

## The Corrosion Behaviour of a Hypereutectic Al-Si Alloy Obtained by Spray Forming in Acid, Neutral and Alkaline Solutions

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**Abstract:** Al-Si hypereutectic alloys produced by spray forming represent an important technological development for application in the aeronautical and automotive industries. Due to some special properties these alloys find application as cylinder liners, mainly due to their high strength and wear resistance. Much research has been carried out to evaluate the mechanical properties of these alloys but the literature on their corrosion performance is still very scarce. In this study, the corrosion behaviour of a spray formed Al-Si-Cu hypereutectic alloy was investigated by electrochemical impedance spectroscopy (EIS) in acid (pH 3.3), neutral (pH 7) and alkaline (pH 11) solutions. Intense localized attack occurred in the acid electrolyte and the impedance decreased with time of immersion. In the neutral medium, the alloy was passivated but localized attack also occurred on weak areas of the passive film. In the alkaline medium, precipitation of corrosion products occurred during the first hours of immersion causing the increase of impedance but thickening of this layer led to cracks growth with time and, consequently, to the exposure of metallic substrate, resulting in the decrease in impedance for longer periods.

### Introduction

The automotive and aeronautics industries developed various high tensile strength aluminium alloys. However, the increase in mechanical properties has caused a decrease in the corrosion resistance due to the precipitates formed in result of alloying elements added for hardening purposes. The silicon, as the main alloying element in Al-Si alloys, increases the flowability of liquid aluminium, reduces the volume contraction during solidification, reduces porosity and the thermal expansion coefficient, and also improves weldability [1,2]. The combination of silicon and magnesium makes the alloy heat treatable [1]. Copper addition increases the mechanical strength, favours the decrease of internal contraction during solidification and improves machining [2].

Due to their good wear properties, the Al-Si alloys have been chosen as material for use in engine parts. In comparison to grey cast iron, Al-Si alloys present improved properties such as lower specific mass, enhanced heat transfer that leads to reduction in engine temperature, decreased wear and tear between the contact surfaces, smoother contact surfaces and similar thermal expansion to other engine aluminium parts. These properties result in noise reduction, elimination of the machining of dissimilar materials, such as aluminium / iron, and improved recycling properties [3].

One of the production methods of Al-Si alloys is the spray forming, specifically for highly alloyed alloys. Similarly to powders production by atomisation, the spray forming involves the atomisation of metals and the deposition of droplets in a substrate, leading to the formation of a preform. The advantages of spray formed alloys have been extensively documented in the literature [4,5]. However, researches on the corrosion behaviour of these alloys are still very scarce. The

objective of this work was to evaluate electrochemical behaviour of a spray formed Al-Si alloys in an electrolyte that simulates the composition of the condensed solution collected from the exhaustion system of automotive vehicles, with pH adjusted to simulate acid, neutral and alkaline solutions.

## Experimental

The material used in this study was obtained in a spray forming pilot plant. The alloy chemical composition is shown in Table 1. Samples were obtained from the spray formed billet, in the perpendicular direction to the spray deposition. Some samples were analysed in the as received condition, others after hot rolling (at 450°C) using a goldsmith's rolling mill in 0,246 mm steps, and others after cold rolling in the same rolling mill.

The corrosion resistance of the studied material was investigated in an electrolyte that simulates the composition of the condensed exhaust gases from automobiles run in Europe, here called condensed synthetic automotive (CSA) solution. This solution was formulated based on the chemical analyses of the condensed gases obtained from exhaust of automobiles, being the composition supplied by ACESITA [6], and shown in the Table 2. This was chosen taking into consideration the application of the studied alloy in cylinder-liners.

