Original Article

Tailoring the microstructure of recycled 319 aluminum alloy aiming at high ductility

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ABSTRACT

Iron has low solubility in solid aluminum and for this reason it can lead to the formation of Fe-rich intermetallic phases (such as β-AlFeSi in Al-Si cast alloys) severely impairing the ductility of the material. Spray forming is an advanced casting process that has been described as a potential technique to highly decrease the β-AlFeSi formation, consequently increasing the ductility. This paper aims to study the effect of pouring and tundish temperature in the microstructure of 319 aluminum alloy with high iron content processed by spray forming. Spray formed ingots and overspray particles were analyzed for two different processing conditions. In order to evaluate the mechanical properties, the spray formed deposits were mechanically conformed by hot swaging. Results showed that the decrease in the β-AlFeSi content strongly depends on the processing conditions. Spray formed deposits processed by hot swaging presented high ductility, allowing a wide range of possibilities to apply casting alloys with high impurity content to more valuable applications beyond the casting industry, therefore decreasing the needs for using primary alloys and contributing to the environment.

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1. Introduction

One of the main problems of recycling wrought aluminum alloys is controlling the chemical composition [1,2]. The presence of iron increases the possibility to form detrimental intermetallic phases in the microstructure [3]. Such phases are usually formed from the liquid and are consequently not possible to be eliminated by heat treatments [4]. They present faceted morphology with sharp edges that lead to (i) a decrease in mechanical properties (especially the ductility) and, consequently, (ii) difficulties in thermomechanical processing [5,6]. Thus, for wrought alloys, iron is limited to a considerably lower
content (below 0.3–0.4 wt.%) to avoid cracking during thermomechanical processing and low fracture toughness of the final products. High iron contents (limited to a maximum of 1.5 wt.%) are acceptable and necessary for alloys processed by high pressure die casting to avoid the welding of the cast part with the metallic die [7].

The solubility of iron in aluminum is negligible, which leads to the formation of intermetallic compounds, a problem that is more significant with the presence of silicon. For casting alloys from 3XX series, which mostly contain silicon in the range of 6–9 wt.%, the most common intermetallic phases are the α-AlFeSi and β-AlFeSi [8]. The α-Al(Fe,Mn)Si intermetallic can be formed when Mn is added to the composition [9], which is an attempt to avoid the formation of the β-AlFeSi phase with its platelet-like morphology, highly harmful to ductility [10]. In contrast to the β intermetallic, the α-AlFeSi or α-Al(Fe,Mn)Si phases present a less detrimental morphology [11]. When the α-AlFeSi is formed as a primary phase, it presents a polygonal morphology; on the other hand, if it is formed at the end of solidification, a Chinese script morphology is found [12]. When conventionally cast, it is reported two ways to reduce the formation of β-AlFeSi in favor of α-AlFeSi or α-Al(Fe,Mn)Si in the microstructure: (i) increasing the cooling rate during solidification [13]; and/or (ii) increasing the Mn content [9,14,15].

Recycling cast and wrought aluminum alloys using the spray forming technique is not a new approach. Different works show results describing the potential of this advanced casting method to produce Al alloys with superior mechanical properties even with high iron contents [16–21]. In Ref. [18], it is suggested that the spray forming process can highly decrease the formation of the β-AlFeSi intermetallic phase in recycled aluminum alloys. However, the mechanisms behind this phenomenon were not clarified due to the lack of information regarding the solidification sequence of spray forming products. More recently, a study was published, which aimed to recycle the A6061 wrought aluminum alloy by spray forming and hot extrusion [19]. The authors achieved the same level of mechanical properties for the recycled material (with a high impurity content) in comparison to the primary alloy through this processing route. For casting aluminum alloys, it is even more challenging due to its high alloying element content (mainly Si and Fe). The possibility of upcycling this material by applying recycled casting aluminum alloys for applications that up to now are just for primary wrought aluminum alloys has an inestimable value due to: (i) the decrease in materials that are destined for landfills and (ii) the reduction of the environmental costs to produce primary aluminum alloys (high energy consumption and production of industrial waste) [22].

