed increased susceptibility to pitting corrosion comparatively to the commercial alloys.

INTRODUCTION

The increasing demand for improved properties materials from many industries has stimulated the technological development of new materials. For the automotive industry, the most required properties are reduced weight, low thermal expansion coefficient and excellent mechanical properties; mainly wear resistance at high temperatures. In this context, various new materials have drawn much interest, mainly the Al-Si alloys. Of particular interest are the Al-Si-Cu alloys with hypereutectic compositions due to their optimum wear resistance properties. This is a consequence of their large volumetric fraction of primary silicon phase [1-5]. In spite of the optimum properties of hypereutectic Al-Si-Cu alloys, it was only with technological advances, enabled

by the spray forming process, that their properties were optimised [2].

Al-Si-Cu hypereutectic alloys produced by spray forming have optimised mechanical properties due to a fine and homogeneous distribution of primary silicon phase in the aluminium matrix [5]. These are light materials with high wear resistance, and this last property is of major importance for some motor parts, such as cylinder liners. In fact, spray formed Al-Si-Cu hypereutectic alloys have been lately used for the fabrication of cylinder liners where wear resistance is essential. Furthermore, these alloys have low thermal expansion coefficient, high resistance at high temperatures and low weight.

Despite of the recognised excellent mechanical and physical properties of the Al-Si-Cu hypereutectic alloys, their corrosion resistance in aggressive environments is not yet well known. Only recently, research has been carried out to evaluate the corrosion resistance of these alloys in alcoholic fuels [6,7]. Studies on the corrosion resistance of these alloys in corrosive electrolytes, that simulate the environments to which they are usually exposed, are still needed. The aim of the present investigation is to evaluate the corrosion resistance of four hypereutectic Al-Si-Cu alloys, three produced by spray forming and one by conventional metallurgy method, in an electrolyte of composition typical of the condensed solution obtained from fuel combustion. The chemical composition of the fuel varies from country to country, and particularly in Brazil, where alcohol is added at large amounts to gasoline. Since these materials have been used in motor cars in Brazil, an evaluation of their corrosion resistance in this kind of fuel media is of fundamental importance.

EXPERIMENTAL

The chemical composition of the Al-Si-Cu hypereutectic alloys studied is shown in Table 1. Alloy 1 was laboratory made and alloys 2 to 4 were commercially

produced. Alloys 1 to 3 were produced by spray forming. Alloy 4 showed eutectics and therefore, it was not likely to be processed by spray forming, instead it was fabricated by conventional metallurgy.

Table 1: Chemical composition (weight %) of hypereutectic Al-Si alloys obtained by atomic absorption spectroscopy and gravimetry (Si).

Alloy	Si	Mg	Ni	Cu	Fe	Al
1	26.64	0.02	0.006	5.20	0.19	Bal.
2	23.19	1.00	0.960	2.70	0.19	Bal.
3	20.76	1.10	0.010	4.00	0.21	Bal.
4	16.13	0.64	0.040	5.00	0.49	Bal.

Test medium

An electrolyte of chemical composition typical of the solution resulting from condensation of gases from petrol fuel combustion, here named automotive synthetic condensed solution (ASCS), was used in this study. ASCS is chemically composed by: ammonium nitrate (0.077 gL^{-1}), ammonium sulphate (1.017 gL^{-1}), potassium chloride (0.1345 gL^{-1}), ammonium hydroxide (0.33 mL L^{-1}) and hydrochloric acid 1 M (5.8 mL L^{-1}). The pH of this solution is 3.3 and its conductivity approximately 4000 mS.

Methods

The corrosion behaviour of the hypereutectic alloys in ASCS was evaluated by electrochemical impedance spectroscopy at increasing times of immersion and by potentiodynamic polarisation measurements after 1 day of immersion. A three-electrode cell arrangement was used for the electrochemical measurements with a platinum wire and a saturated calomel electrode (SCE) as counter and reference electrodes, respectively. The working electrodes were prepared by cold resin (epoxy) mounting of the four hypereutectic alloys, electrically connected to a copper wire. The electrodes surface was prepared by grinding with silicon carbide paper up to grade #2000, followed by polishing with diamond paste $1 \mu\text{m}$, rinsing with alcohol and drying under a hot air stream.