The pH of the as prepared CSA electrolyte was 3.3 and its conductivity was 4 mS. Electrolytes based on the CSA composition and with pH adjusted to 7 and 11 were also prepared by the addition of ammonium hydroxide. The working electrodes were prepared by epoxy cold mounting of the samples, after electrical contact has been provided by a copper wire bonded into one of the Al-Si alloy surfaces. After resin cure, the surface for exposure to the electrolyte was prepared by grinding in SiC emery paper and mechanical polishing with 6 µm and 1 µm diamond paste, followed by final polishing with colloidal silica particles of 0.25 µm. The EIS tests were accomplished using a Solartron 1260 frequency response analyser coupled to a Solartron 1287 potentiostat, controlled by the  $Z_{view}$  and  $Corr_{view}$  software. The frequency range studied was from  $1 \times 10^5$  Hz to  $5 \times 10^{-3}$  Hz, with voltage perturbation amplitude of 10 mV. Experiments were performed in naturally aerated solutions at 25 °C. The evolution of the electrochemical behaviour was accompanied by EIS tests at increasing time.

## Results and discussion

The chemical composition of the Al-Si-Cu hypereutectic alloy used in this study is shown in Table 1. The elements composition, with the exception of Si, was determined by spectrophotometer atomic absorption and the Si content was obtained by gravimetry. The very high Si content in the alloy was only possible due to the fabrication process used, that is, spray forming. The large amount of Cu in the alloy can alter the alloy properties such as corrosion resistance comparatively to other commercial alloys of similar composition.

Table 1. Chemical composition of the Al-Si-Cu hypereutectic alloy of atomic absorption and gravimetry (Si) for the aluminium-silicon hypereutectic alloy (mass%).

Element	Si	Mg	Ni	Cu	Fe	Al
Mass%	26.64	0.02	0.006	5.2	0.19	balance

Fig. 1 shows the evolution of the Al-Si-Cu alloy electrochemical behaviour with time of immersion in the acid solution. The Nyquist diagrams show a flattened capacitive semicircle from high to medium frequencies that was followed by a segment suggesting a second time constant. The evolution of the diagrams showed that the impedance decreased with time. The Bode phase angle diagrams also suggest the existence of at least two time constants. For shorter times (1 to 3 days of immersion) these diagrams indicated the presence of a “shoulder” after the peak at higher

frequencies that disappeared for longer periods. The phase angle peak at higher frequencies moved into lower frequencies between 1 and 5 days of test, suggesting the slowing down of the kinetics of this process during this period. The time constant at lower frequencies (inferior to 0.1 Hz) could be related to localized attack in the alloy.

The flattened semicircle in the Nyquist diagrams also suggested the interaction of two time constants from high to medium frequencies for periods between 1 and 4 days of immersion. It is possible that these are related to the interaction of the dissolution of the more active phases in the alloy coupled to charging of the double layer and transfer charge processes related to the Al rich phase attack. As already mentioned the indication of the interaction of two time constants in the high to medium frequencies is more evident for shorter times of immersion, when a “shoulder” was indicated in the frequency range between 10 and 100 Hz. The selective attack and consequently removal of the more active phases in the alloy comparatively to the matrix must have been the reason for this result. The impedance decrease with time, on the other hand, might have resulted from the intensification of the localized attack with time in the acid medium. It is known that aluminium loses its passivity in environments with pH lower than 4. Other interfacial processes may also contribute for the time constant at higher frequencies, taking into consideration the complex microstructure of the alloy, as shown in Fig. 2 (a). The Bode phase angle diagrams show that between 1 and 4 days, the phase angle peak decreases and moves to lower frequencies, suggesting increasing slower kinetics. This could have been caused by the increasing removal of the more active phases comparatively to the Al rich matrix, due to their selective attack and, consequently, to surface “cleaning”, decreasing the galvanic effects associated to it. On the other hand, the removal of the more active phase might have produced porosities on the surface, favouring localized attack on these areas. Although the Bode phase angle diagrams did not vary significantly between 5 and 6 days, the Nyquist diagrams indicated a decrease in impedance during this period. These results support the hypothesis of the intensification of the localized attack in this medium.