Recently, a new approach regarding the study of microstructure evolution in spray forming products was proposed and provided new insights regarding the microstructure evolution [23,24], thus making it possible to tailor the final microstructure in a desirable way. This model separates the solidification in two different stages: (i) in the atomization and (ii) in the deposition. The liquid metal is atomized by an inert gas, and in this stage, high cooling rates are imposed to the material (estimated to be in the order of $10^2$–$10^5$ K/s [24]. During the flight from the atomization nozzle to the substrate, different cooling rates are imposed to the droplets depending on their size; thus, solid, semisolid and liquid particles hit the substrate [25]. The deposit is formed by the consolidation of these droplets. In this stage, the surface achieves an equilibrium temperature that must be within the solidification interval of the alloy in order to obtain a low-porosity ingot [24,26]. This condition can be obtained by careful setting of the processing parameters, among them the pouring and tundish temperatures, as well as the atomization pressure and the flight distance. The temperature equalization is achieved by heat exchange from the droplets of different sizes that reach the deposition zone: the already solidified droplets, whose mean temperature lies below $T_{\text{solidus}}$, heats up, and the liquid droplets, whose temperature lies above $T_{\text{liquidus}}$, cool down. Consequently, depending on the fraction of each type of droplet, the final temperature of the deposit surface lies within the solidification interval of the alloy. Grant [25] as well as Grant and Cantor [27] proposed a method to estimate the time that the deposit takes to achieve this temperature and it was estimated to occur in milliseconds for most of the metals.

Therefore, during the deposit build-up, the deposit surface temperature lies in the solidification range of the alloy and, at this point, the cooling rates are considerably lower when compared to the atomization stage. Different studies in the literature indicate that the cooling rate of the deposit lies between 0.1 and 10 K/s [23–25]. One of the major consequences of the temperature equalization is that the lower melting temperature phases present in the completely solidified particles tend to re-melt, while the primary phases are retained in solid state at the deposition zone. By cooling down, these primary phases act as solid nuclei to solidify the remaining liquid and other phases may form depending on the chemical composition of the liquid and the cooling conditions. Due to convective currents and turbulence provided by atomization gas and incoming droplets, the solid nuclei are uniformly distributed with non-oriented heat exchange. Considering the aspects cited above, the sequence of events leads to the microstructure of equiaxed grains of the primary phase with secondary phases at the grain boundaries [23,24].

The aim of this work is to bring out new insights regarding the formation of Fe-rich intermetallic phases in spray-formed 319 aluminum alloy under the new knowledge of the aforementioned solidification mechanism. The focus is on the most common iron intermetallic phases and their formation was analyzed regarding the different solidification stages of the spray forming process. Once the main solidification mechanism is established, the final microstructure can be tailored, decreasing the formation of the deleterious β-AlFeSi intermetallic phase in recycled 319 aluminum alloy, even with high iron contents. This is of utmost importance in order to improve the ductility of these materials, which allows their thermomechanical processing, opening new possibilities to substitute primary wrought alloys (costly and whose production relates to environmental issues). Therefore, the mechanical properties of these hot forged products were also evaluated to assess the enhancement in performance that this processing route can render to this cast alloy.
Table 1 – Parameters for L1 and L2 spray forming runs.

<table>
<thead>
<tr>
<th></th>
<th>L1</th>
<th>L2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pouring temperature K (°C)</td>
<td>993 (720)</td>
<td>1033 (760)</td>
</tr>
<tr>
<td>Tundish temperature K (°C)</td>
<td>1023 (750)</td>
<td>1043 (770)</td>
</tr>
<tr>
<td>Atomization pressure (MPa)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Flight distance* (mm)</td>
<td>330</td>
<td>330</td>
</tr>
<tr>
<td>Nozzle diameter (mm)</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Atomization gas</td>
<td>Na</td>
<td>Na</td>
</tr>
<tr>
<td>Atomization time (s)</td>
<td>60</td>
<td>60</td>
</tr>
</tbody>
</table>

* Distance between the quartz nozzle and the substrate.