EIS measurements were accomplished with a 1260 Solartron frequency response analyser coupled to a Solartron 1287 potentiostat. All EIS measurements were performed in potentiostatic mode and at the open circuit potential, E_{ocp} . The amplitude of the perturbation signal was 10 mV, and the frequency range studied from 10^5 to 5×10^{-3} Hz, with 6 points per decade. The electrolyte was quiescent, naturally aerated and at a temperature of (20 ± 2) °C. The electrochemical impedance measurements were obtained at increasing test times from 1 day until 6 days of immersion. All tests were carried out in triplicate.

Potentiodynamic polarisation measurements were carried out by means of a Solartron 1287 potentiostat coupled to a computer, in the potential range from the open circuit potential (E_{ocp}) up to 1500 mV (SCE) or to a limit current of 10^{-1} A/cm^2 , with the scanning rate of 1 mV/s.

RESULTS AND DISCUSSION

Figures 1 and 2 show the evolution of the electrochemical impedance spectroscopy (EIS) results with time of immersion for the four alloys studied.

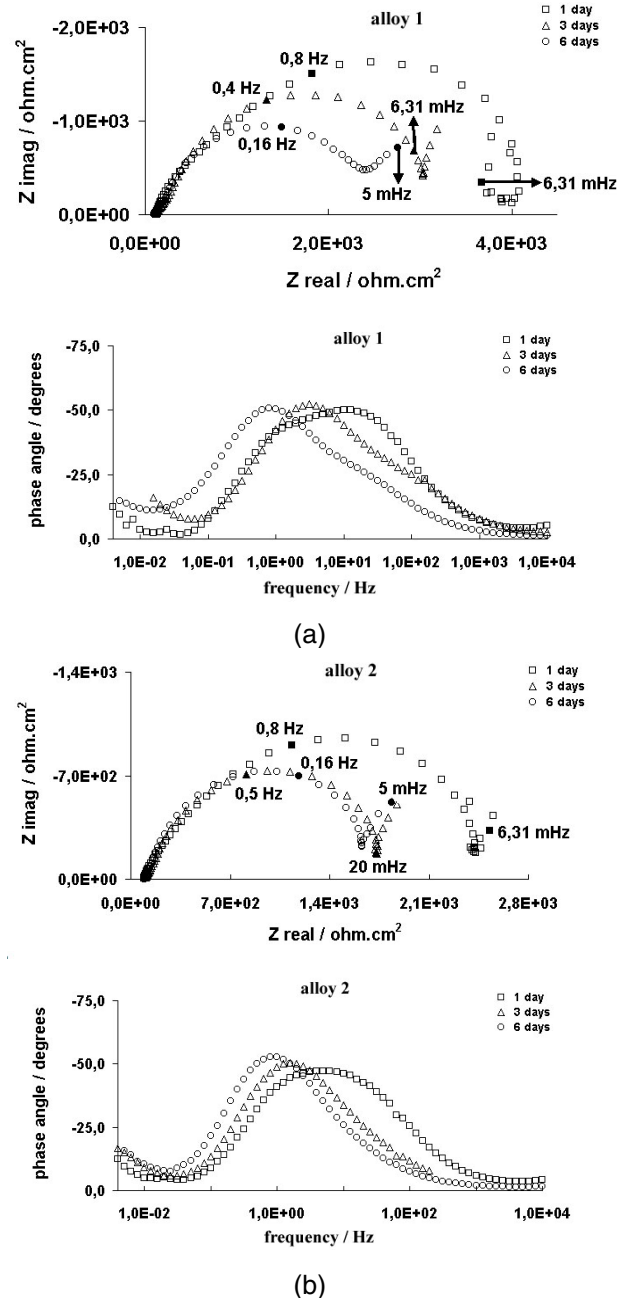


Fig. 1. EIS results for hypereutectic Al-Si-Cu alloys at increasing immersion periods in naturally aerated ASCS, showing Nyquist and Bode phase diagrams for (a) alloy 1 and (b) alloy 2.