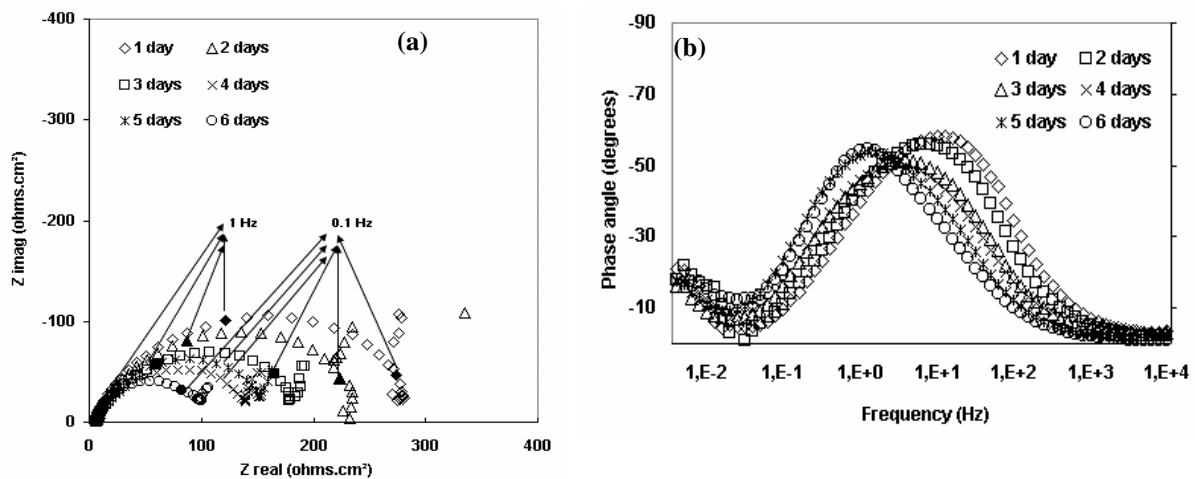


Figure 1. (a) Nyquist and (b) Bode phase angle diagrams for the Al-Si-Cu hypereutectic alloy in CSA (pH 3.3) as a function of time of immersion.

The micrographs of Fig 2 show the surface of Al-Si-Cu alloy in two conditions; (a) after metallographic preparation and before immersion in the electrolyte and (b) after six days of immersion in the CSA electrolyte. The preferential attack of the matrix comparatively to the primary Si phase is clearly seen in Fig. 2 (b). This last phase appears as if they were emerging from the matrix. The susceptibility to localized attack of this alloy is also indicated in this figure, showing pits either previous to or after six days of immersion in the electrolyte (CSA pH 3.3).

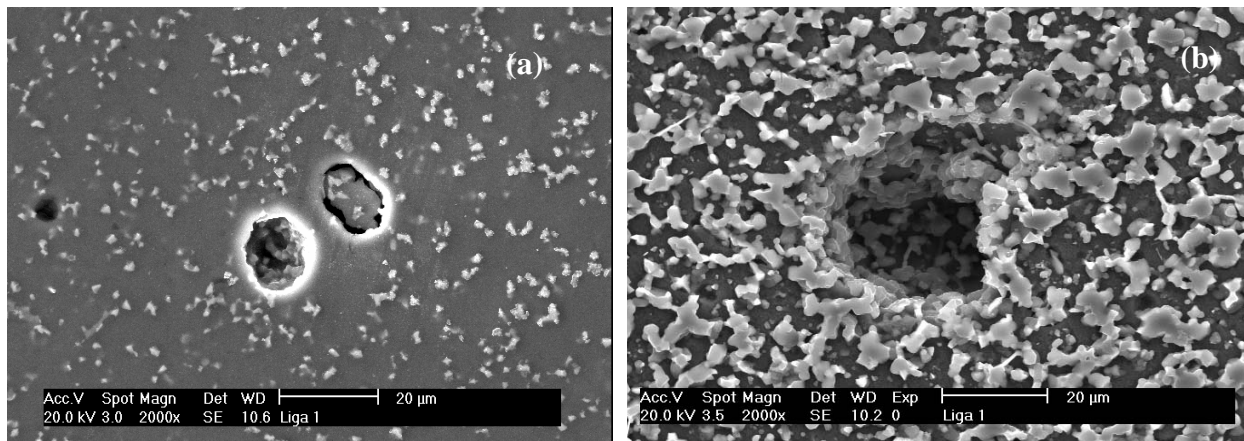


Figure 2. SEM micrographs of the Al-Si-Cu alloy: (a) previous to immersion and (b) after 6 days of immersion in CSA (pH 3.3).