Table 2 – Chemical composition* of the spray formed samples (weight%).

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Mg</th>
<th>Zn</th>
<th>Ni</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>5.92</td>
<td>3.54</td>
<td>0.66</td>
<td>0.13</td>
<td>0.02</td>
<td>0.61</td>
<td>0.08</td>
<td>Bal.</td>
</tr>
<tr>
<td>L2</td>
<td>5.45</td>
<td>3.34</td>
<td>0.65</td>
<td>0.13</td>
<td>0.01</td>
<td>0.58</td>
<td>0.07</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

* Determined by optical emission spectroscopy.

Fig. 1 – Thermocouple position in relation to the substrate.

2. Materials and methods

Ingots of approximately 2.5 kg of 319 aluminum alloy were produced using a close-coupled spray forming equipment produced by Gateway Engineering, England. The induction furnace was used to melt the alloys and a resistance furnace was used to heat the tundish and control its temperature preventing the early solidification of the liquid metal before it enters the atomization nozzle. Two spray-formed ingots with different processing parameters were produced, L1 and L2, also described as presenting a “colder” spray forming conditions and “hotter” spray forming conditions, respectively (Table 1). The main difference between them was the pouring and tundish temperature, lower for the condition hereinafter called L1, and higher for condition L2.

The chemical composition was kept the same as presented in Table 2. For both conditions, a K-type thermocouple was positioned 20 mm above the center of the substrate in order to record the temperature evolution of a single point inside the ingot (see Fig. 1).

Thermodynamic calculations using the Thermo-Calc® software, version 4.0 and TCAL3 database, were conducted to verify the equilibrium phase transformation path and the Scheil solidification model of the studied alloy [28]. The spray-formed deposits and overspray powders were prepared using a conventional metallographic procedure (embedding, grinding and polishing) and in order to preserve the phases, the samples were not etched. Their microstructures were characterized by Scanning Electron Microscopy (SEM) using Phillips XL-30 FEG and FEI Inspect S50 both coupled with energy dispersive X-ray spectroscopy (EDX). The Fe-rich intermetallics were characterized by Transmission Electron Microscopy (TEM) using a Tecnai G2 F20 (TEM/STEM) at 200 kV with a field emission gun (FEG); disks with 3 mm of diameter were grinded until 80 μm of thickness and a Precision Ion Polishing System (PIPS) was used as a final step for the sample preparation. X-ray diffraction (XRD) using Bruker D8 Advance ECO equipment with Cu radiation, coupled with a high-speed detector SSD160, was carried out to identify the present phases in both spray-formed deposits and overspray particles. Two main conditions were used: from 2Θ = 10⁰ to 90⁰ in a scanning rate of 5.3 /min and from 2Θ = 15⁰ to 30⁰ in a scanning rate of 0.5 /min in order to observe the phases that are presented in low amounts in the microstructure.

It is well known from the literature that one of the main disadvantages of the spray forming process is the inherent porosity of the deposits [25]. For this reason, in order to decrease the porosity and reduce the effect of this variable in the mechanical tests, five samples of each deposit were machined to cylinders with 25 mm diameter and processed by hot swaging at 573 K. For this process, the specimens were placed in a resistance furnace for 15 min to homogenize the temperature and the area of the cylinder was reduced to a ratio of 5:1. The porosity was measured before and after forging through image analysis of 20 pictures for each sample (Software Image J).

The mechanical tests were performed for both L1 and L2 samples after hot swaging and they were compared to as-cast 319 Al alloy (named as “AC” henceforth). The tensile tests were performed according to ASTM EB/8EM-16 standard using an Instron Universal testing machine, model 5500R. Cylindrical samples with 20 mm of gauge length and 2.5 mm of gauge diameter were tested with a strain rate of 0.1 s⁻¹. The conventionally cast sample was obtained from an engine head cast in sand mold (the samples were machined from the region of the part that presented the lower levels of porosity). The mechanical results were also compared to the recycled 6061 wrought aluminum alloy, produced by a similar route by Pereira et al. [19]. The phase fraction and the porosity levels were evaluated by image analysis using ImageJ software.

