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# Corrosion Resistance in chloride solution of the AlSi10Mg Alloy obtained by means of LPBF

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## Abstract

The paper deals with the corrosion resistance in chloride solutions of an AlSi10Mg alloy obtained by LPBF process. Potentiodynamic tests were carried out in solutions having different chloride contents. The results emphasize the role of chloride concentration on localized corrosion. The increase of concentration reduces pitting potential. In addition, the influence of the post-processing heat treatment temperature was recognized. Penetrating attacks occurred either on after low temperatures stress relieving or specimens without any treatment, promoted by selective dissolution of the  $\alpha$ -Al phase stimulated by galvanic coupling with noble silicon precipitates at the border of the melt pool. Such penetrating morphology was not observed after heat treatments at high temperature.

## Keyword

Additive Manufacturing; Laser Powders Bed Fusion; Aluminium Alloy; Heat Treatment; Pitting Potential;

## Introduction

Laser Powder Bed Fusion (LPBF) is an additive manufacturing technique for fusion of metal powders, layer by layer, by using a laser moving in accordance with the 3D CAD model<sup>1</sup>. This production method has advantages in terms of cost reduction and manufacturing time. It eliminates the swarf typical of traditional subtractive machining and permits to obtain new complex forms<sup>2</sup>. The manufacture of aluminium components by this technique requires a careful laser scanning strategy to avoid the formation of oxide at the interface between adjacent traces and to limit the porosity<sup>3</sup>. The LPBF machine should be equipped with an inert atmosphere room, being the reactive nature of the metal. Nowadays, the hypoeutectic AlSi10Mg alloy is considered the best aluminium alloy for this technique, allowing to achieve high-density and good mechanical properties<sup>4-6</sup>. It is relatively easy to process by laser applications because its composition lead to a narrow solidification range. A small addition of magnesium (0.3 – 0.5 wt%Mg) is able to induce precipitation hardening by forming dispersed Mg<sub>2</sub>Si phase during natural or artificial ageing. In addition, the alloy shows adequate corrosion resistance in mild environments and atmospheric exposure, because of the natural ability to form a stable and adherent passive oxide layer. Thanks to very fast cooling compared with traditional casting, LPBF process gives very fine microstructures having high mechanical properties<sup>7,8</sup>, but the components made with this innovative process have rough surfaces affecting the corrosion resistance. Previous works demonstrate that surface treatments as polishing and shot peening enhance corrosion resistance of surfaces as produced

by manufacturing. Furthermore, selective attacks were observed at the border of the melt pools, caused by the galvanic corrosion promoted by the inhomogeneous precipitation of cathodic silicon particles<sup>9-15</sup>

The aim of work is the study of localized corrosion resistance of an AlSi10Mg alloy obtained by means of LPBF. The behaviour was evaluated in chloride solutions, by measuring the pitting potential ( $E_{\text{pit}}$ ) as a function of chloride ion activity. The effect of post processing heat treatments at 200, 300 and 400°C for 2 hours was also studied.

## Materials and Method

The tests were performed on disk specimens with 15 mm diameter and 5 mm height. Table 1 reports the alloys composition. The specimens were obtained with the base face placed to the building platform – i.e. perpendicular to the building direction.

After manufacturing, some specimens were heat treated at 200, 300, and 400°C for 2 hours and air cooled. The untreated specimens - without any further heat treatment - are named UT.

Before test, the surface was polished by abrasive papers and 0.4  $\mu\text{m}$  colloidal alumina in order to remove the oxide layer formed during manufacturing. Afterwards, the specimens were lead in air for 48 hours in order to stabilize their passive film.

The electrochemical tests were performed in one litre ASTM G5 standard cell by using a sample holder with exposed area of 1  $\text{cm}^2$ , a standard calomel reference electrode (SCE) and two graphite counter electrodes. Potentiodynamic tests were carried out at 10 mV/min scan rate from -50mV with respect to free corrosion potential up to reach 10  $\text{mA}/\text{cm}^2$  until anodic current density. Before tests, the open circuit potential was monitored for 10 minutes to attain stable values of free corrosion potential. The tests were performed at room temperature, in aerated tests solution containing different chloride concentrations (Table 2). Sodium sulphate was added in order to maintain constant the sodium content and almost constant the electrolyte conductivity.