The Bode phase diagram corresponding to alloy 1 after

1 day of immersion in ASCS suggests the presence of three time constants. These are indicated by two peaks in the frequency range from 100 Hz to 1 Hz, and the increase in the phase angle, after a minimum, at low frequencies, suggesting three electrochemical processes associated to the hypereutectic alloys in the test solution. For alloy 2, the results for 1 day of test, suggests that the two time constants at medium frequencies (10 Hz to 1 Hz) interact, as indicated by the large peak in the Bode phase diagram. For alloy 1 after day of immersion, the phase angle peak at high frequencies decreases with time and it practically disappears in the diagrams corresponding to alloy 2, from 3 days onwards. This suggests that the contribution of this process to the electrochemical response of the system investigated is gradually decreasing. Another common characteristic in the Bode diagrams is the displacement of the second phase angle peak to lower frequencies as the time increases, indicating a decrease in the kinetics of this process. This time constant is likely related to charge transfer processes.

Nyquist diagrams for alloys 1 and 2 show a depressed capacitive loop from medium to low frequency region. Nyquist diagrams corresponding to alloy 1 show also a consecutive diminution of impedance with immersion time, while a major decrease of impedance was detected for alloy 2 between 1 and 3 days of immersion. For this last alloy, only a slight decrease occurred from 3 days afterward. In the Nyquist diagrams, a straight line is seen at low frequencies (below 20 mHz).

Similar responses were obtained for alloys 2 to 4, all showing a large peak for 1 day of immersion, a major decrease of impedance between 3 and 5 days of immersion and the dislocation of the second peak to lower frequencies. The evolution of the peak at higher frequencies (faster kinetics) was similar for all four alloys studied, showing a significant decrease between 1 and 3 days of immersion.

In a previous work [8], it has been suggested that corrosion on Al-Si hypereutectic alloys starts at the matrix/precipitates interface. These precipitate particles were Al and Cu rich, and could be CuAl_2 intermetallics. Considering that the electrical conductivities of Al ($3.77 \times 10^7 \text{ ohm}^{-1} \text{ m}^{-1}$) and Cu ($5.98 \times 10^7 \text{ ohm}^{-1} \text{ m}^{-1}$) are higher comparatively to that of Si ($1 \times 10^3 \text{ ohm}^{-1} \text{ m}^{-1}$), and that the hydrogen evolution reaction is more polarised on Al (i_0 of approximately 10^{-10} A/cm^2) than on Cu (i_0 around 10^{-7} A/cm^2) [9]. It is most likely that the cathodic hydrogen evolution reaction occurs on the copper rich intermetallics. This last reaction partially balances the anodic reaction due to dissolution of the Al matrix in the acidic test solution, leading to corrosion at the matrix / intermetallics precipitates interface due to a galvanic effect between the two phases. Moreover, the active dissolution of aluminium (matrix) could also be partly balanced by the reaction (1):

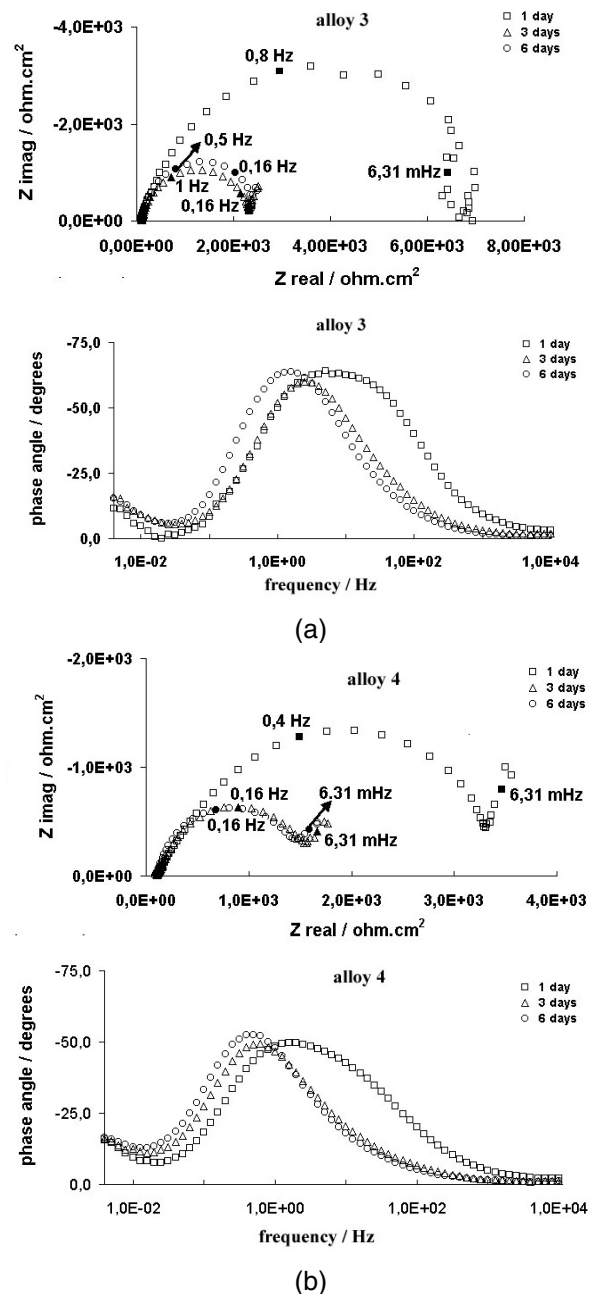
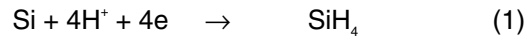