3. Results

Fig. 2 presents the calculated equilibrium solidification path for the L1 composition (Al - 5.92 wt.%Si - 3.54 wt.%Cu - 0.66 wt.%Fe - 0.13 wt.%Mn). Although not shown, it is worth mentioning that L2 presented equivalent results because of its similar chemical composition. Both α-Al(Fe,Mn)Si and β-AlFeSi intermetallic phases are stable in equilibrium conditions. The solidification path comprises the formation of (α-Al) as a primary phase followed by the formation of β-AlFeSi at approximately 863 K (590 °C). The solidification ends
with the formation of the $\alpha$-Al(Fe,Mn)Si intermetallic and (Si) from 833 K (560 °C) to 798 K (525 °C). It should be mentioned that the diagram presented in Fig. 2 was only used as a reference to understand the solidification path of the alloy. It does not mean that the solidification of the spray formed deposits occurs in equilibrium conditions.

Fig. 3 presents the temperature evolution of the interior of the deposit. In order to help understand the deposit solidification, the cooling rates were calculated for three different stages. Besides that, it is important to point out in Figs. 2 and 3 that the highest temperature achieved by the thermocouple was within the solidification interval of the alloy. The deposition takes approximately 60 s to be completed and the solidification was not over at this point, since the temperature inside the deposit is still higher than the solidus temperature. After deposition, the cooling rate is relatively low and within the same range (-0.45 K/s) predicted by [25]. This result confirms that spray forming is not a rapid solidification process and the long solidification time helps to explain why the dendritic/cellular microstructure of the overspray droplets disappears, as will be discussed further in this work.

![Equilibrium phase transformation path evaluated the L1 composition](image)

**Fig. 2** – Equilibrium phase transformation path evaluated the L1 composition: (a) overview of the diagram; (b) magnification to distinguish low volume fraction phases.

![Temperature evolution in the interior of the deposit L2](image)

**Fig. 3** – Temperature evolution in the interior of the deposit L2.

<table>
<thead>
<tr>
<th>Phase ID</th>
<th>Al</th>
<th>Si</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>95.67</td>
<td>0.85</td>
<td>3.48</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>B</td>
<td>56.39</td>
<td>1.36</td>
<td>42.25</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>C</td>
<td>16.87</td>
<td>82.63</td>
<td>0.49</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>D</td>
<td>58.20</td>
<td>9.17</td>
<td>5.13</td>
<td>21.45</td>
<td>6.05</td>
</tr>
</tbody>
</table>

**Table 3** – EDX measurements from the phases labeled in Fig. 6 (L1 deposit), in wt.%

### 3.1. Fe-rich intermetallics

Fig. 4a represents the full diffractogram for the deposits. However, it is only possible to observe the presence of the main secondary phases in this analysis: (Si) and (θ-Al$_2$Cu), not the presence of Fe-rich intermetallic phases. For this reason, a XRD measurement with lower scanning rate was made and is shown in Fig. 4b for the deposit and Fig. 4c for the overspray particles. From this result, the β-AlFeSi intermetallic could be detected for the L2 deposit.

Fig. 5 shows the overspray powder microstructure from both spray forming runs. These are typical microstructures of rapid solidified hypoeutectic Al-alloys with cellular/dendritic ($\alpha$-Al) phase and secondary phases at the intercellular/interdendritic arm spacing. The secondary phases that can be observed are the (Si), the Cu-rich phase (θ-Al$_2$Cu) and the $\alpha$-Al(Fe,Mn)Si in a polyhedral morphology. As expected, due to the rapid solidification conditions, the β-AlFeSi intermetallic was not observed at the overspray particles with a maximum diameter of 100 μm. This fact corroborates with what is presented in Fig. 4c, in which the diffractograms of the droplets do not show any evidence of the β-AlFeSi phase, presenting just the $\alpha$-Al(Fe,Mn)Si intermetallic. In fact, these results are in accordance with the literature, since rapid solidification is one of the main methods to avoid the presence of β-AlFeSi in aluminum alloys with high Fe content [9,13].

