On the impact of Si content and porosity artifacts on the anodizing behavior of additive manufactured Al-Si alloys

Reynier I. Revilla *, Yorfred Rojas, Iris De Graeve

Vrije Universiteit Brussel (VUB), Dept. of Chemistry and Materials, Research Group of Electrochemical and Surface Engineering (SURF), Pleinlaan 2, 1050 Brussels, Belgium

*Corresponding author. E-mail address: rrevilla@vub.be (R. I. Revilla)

ABSTRACT:
This work analyzes the galvanostatic anodizing behavior of additive manufactured (AM) Al-Si alloys. Two main factors were studied here: 1) the influence of Si content on the anodizing behavior and on the porous structure of the anodic oxide film, and 2) the effect of pre-existing internal pores on the anodizing behavior of these materials. Three different alloys were anodized in H₂SO₄ electrolyte, with 7%, 10%, and 12% Si. The voltage responses of the different samples during anodizing were compared and the formed oxide was analyzed. The amount of Si in the AM Al-Si alloys was found to have a great influence on the anodizing voltage and consequently on the porous structure of the anodic oxide layer. However, the anodic oxide growth rate was nearly independent of the Si content in the samples. Moreover, the effect of internal porosity resulting from the metal additive manufacturing process on the anodizing behavior of these specimens was also analyzed. An outer anodic oxide layer decorated the pre-existing internal pores that were reached by the anodic oxide front. These internal pores were also characterized by the systematic appearance of cracks resulting from the volume expansion of anodic oxide layers advancing in opposite directions.
**Introduction**

Al-Si alloys, extensively used in the automotive, aeronautic, and aerospace industry [1], are usually prepared by casting. Nevertheless, over the past few years, metal additive manufacturing (MAM) has shown great potential for the fabrication of dense and complex Al-Si components [2-6]. During this process, metallic parts are built-up in a layer–by–layer fashion using a metal powder feedstock [2-6]. Metal powders used in MAM are already pre-alloyed, which together with the extremely fast cooling rates associated with this process, promote the formation of a very fine microstructure and distribution of alloying elements [2-6].

The microstructure of additive manufactured (AM) Al-Si alloys has already been described in a great number of works [7-15]. As-built specimens exhibit a very fine distribution of Si, forming a 3-dimensional network that encloses the α-Al in very small cells. The size of these cells varies over the melt pool due to the thermal gradient created by the moving heat source. Fine cells are formed towards the middle of the melt pools (MP), while coarser cells are observed in the melt pool borders (MPBs) [9,14,15]. The cross sections of these cells are also known to present an approximately round shape in the plane parallel to the building platform (XY), whereas in the plane perpendicular to the building platform (XZ) rather elongated cells have been described [9,14,15]. In an earlier study we found that by increasing the amount of Si, a greater level of connectivity is seen in the Si phase [15]. A thinner and partially discontinuous Si network was noticed for AlSi7Mg0.6 samples, while a thicker and much more connected Si network was observed for AlSi12 specimens in earlier studies [15]. Previous works have also demonstrated that the Si network formed in AM Al-Si specimens is predominantly composed of Si nanocrystals [10,14]. However, a lamellar microstructure of alternating layers of Al and Si phases, common for eutectic Al-Si structures, has been reported at the MPBs [16]. Moreover, the MPBs have also been found to be slightly enriched in Si content compared to the core of the MPs [16]. This has been associated with the relatively lower cooling rate at the MPBs compared to the core of the MPs [9,14-16].

The special microstructure resulting from the additive manufacturing process has been shown to affect not only the corrosion performance, but also the anodizing behavior of AM Al-Si alloys. A great number of works have been dedicated in recent years to study the corrosion mechanism of these specimens [15,17-32]. Nevertheless, only a few studies have focused on the anodizing behavior of AM Al-Si alloys [14,16,33]. These studies have shown that the anodizing voltage-time response and oxide film characteristics are significantly affected by the unique microstructure produced by MAM [14,16,33]. A previous analysis using x-ray photoelectron spectroscopy (XPS) revealed that unlike the cast alloy, where only the superficial Si is oxidized during anodizing, most of the Si in the anodic oxide layer of the AM specimens is oxidized [16]. This full oxidation of Si in the AM materials causes a major reduction in anodizing efficiency compared to the cast alloy, and a much greater voltage response during galvanostatic anodizing compared to the cast alloy [14,16]. An anisotropic anodizing behavior has also been observed in AM AlSi10Mg specimens [14,16,33]. In general, the voltage measured is much higher during galvanostatic anodizing of
surfaces oriented in the XY direction than surfaces oriented in the XZ direction. This has been linked in earlier works to differences in the size of the Al cells in the different planes [16]. All the past works dedicated to study the anodizing behavior of AM Al-Si alloys have been conducted using AlSi10Mg [14,16,33]. In the present work, the anodizing behavior of AM Al-Si specimens containing 7%, 10%, and 12% Si was analyzed. Here, the influence that the amount of Si in the AM Al-Si alloys have on the anodizing voltage and on the porous structure of the anodic oxide layer was investigated. The anodizing was conducted galvanostatically in H₂SO₄ electrolyte as it has been done in past studies [14,16,33]. A comparison between the voltage responses during anodizing for the different samples was carried out. The samples’ anodic oxide layers were characterized using optical microscopy and Field Emission Scanning Electron Microscopy (FE–SEM). Additionally, the influence of defects such as porosity on the anodic oxide layer was analyzed.