## Results and discussion

Figure 1 shows the potentiodynamic curves. The curves are grouped in function of chloride concentration. The curves at the lowest chloride concentration and on untreated specimens show evident passive behaviour with large range of passivity. The extension of the passive range progressively decreases as the chlorides concentration increases, leading to practically active anodic curve at the highest chloride concentration - equal to 35 g/L - independently upon the post processing heat treatment. At so high chloride concentrations, the anodic curves show typical Tafelian behaviour, thus indicating that localized corrosion attack already initiated since early immersion.

The specimens heat treated at 400°C always show an active corrosion behaviour only except at the lowest chloride concentration, for which the passive range is however quite small.

Figure 2 shows pitting potential for the potentiodynamic anodic polarization curves having a clear range of passivity as function of the activity of chloride ions, measured on specimens heat treated at 300°C or un-treated (UT). The free corrosion potential values for the curves having almost active behaviour are also showed, The chloride activity is calculated according to Dash et al<sup>16</sup> (Table 3). All the experimental results will be discussed by using such parameters instead of chlorides concentration.

Pitting potentials were estimated by the potentiodynamic curves. The pitting potential has been assumed equal to the value of potential for which the anodic current density quickly increases above the current density of passive range, at high potentials. The pitting potential was assumed as a parameter that indicates the resistance to localized corrosion.

For the UT condition, the pitting potential values decrease as the chlorides activity increases. At the highest chloride ions activity, it approaches free corrosion potential because localized attack initiated since early immersion. After heat treatment at 300°C, the specimens show a similar behaviour, but with lower pitting potentials, just showing an active behaviour in the solution having 0.05 mol/L chloride ion activity.

Pitting potential data are scattered because the statistical presence of emerging porosities on the metal surface affects localized attack initiation. The emerging porosities act as preferential sites for localized corrosion initiation. Inside porosities, the oxide formed at high temperature – i.e. during the manufacturing process – is still present, thus promoting initiation due to the fact that its protectiveness is fairly low compared to the oxide naturally formed at air <sup>9</sup>.

Despite data are very scattered, a logarithmic correlation between pitting potential and activity of the chloride is well defined. Such a correlation is emphasized by the model proposed by McCafferty<sup>17</sup>. However, the results show a slope that differs from the value estimated by McCafferty for pure aluminium. The AlSi10Mg alloy considered in this experimental work contains cathodic second phases that can stimulate the corrosion of  $\alpha$ -aluminium matrix by galvanic coupling.

The distribution of such cathodic precipitates depends on the thermal cycle during manufacturing and the subsequent post processing heat treatment. The effect of heat treatment on the corrosion behaviour is underlined in the Figure 3, which reported the pitting potential and the free corrosion potential at the lowest chloride ions activity – 0.008 mol/L – as a function of heat treatment temperature. The specimens heat treated in the range 200-400° C for 2 h show a reduction of pitting potential with respect to the UT specimens, with values that approach the free corrosion potential. The lowering of pitting potential denotes a reduction of resistance to localized corrosion after the heat treatment at temperature usually considered for stress relieving.

The observation of corrosion morphology by Scanning Electron Microscopy showed that the localized attack occurs by selective dissolution of the  $\alpha$ -Al phase. On UT specimen it takes place along the melt pool borders, mainly in the Heat Affected Zone (Figure 4-a), thus directly related with texture produced by the additive manufacturing. Similar corrosion morphology was noticed after heat treatments at 200°C and 300°C. Otherwise, after heat treatment at 400°C (Figure 4-b) the attack is spread out over entire surface without showing any morphology related with the laser tracks.

The corrosion morphology observed into the pit is due to the unique microstructures produced by LPBF process, modified by the post processing heat treatment. The local fusion of overlapped layers of metallic powder creates small “melt pools”. Due to the very fast solidification, the  $\alpha$ -Al phase remains supersaturated and excess silicon segregates at grain boundaries, thus giving rise to intercellular network of silicon. The network is interrupted in the heat affected zone (HAZ) just below laser scan tracks overlap. In this zone, the silicon particles coarse and idiomorphic crystals can be noticed (Figure 5-a), due to the silicon diffusion during heating.