Fig. 6 shows the microstructure of deposit L1 and Table 3 presents the EDX of labeled phases. After careful analysis, the presence of β-AlFeSi intermetallic was scarce to be observed. This result is in accordance with the XRD pattern of the sprayformed L1 deposit (Fig. 4b), where no diffraction peak of the β-AlFeSi could be observed demonstrating that this phase is present in a small amount. On the other hand, the polygonal $\alpha$-
Al(Fe,Mn)Si particles are homogeneously distributed along the microstructure. Fig. 7 shows the microstructure and Table 4 presents the EDX of the labeled phases for the L2 deposit. It can be observed that the higher pouring and tundish temperatures (L2 condition) lead to the presence of platelet-like \( \beta \)-AlFeSi and polygonal \( \alpha \)-Al(Fe,Mn)Si intermetallic phases. This result is in accordance with the XRD pattern presented in Fig. 4b.

Fig. 8 presents both Fe-rich intermetallics analyzed through STEM mode (Scanning-Transmission Electron Microscopy) with the electron diffraction pattern taken from each intermetallic class in order to obtain crystallographic information of each phase. As described in the literature, the \( \alpha \)-Al(Fe,Mn)Si intermetallic presents a cubic structure (space group: \( \text{I} \text{m} - 3; a = 1.256 \text{ nm} \) [29]) and the \( \beta \)-AlFeSi intermetallic presents a monoclinic structure (space group: \( \text{A} 2/\text{a}; a = 0.6161 \text{ nm}, b = 0.6175 \text{ nm}, c = 2.0813 \text{ nm}; \beta = 90.42^\circ \) [30]).
Even though this work focuses on the Fe-rich intermetallics, it can also be seen that the Cu-rich phase (α-Al2Cu) was presented as a typical eutectic morphology (lamellae with α-Al, Fig. 6). It should be remembered that the composition of this alloy, which permits solution heat treatment and aging, does not predict the formation of the (α-Al)/(α-Al2Cu) eutectic morphology at solidification under equilibrium conditions. As can be observed in Fig. 2, the Cu-rich phase (α-Al2Cu) would be the last to form by solid state precipitation in equilibrium conditions.

3.2. Porosity and hot swaging processing

The porosity levels of the deposited samples before and after hot swaging are presented in Table 5 in volume percent. The results indicate that hot swaging at 573 K was effective to reduce the porosity of the deposits. It is worth mentioning that the thermomechanical processing of such alloys was only possible because of the refined microstructure obtained from the spray forming process and higher ductility of the as-spray samples. When conventionally casted, the 319 aluminum alloy presents a coarser microstructure with the presence of high amounts of deleterious phases. Even the Chinese script morphology of the α-Al(Fe,Mn)Si intermetallic may significantly decrease the ductility of the alloy when in high amounts [9] and the elongation at fracture values lie between 0% and 2% when tested at room temperature [31]. For this reason, the thermomechanical processing may be relatively difficult to perform without inducing cracks on the material.

Fig. 9(a and b) presents the microstructures of deposits L1 and L2 after hot swaging, respectively. In comparison to the as-spray samples (Figs. 6 and 7), the microstructures in general were refined by the thermomechanical processing in conjunction with the lower levels of porosity.

Table 5 – Porosity level before and after thermomechanical processing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Before hot swaging</th>
<th>After hot swaging</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>(2.8 ± 1.4) vol.%</td>
<td>(0.3 ± 0.2) vol.%</td>
</tr>
<tr>
<td>L2</td>
<td>(3.2 ± 3.4) vol.%</td>
<td>(0.3 ± 0.3) vol.%</td>
</tr>
</tbody>
</table>

Fig. 6 – SEM image of the L1 deposit.