Fig. 2. EIS results for hypereutectic Al-Si-Cu alloys in naturally aerated ASCS at increasing immersion periods, showing Nyquist and Bode phase diagrams for (a) alloy 3 and (b) alloy 4.

Due to the low pH (3.3) of the test solution used, it could be expected that the oxygen reduction reaction would have no main contribution to the overall cathodic rate. However, the EIS response at low frequencies suggests a diffusion-controlled process and this could be related to the reaction (2) that might be controlled by oxygen diffusion to the metallic interface.



Figure 3 shows micrographies of the hypereutectic Al-Si-Cu alloys surface obtained SEM after 6 days of

immersion in the naturally aerated electrolyte (ASCS). The numbers indicate the various phases present in these alloys and correspond to (1) primary silicon phase, (2) matrix, (3) copper rich phase, and (4) the eutectic. These phase were identified by energy dispersive spectrometry

Pitting was only seen on alloy 1, confirming the results of a previous work that indicated a higher pitting susceptibility associated to this alloy [8]. Selective corrosion attack of the Al matrix occurred for all hypereutectic alloys tested, and the primary silicon phase was not attacked. The particles of this last phase appear in Fig. 3 as emerging from the matrix phase. It is proposed that on this last phase, reaction (1), presumably of fast kinetics, occurs. The high supply of hydrogen ions in the test solution used ($\text{pH} = 3.3$) and the high volume fraction of primary silicon particles in the studied alloys, as Fig 3 indicates, must result in a fast kinetics for this reaction. The surface of alloy 4, which was prepared by conventional metallurgy method, shows preferential attack on the aluminium matrix phase (Fig. 3 (d)), mainly at the interface matrix-primary silicon phase, this last phase being left intact. Corrosive attack of the eutectic also occurred.

It is proposed that the electrochemical process of faster kinetics (response at higher frequencies) is due to charge transfer processes associated to reaction (1), and that associated to the second peak in the Bode diagrams, to the anodic dissolution of the matrix. This last reaction can be balanced by the hydrogen evolution reaction on the intermetallics particles, and by reactions (1) and (2). The EIS results suggest that the contribution of the process of faster kinetics decrease with immersion time. This could occur due to the reaction of silicon particles with hydrogen ions forming silicon hydride, according to (1). The higher contribution of this process for alloy 1 comparatively to the other alloys, as indicated in the Bode phase diagrams, could be explained by the larger volume fraction of primary silicon phase in this alloy, resulting from its also greater silicon content, requiring longer periods for reaction (1) completion.

The EIS spectra of all the alloys tested also show similarities for the process with response at medium frequencies (around 1 Hz). The kinetics of this process slows down as time increases, mainly between 1 day and 3 days of immersion, and it is fairly steady between 3 days and 5 days of test. This is a common feature for all tested alloys therefore; it is reasonable to presume that it is related to charge transfer processes associated to the active dissolution of the Al rich matrix phase. Furthermore, the decrease in the kinetics of the anodic process with time that could result from the conversion of Si to SiH_4 would also decrease the overall cathodic rate and, consequently, the dissolution (anodic) rate.