The modification of corrosion behaviour after heat treatment derives by microstructural changes. The heat treatment at 400°C deeply modifies the microstructure so much that melt pools cannot be distinguished anymore after 2 hours heating.

During the heat treatment, silicon segregates due to oversaturation in the  $\alpha$ -Al phase. Its precipitation affects the amount and distribution of silicon crystal at the border of melt pool (Figure 5-b). At 400°C – as melt pools microstructure disappear - uniform matrix of  $\alpha$ -Al phase with coarse dispersed particles of silicon form (Figure 6).

Silicon segregation already begins at temperatures around 200 °C, as demonstrated by Manfredi et al.<sup>18</sup> through Differential Scanning Calorimetry (DSC) measurements.

The distribution and amount of silicon particle in the  $\alpha$ -Al phase increases with time and temperature of heat treatment and can affect the alloy corrosion behaviour because of their different practical nobility<sup>19</sup>. Although silicon is not a so efficient cathode for sustaining the corrosion process, several authors confirmed its role on the corrosion rate. Osòrio et al<sup>20</sup> reported the increase of the corrosion rate of ipo-eutectic Al/Si alloy by increasing the silicon content. Wu and Liao<sup>21</sup> underlined that the corrosion rate of the  $\alpha$ -Al phase of Al-12Si-Mg alloy close to silicon particles in dilute sulphuric acid is enhanced due to the cathodic behaviour of the silicon particles. In addition, the presence of silicon inside the oversaturated  $\alpha$ -Al phase increases its electrochemical potential. Revilla et al<sup>22</sup> measured the Volta potential differences between Al and Si inside and outside the melt pool borders of specimen without heat treatment. The authors concluded that such difference is much higher inside the melt pool border than outside.

The corrosion morphology modification is related to the silicon segregation and precipitation induced by the heat treatment. The uneven distribution of silicon found in absence of the heat treatment promotes preferential dissolution of the border of the melt pool with respect to the centre. The heat treatments at 200° and 300°C increases the silicon precipitation without destroys the melt pool macrostructure, so the preferential corrosion of the border of the melt pool is also observable.

On the other side, the aluminium matrix depleted in silicon due to heat treatments showed lower pitting potential compared to UT specimens thus leading to more distributed attacks morphology after heat treatment at 400°C, which spread out over the exposed surface. After heat treatment at this temperature, the lowest localized corrosion resistance was noticed due to the coalescence of the coarse silicon particles surrounded by  $\alpha$ -Al phase.

## Conclusion

The effect of chloride content and heat treatment on the resistance against localized corrosion of AlSi10Mg alloy, produced by means of LPBF, was evaluated through potentiodynamic tests in different chloride solutions.

The pitting potential values decrease as the chlorides activity increases and after the heat treatment at 200, 300 e 400°C for 2 hours. A logarithmic correlation between pitting potential and activity of the chloride was established.

The corrosion morphology of localized attack modifies as function of heat treatment temperature due to the different distribution and size of silicon phases. Penetrating selective attack at the border of the melt pool was found in as-produced LPBF AlSi10Mg due to the uneven distribution of silicon particles. This corrosion morphology was observed also on the specimens heat treated at 200 and 300°C, because the low temperature treatment not destroy the melt pool macrostructure.

The coalescence and growth of silicon particles and the modification of their distribution promoted by heat treatment at 400°C lead to the occurrence of less penetrating attack, which is spread out over the entire metal surface.

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Table 1: nominal chemical composition of powder

Alloy (% weight)	Si	Fe	Cu	Mn	Mg	Zn	Ti
AlSi10Mg	9-11	≤0.55	≤0.05	≤0.45	0.2 - 0.4	≤0.1	0.01

Table 2: composition of test solutions.

NaCl		Na <sub>2</sub> SO <sub>4</sub>
(g/l)	(mol/l)	(g/l)
35	0.6	0
3.5	0.06	38.34
1	0.02	41.18
0.5	0.01	41.89

Table 3: activity of chloride ions

NaCl		$\gamma_{Cl^-}$	aCl <sup>-</sup>
(g/L)	(mol/L)		(mol/L)
35	0.6	0.563	0.34
3.5	0.06	0.785	0.05
1	0.02	0.858	0.015
0.5	0.01	0.962	0.008