Fig. 7 – SEM image of the L2 deposit.

Fig. 8 – STEM imaging mode with electron diffraction patterns of the (a) α-Al(Fe,Mn)Si intermetallic and (b) β-AlFeSi intermetallic.
3.3. As-cast 319 aluminum alloy

The chemical composition of the as-cast (AC) sample, used in this work as a reference for mechanical properties of a conventionally casted 319 Al alloy, is presented in Table 6. It can be observed that both the Si and Mn contents are slightly higher than the L1 and L2 compositions. However, the Fe content is quite the same, remaining in the error of the measurement. The microstructure of the AC sample is presented in Fig. 10 and high amounts of $\alpha$-Al(Fe,Mn)Si can be seen in a Chinese script morphology.

3.4. Mechanical properties

The mechanical properties obtained from the AC sample were evaluated in order to be a comparable value to the L1 and L2 samples processed by spray forming and hot swaging. Table 7 presents the mechanical properties of the aforementioned samples and the results show that the AC sample almost did not present any elongation at fracture. On the other hand, both the L1 and L2 presented higher ductility, reaching the magnitude of some wrought aluminum alloys. These results indicate what was expected according to the evaluated microstructures, in which the AC sample presented much coarser phases and higher porosity levels (2.1 ± 2.2) vol.%. After hot swaging, the porosity level of the spray formed deposits was decreased to almost zero (Table 5) and this lower porosity contributed to higher ductility of these samples.

Regardless of the microstructure refinement and the porosity levels, Fig. 11 presents the phase fraction in comparison to the elongation at fracture for the AC, L1 and L2 samples. The (Si) and ($\theta$-Al$_2$Cu) phases presented almost the same level in all the microstructures and can be comparable to the values obtained by the thermodynamic calculations presented in Fig. 2, even though the predictions were made considering the thermodynamic equilibrium. The lowest level of the $\beta$-AlFeSi
intermetallic was presented for the L1 condition, which also presented higher elongation in comparison to L2 condition. Because of the higher Mn content of the AC, it can be observed that this sample presented high levels of α-Al(Fe,Mn)Si intermetallic; it is reported in the literature that when in high amounts, this phase can also be detrimental to the mechanical properties [9].

4. Discussion

From the results presented in Figs. 5–7 and 11, together with XRD results in Fig. 4, it can be observed that the deposits show low amounts of iron-containing intermetallics. By adjusting the processing parameters, the microstructure of the deposits can be tailored to form preferentially the polygonal α-Al(Fe,Mn)Si, which consumes the available iron, and consequently reduces the β-AlFeSi content. The main reason for the decrease in the β-AlFeSi intermetallic content for L1 deposit was the lower pouring and tundish temperature, which led to a colder condition of the deposit. In fact, the whole spray forming processing conditions give rise to a unique microstructure evolution, which is formed at two different stages: during atomization and during deposition, as the approach regarding the solidification of spray formed products was recently described [23,24]. The phases that were first formed in the atomization stage were evaluated through the microstructural analysis of the overspray particles. It could be seen that these particles directly influence the phases present in the deposit, but it is not determinant to the final microstructure. Both the conditions (L1 and L2) demonstrated equivalent overspray particles with the same microstructure and XRD results regarding the Fe-rich intermetallic phases, in which the presence of the α-Al(Fe,Mn)Si intermetallic was just seen.

In contrast, the microstructures of the L1 and the L2 deposits were quite different in which the first presented a considerably lower amount of the more detrimental intermetallic phase (β-AlFeSi). According to the solidification models for spray forming products, colder processing temperatures led to higher amounts of completely solidified particles reaching the deposition zone. Therefore, the solid to liquid fraction must be higher for this condition than for the hotter condition (L2) and the equilibrium temperature at the deposition zone must be at a lower level. Thus, the heat content was lower for the L1 condition and it decreased the probability to re-melt the already solidified α-Al(Fe,Mn)Si nuclei that was formed in the atomization stage. On the other hand, the probability of re-melting the α-Al(Fe,Mn)Si nuclei is higher for higher processing temperatures (L2). The analysis of the results for both conditions (L1 and L2) are based on the fact that the re-melting process depends on the heat supply of completely liquid droplets that arrives at the deposition zone (understood as the fraction of liquid droplets). If the temperature at the deposit is high enough, it can provide enough heat to completely re-melt the α-Al(Fe,Mn)Si phase and increase the iron content in the remaining liquid phase as the solubility of iron in the (α-Al) is negligible.