**Materials and methods**

**Samples**

Three different additive manufactured Al-Si alloys were used during the experiments: AlSi7Mg0.6, AlSi10Mg, and AlSi12. These alloys are the same as those used in our previous study concerning the corrosion behavior of these materials [15]. These three samples were fabricated using LaserForm AlSi7Mg0.6, LaserForm AlSi10Mg, and LaserForm AlSi12 powder, respectively. The chemical compositions of the metal powders used to fabricate the samples are shown in Table 1.

The samples were manufactured using selective laser melting (SLM) with the same procedure as the one used for the fabrication of the samples described previously [15]. The AlSi10Mg and AlSi12 samples were prepared using a ProX DMP 320 machine (3D Systems Leuven), while the AlSi7Mg0.6 sample was prepared using a ProX 300 machine (3D Systems Leuven); both equipped with a 500 W laser in an argon atmosphere with resulting oxygen content of < 50 ppm. Rectangular cuboids of 5×30 mm² and a height of 10 mm were fabricated. For the AlSi10Mg and AlSi12 samples, a 30 µm layer thickness was used, while a 40 µm layer thickness was employed for the AlSi7Mg0.6 sample. A laser energy density of 59 J/mm³, 51 J/mm³, and 52 J/mm³ was used for the AlSi7Mg0.6, AlSi10Mg, and AlSi12 specimens, respectively. The specific process parameters (resulting in the energy density used) were optimized for each alloy type in order to obtain high density parts with the lowest possible level of porosity.

No post heat treatment was applied on the AM specimens. All the samples were mechanically ground and polished, finishing with 0.04 µm standard colloidal silica suspension (OP–S). In order to image the microstructure of the samples, the surfaces were etched with Keller’s reagent. In all the experiments, the surface parallel to the building platform, XY, and the surface perpendicular to the building platform, XZ, were analyzed.

Small amounts of Mg are present in some of the Al-Si specimens analyzed (see Table 1). Sample AlSi10Mg has 0.2% – 0.45% Mg, and sample AlSi7Mg0.6 has 0.45% – 0.7% Mg. In traditional cast Al-Si alloys, Mg is known to form Mg₂Si precipitates. Nevertheless, in AM Al-Si samples,
due to the extremely high cooling rates associated with the MAM process, the presence of these precipitates has not been confirmed. Instead, Mg has been found to be highly dispersed within the AM samples [16,17]. The Mg present in these specimens could be oxidized during the anodizing process. However, due to the relatively low amounts of Mg present in these alloys, and the high dispersion of it within the samples, we believe that Mg has no major influence on their anodizing behavior.

Anodizing

Anodizing was carried out galvanostatically in a stirred 3M H₂SO₄ electrolyte at 10 mA/cm² and at room temperature. These anodizing conditions were the same as those used in our previous works [14,16,33] in order to facilitate comparisons. An ES 0300-0.45 power supply from Delta Elektronika was used. The anodic potential was measured as a function of anodizing time using a two electrode cell configuration with the sample as working electrode and a platinum counter electrode. Prior to anodizing, the samples were ultrasonically cleaned in acetone and ethanol, with immersion times of 3 min. After anodizing, the samples were washed with distilled water and dried with a cool air stream.

The anodizing was conducted on polished samples, as in our previous studies [14,16,33], in order to better understand the effect of microstructure on the anodizing behavior. Nevertheless, it is important to keep in mind that for commercial applications an etching-desmutting process is generally used. This process can have an influence on the morphology of the porous anodic oxide. Additionally, for AM metal parts other factors such as surface roughness, the presence of unmelted powder on the surface, as well as post-treatments such as shot peening or sandblasting (often used in AM Al-Si alloys), can also affect the morphology of the anodic oxide.

Characterization by FE–SEM and optical microscopy

The optical characterization of the samples was conducted using a Leica DMi8 microscope with built-in image software. A FE–SEM JEOL JSM–7100F scanning electron microscope was also used. Secondary electron images of the specimen’s microstructure were obtained using 15 kV acceleration voltage, 10 nA probe current, 10 mm working distance. Backscattered electron images were used for the anodic oxide layer characterization. Here, 5 kV acceleration voltage, 5 nA probe current, and a working distance of 4 mm were used.