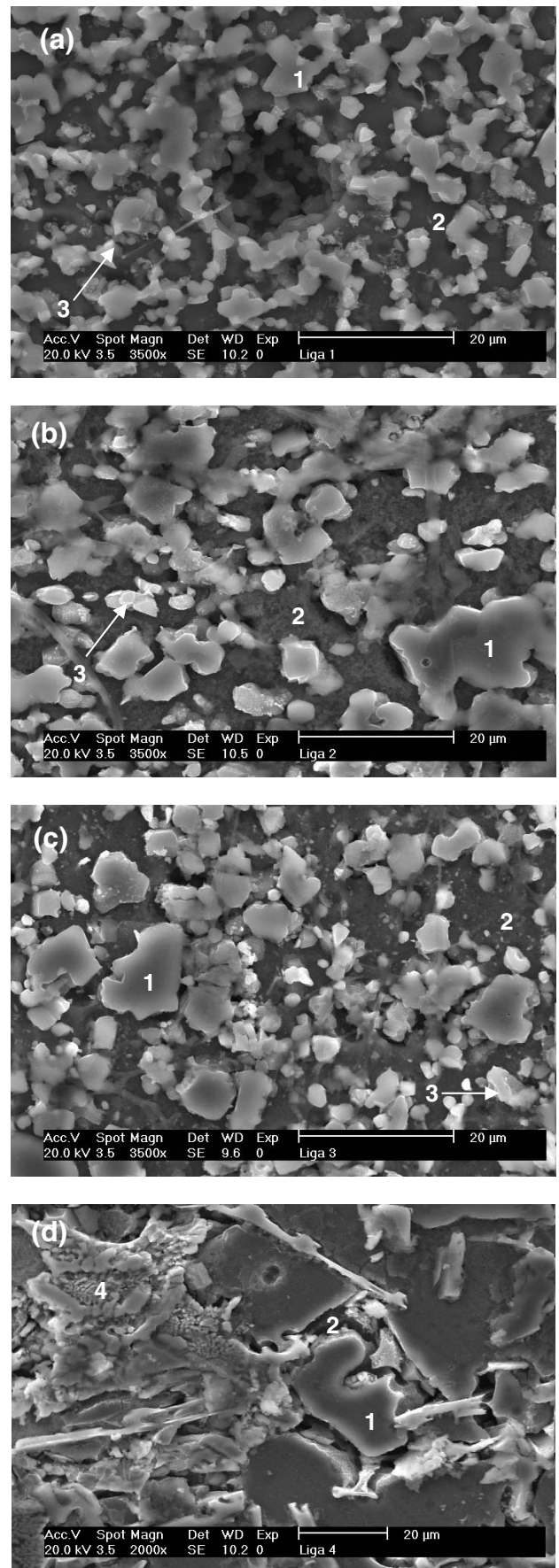


Fig. 3. SEM micrographies of Al-Si-Cu hypereutectic alloys, after 6 days of immersion in naturally aerated ASCS. (a) Alloy 1, (b) alloy 2, (c) alloy 3, (d) alloy 4.

The EIS data at low frequencies indicate similar responses for all studied alloys and it is likely due to faradic processes. The results suggest a diffusion-controlled reaction that could be associated to oxygen transport to the interface, according to reaction (2).

The potentiodynamic polarisation curves, results not presented in this work, supported a higher pitting susceptibility associated to alloy 1 comparatively to the other tested alloys. This increased susceptibility to pitting could be related to the larger copper content in this alloy leading to an also larger volume fraction of copper rich intermetallics precipitates in this alloy, but this needs further investigation.

CONCLUSION

The corrosion behaviour of four Al-Si-Cu hypereutectic alloys in a synthetic solution simulating the condensed solution from automotive fuel combustion products has been evaluated by electrochemical impedance spectroscopy. The results indicated a preferential attack of the aluminium matrix phase in all alloys studied. The alloy with higher copper content and prepared by spray forming was associated to increased pitting susceptibility comparatively to the other alloys. A diffusion-controlled process was indicated in the EIS response at low frequencies, likely due to oxygen transport to the metallic interface.

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