Therefore, in the final stages of solidification, the remaining iron present in the liquid phase has two possibilities: i) to participate in the growth of already formed α-Al(Fe,Mn)Si nuclei or ii) to nucleate β-AlFeSi. From this work, it can be observed that for the L1 condition, iron atoms presented at the remaining liquid contributed to the growth of the already α-Al(Fe,Mn)Si nuclei instead of nucleating β-AlFeSi. On the other hand, higher temperature conditions tend to re-melt a higher amount of the α-Al(Fe,Mn)Si nuclei, giving conditions to β-AlFeSi nucleation due to the higher iron content segregated to the liquid. A higher re-melt level of α-Al(Fe,Mn)Si also explains the presence of smaller particles of this intermetallic in the L2 run compared to L1 (see Figs. 6, 7 and 9).

From the above, it can be derived that the same phases formed at the droplets can lead to a different microstructure depending on processing parameters used on spray forming. Therefore, it is expected that any adjustment in spray forming parameters, which will lead to a colder condition (for example, higher atomization pressure, higher flight distance, lower pouring and tundish temperatures) will decrease the probability of the detrimental β-AlFeSi intermetallic phase to be formed and a polyhedral α-Al(Fe,Mn)Si will tend to occur in a higher content than predicted by equilibrium calculations. However,

![Fig. 12 – Scheil-Gulliver solidification path for L1 composition.](image-url)
it is worth pointing out that irrespective of the processing parameters, the total amount of iron intermetallics is considerably lower compared with the results of conventionally cast alloy.

In order to better understand the overall solidification process and through the thermocouple measurements taken from the interior of the deposit, the presence of (θ-Al2Cu) in a eutectic morphology can be explained by the occurrence of microsegregation at the end of solidification. Fig. 12 represents the phase evolution obtained by the software Thermo-Calc to the L1 composition (Al-5.92 wt.%Si-3.54 wt.%Cu-0.66 wt.%Fe-0.13 wt.%Mn) following the Scheil-Gulliver solidification model. The relative low diffusivity of Cu in the solid Al matrix together with the fact that the partition coefficient of Cu in Al is less than unity leads to the formation of this phase at the end of the solidification in non-equilibrium conditions, and not as precipitates in solid state, as predicted by the equilibrium solidification path (Fig. 2).

The discussion of this phase presence in a eutectic morphology is important to this work because it confirms what was presented earlier. At the end of the deposit solidification, the cooling rates are considerably lower compared to the atomization stage, making the segregation of this solute possible and, consequently causing a eutectic reaction. According to the solidification model presented here for spray forming products, the (θ-Al2Cu) phase at the completely solidified droplets was re-melted due to its lower melting temperature after heat exchange from the different types of droplets. After temperature equalization, it is highly probable that the solidification tends to follow the Scheil-Gulliver model mainly because of the low diffusion of copper in solid aluminum. Thus, the end of the deposit solidification tends to follow the Scheil-Gulliver solidification model, leading to a high solute segregation to the grain boundaries. At the end of the deposit solidification, the Cu amount in the liquid was so high that it achieved a composition that led to the eutectic reaction.