The evolution of the Nyquist and Bode diagrams of the Al-Si-Cu alloy in the neutral CSA medium, between 1 and 6 days of immersion, is shown in the Fig. 3 (a) and (b). The Bode phase angle diagrams clearly indicate two time constants and the Nyquist diagrams show a significant increase of the impedance between 1 and 4 days, a slight decrease between 4 and 5 and it was fairly stable between 5 and 6 days. These results suggest the formation and growth of a surface layer from 1 to 4 days of immersion. It is known that Al is passive in the pH range from 4 to 9, that is, in the pH of this electrolyte. The increase in the second peak with time also suggest that increase in the capacitance associated to this process. It is likely that it is related to the charge transfer processes at the interface that become increasingly hindered by the presence of a growing layer on the surface. The time constant at higher frequencies could be associated to the galvanic effects on the surface due to the presence of various phases with different electrode potentials. The decrease in impedance between 4 and 5 days could be due to localized attack at some weak areas of the passive film by chloride ions present in the electrolyte. The decrease in impedance followed by its increase for periods longer than 4 days indicates the competition between the chloride ions leading to localized attack and the oxygen dissolved in the electrolyte leading to passivation. Consequently, the observed variations could be related to the localized attack and breakdown of the passive film in the surface, followed by its repassivation. The Nyquist diagrams indicate the presence of another time constant at frequencies inferior to 0.1 Hz suggestive of localized attack supporting the hypothesis proposed above.

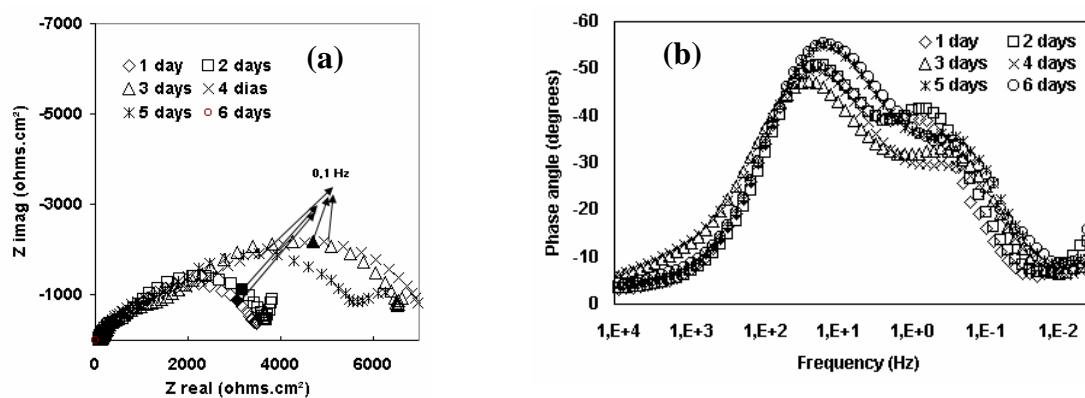


Figure 3. (a) Nyquist and (b) Bode phase angle diagrams of the Al-Si-Cu alloy in CSA neutral (pH 7) solution at various times of immersion.

Fig. 4 shows the alloy surface after 6 days of immersion in the neutral electrolyte. The presence of chloride ions in the electrolyte associated to the highly complex microstructure of the alloy contributes to its high susceptibility to localized attack.