Consequently, the solidification sequence can be summarized as follows:

Atomization step: rapid solidification, dendritic network with interdendritic segregation. Deposition step: (1) at first, an equilibrium temperature and respective solid to liquid fraction will be reached within the solidification interval of the alloy due to the heat balance among the droplets that hit the substrate to form the deposit. When the equalization temperature is reached, the lower cooling rate and very small size of the droplets leads to almost equilibrium solidification conditions and low solubility elements will be rejected by the solid to the liquid. Both solid and liquid phases will homogenize; (2) by cooling down, due to liquid convection caused by the impacting droplets and insufficient time to solute redistribution on the growing solid, the Scheil mechanism can be considered and this was confirmed by the segregation of copper and formation of Cu-rich phases on the grain boundaries in a eutectic morphology. To the best of our knowledge, this approach is totally new and not reported so far for spray formed Aluminum alloys.

From the perspective of the mechanical properties, the spray forming provides not just a finer microstructure but can also be a processing technique that makes possible to control the iron-containing intermetallic phases. Even though different works in the literature present outstanding mechanical property results for Al-Si casting alloys, most of them are based on low iron-containing alloys processed by rapid solidification techniques with posterior heat treatments [32]. The main difference of this work is that spray forming presents a high production rate compared to rapid solidification techniques and is tolerant to high iron contents making it a promising route for recycling aluminum alloys not just for reproducing the original properties of the recycled alloy, but also for increasing the mechanical properties, especially the ductility at a level that allows theromechanical processing. Therefore, it opens the possibility of using cast recycled alloys in more valuable applications substituting the primary wrought aluminum alloys. Pereira et al. [19] recently adopted a similar methodology to recycle highly contaminated 6061 wrought aluminum alloy (1.4 wt.% Fe) and achieved 142 MPa of yield strength and 12% of elongation at fracture. The results obtained in this work for a casting aluminum alloy presented higher yield strength (231 MPa for L1) and a comparable elongation at fracture (7.5% for L1). The phase percentage of the β-AlFeSi below 0.5% for the L1 sample has a direct impact on the achieved mechanical properties. On the other hand, the samples L2 presented more than double of the amount of this deleterious intermetallic in the microstructure. Summarizing, spray forming is a processing technique that should be considered when one intends to upcycle aluminum alloys with high impurity content. Moreover, concerning the knowledge acquired by this work, it is also possible to control the presence of Fe-rich intermetallics, which will directly affect the mechanical properties (Fig. 11). Indeed, this paper shows that by this processing route it was possible to increase the ductility of a common cast Al-Si alloy to unexpected values never attained before. In addition, it is worth pointing out that no attempt was made to change the morphology of the silicon particles through modification or heat treatment, even though it is the major secondary phase in the alloy (phase percentage in the range between 8 and 9%). Considering the well-known effect of the platelet-like silicon particles on impairing the ductility of Al alloys, even a higher increase in the ductility of the alloys can be foreseen, if one succeeds in changing its morphology.

5. Summary and conclusions

In this paper, it was studied the effect of pouring and tundish temperature in the microstructure of 319 aluminum alloy with high iron content processed by spray forming. The focus was to evaluate the formation of the intermetallic phases α-Al(Fe,Mn)Si and β-AlFeSi. The main conclusions are as follows:

- The overspray particles only presented the α-Al(Fe,Mn)Si intermetallic phase, while the deposit with higher pouring and tundish temperature (L2) presented the β-AlFeSi on its structure.
- The solidification process and the sequence of phase formation was strongly affected by the processing parameters. Higher pouring and tundish temperatures led to higher amounts of β-AlFeSi in the microstructure due to higher
re-melting of the α-Al(Fe,Mn)Si phase solidified at the atomization step.

- The Cu-rich intermetallic phase was presented as a eutectic morphology implying that this phase was formed at the end of the deposit solidification, which tends to follow the Scheil-Gulliver solidification model.

- Higher levels of Fe-rich intermetallic phases led to lower mechanical properties, especially the elongation at fracture. For the spray forming experiments, lower amounts of β-AlFeSi phase (L1) led also to higher elongation values.

Finally, in this work, it shows the possibility of producing a recycled casting Al alloy with high iron content showing a significant improvement in the ductility.

Conflicts of interest

The authors declare no conflicts of interest.

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