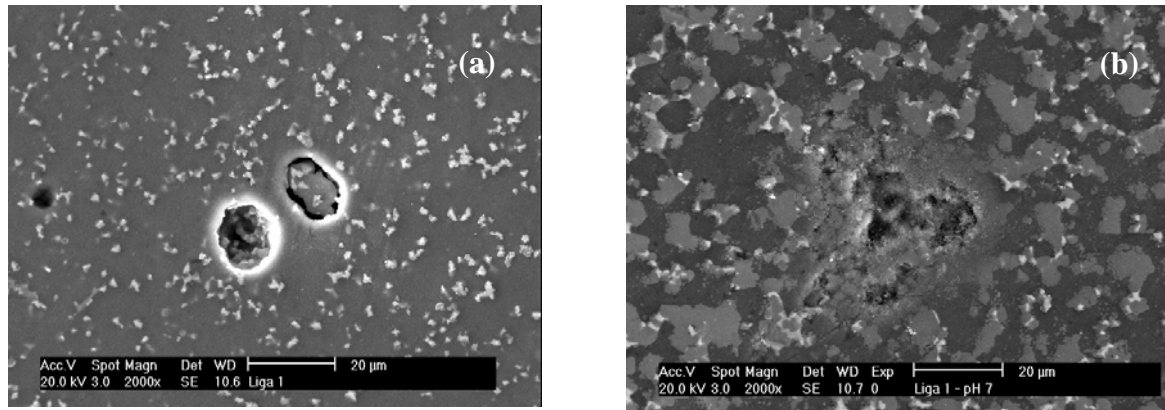


Figure 4. Micrographs of the Al-Si-Cu alloy surface (c) previous to immersion and (d) after 6 days of immersion in CSA pH 7.

Fig. 5 (a and b) shows the evolution of the impedance diagrams with time of immersion in CSA with pH 11, until six days. For one day of test, only a time constant is clearly identified, showing a phase angle peak at frequencies inferior to 0.1 Hz. The corresponding Nyquist diagram indicates a very flattened capacitive semicircle likely due to the surface irregularities and the attack of the matrix at this solution. As mentioned previously the Al is attacked in solutions of pH superior to 10. For 2 days of immersion, however, two time constants are easily seen on the Bode diagrams. This time constant with a phase angle peak between 1 and 100 Hz was seen from 2 until 6 days of immersion. This is probably related to the deposition of corrosion products in the alloy surface during the first day of immersion in the electrolyte. The intense attack that occurred in this medium in fact led to the development of a black corrosion product on the Al-Si-Cu alloy that was easily identified to the naked eye on the surface after removal from the electrolyte. This phase angle peak moved to lower frequencies between 2 and 4 days of test, indicating deterioration of this layer, likely due to its thickening leading to defects development on it. The time constant at lowest frequencies suggests diffusion related processes, probably due to reactive species to the surface or corrosion products through this layer. Between 4 and 6 days immersion, the diffusion controlled processes at lower frequencies are no longer indicated, probably due to the growth of defects, such as cracks or pores that would permit easy access of the species to or out of the surface. The Bode diagrams indicated the capacitive increase of the processes associated to the two time constants between 4 and 6 days, likely due to thickening of the corrosion products layer.

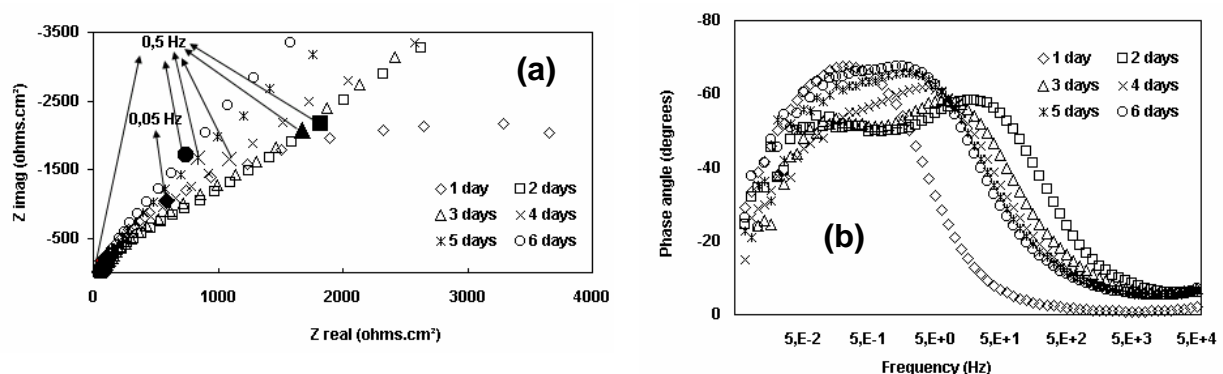


Figure 5. (a) Nyquist and (b) Bode phase angle diagrams for Al-Si-Cu alloy as a function of immersion time in CSA pH 11.

The precipitation of corrosion products in the surface in result of the intense attack of the Al rich matrix during the first hours of test was supported by surface observation by Scanning Electron Microscopy, previous to and after six days of immersion (Fig. 6). The increase in the proportion of primary Si on the alloy surface is clearly indicated. The presence of cracks is also seen after 6 days of immersion in the electrolyte, supporting the hypothesis previously proposed.

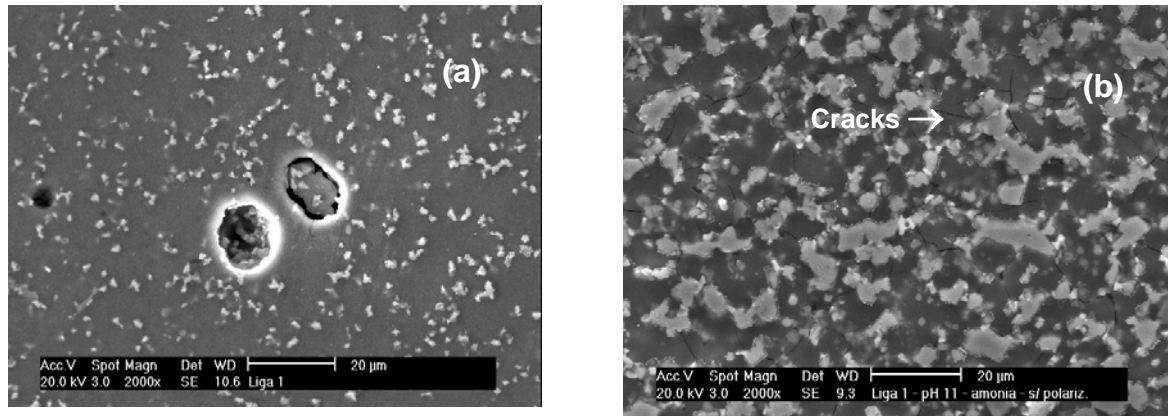


Figure 6. Micrographs of the Al-Si-Cu alloy surface (a) previous to immersion and (b) after 6 days of immersion in CSA pH 11.

The presence of a layer of corrosion products layer easily identified by visual observation of the alloy surface after removal from the electrolyte. A greyish coloured layer was seen, on its surface after 6 days of immersion in the CSA (pH 11) electrolyte.

## Conclusions

The corrosion resistance of an Al-Si-Cu hypereutectic alloy produced by spray forming was investigated in electrolytes whose composition simulates that of the condensed exhaustion gases resulting from combustion in automotive vehicles. The pH of this solution was 3.3. The electrochemical behaviour of the alloy was studied in this electrolyte and two other electrolytes of similar composition with pH adjusted either to 7 or to 11. Intense localized attack occurred in the acid electrolyte and the impedance decreased with time of immersion. In the neutral medium, although the alloy was passivated localized attack occurred on weak areas of the passive film likely due to the chloride ions in the electrolyte. In the alkaline electrolyte, corrosion products precipitated during the first hours of immersion causing the increase in impedance from 1 to 4 days of immersion. The thickening of this layer led to cracks growth with time and, consequently, the exposure of metallic substrate, resulting in the decrease in impedance for longer periods. The results pointed out to the effect of the electrolyte pH on the corrosion mechanism of the studied alloy in electrolytes of similar chemical composition.

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