Results

Anodizing: voltage vs. time response

The voltage response during anodizing was monitored as a function of time. Figure 1 shows representative voltage vs. time plots of the anodizing conducted in the XY plane of the samples. Only results obtained in the XY surface are shown in this figure since the same trend was obtained for the XZ plane. A steep increase of the potential in the first few seconds (< 3s) of anodizing can be seen in Figure 1 for all the samples in the given conditions. All the specimens presented nearly the same behavior in this initial stage of anodization (independently of Si content), in which the rise of the voltage with time was approximately linear. According to the well-reported anodizing film formation mechanism [34,35], this initial linear increase in potential is associated with the
formation of a barrier-type oxide layer. After approximately 2 to 3 s a slight change in slope accompanied by a continued increase of the potential was seen for all the samples. This phenomenon was already described in earlier studies, and it has been associated with a continuous anodization of the Si phase in AM Al-Si alloys [14]. After 1.5 to 3 min of anodizing under the given conditions, a drastic change in the slope of the voltage vs. time curves towards a relatively steady state was then seen for all the specimens (see Figure 1). Nevertheless, marked differences were observed in the voltage values reached for the different Si containing AM specimens. As can be seen in Figure 1, the voltage measured during anodizing increases by increasing the amount of Si in the alloy.

Figure 2 shows, per sample analyzed, a comparison of the voltage vs time response between the XY and the XZ plane. During the anodizing of the XY surface of the AM specimens, significantly higher voltages were obtained compared to those measured during the anodizing of the surface oriented in the XZ direction. The same behavior was described in past works for the AM AlSi10Mg specimen [14,16]. Figure 2 confirms that the asymmetric anodizing behavior described earlier for AM samples containing 10% Si [14,16] is also present in AM AlSi12 and AM AlSi7Mg0.6 specimens.

**Thickness of the anodic oxide film**

By using optical microscopy, cross sections of the anodized specimens were analyzed and their thickness measured. This was done at different anodizing times. Figure 3a portrays the thickness of the anodic oxide layer as a function of anodizing time. Very similar oxide growth was seen for all the specimens analyzed. An approximate growth rate of 0.2 µm/min was measured for all the samples independently of the Si content in the alloy. The same value has been reported in previous works [14,16,33].

On the other hand, a closer look at the thicknesses measured revealed that for the same conditions (same anodizing time) by increasing the Si content slightly thinner anodic oxide layers are obtained. Two examples are shown in Figure 3b (one for the XY plane and one for the XZ plane) for two anodizing times. Even though the thickness values for the different samples at the same anodizing time cannot be considered statistically different from each other (due to overlap in their standard deviation), a consistent tendency towards slightly thinner anodic oxide layers was seen for greater amounts of Si in the alloys. This implies that increasing the amount of Si in the alloy slightly reduces the anodic oxide growth rate.

The values of the standard deviation obtained for the thickness of the anodic oxide layers are plotted in Figure 4. The standard deviation could be taken as a measure for the uniformity of the oxide film. A clear increase in standard deviation can be seen in Figure 4 by increasing anodizing time. However, what is more interesting, a slight increase in standard deviation was noticed for anodic oxides grown in the XY plane compared to those grown in the XZ plane. This means that slightly more uniform oxide layers are obtained when the XZ surface of the AM specimens is anodized compared to when the anodizing is conducted in the XY surface. This phenomenon was observed for all the AM Al-Si samples analyzed.
Anodic oxide layer characterization

A characterization of the anodic oxides’ cross sections was carried out using scanning electron microscopy. Backscattered electron images were used to distinguish compositional differences. Representative backscattered electron micrographs of the specimens at different magnifications are shown in Figure 5. In all the cases shown in Figure 5, the anodizing was conducted on the XY plane. The anodic oxide layer can be easily identified in those images since oxygen (with a lower atomic number than Al and Si) darkens the response. Moreover, the Si network and Al cells are also easily distinguished (see Figure 5). The dark appearance of the Si network within the anodic oxide film reveals that most of this Si is in the oxide form. This was already demonstrated in previous studies for AM AlSi10Mg [16,33]. Interestingly, this is also the case for AlSi7Mg0.6. However, as can be seen in Figure 5a-f, small unanodized areas can be sometimes observed in the anodic oxide layer (yellow arrows in Figure 5). These unanodized spots are usually located underneath of large Si particles. Similar observations were reported in earlier studies for cast Al-Si alloys [36]. Zhu et al. found that in cast Al-Si alloys the Si particles can, depending on their shape, prevent the oxidation of some of the Al phase underneath it [36]. Additionally, it was noticed that the number of unanodized areas increased by increasing the amount of Si in the specimens, or in other words, by increasing the connectivity and thickness of the Si network. An elemental composition analysis of a great number of these unanodized spots was conducted by means of EDS analysis. Figure 6 shows a selected image in which several EDS spectra were taken in different regions. The elemental composition calculated from these spectra is shown in Table 2. From the EDS analysis it was found that most of the unanodized parts within the anodic oxide film were constituted mainly of non-oxidized Al. An example of this is shown in Spectrum 1 (see Figure 6 and Table 2). Small amounts of Si and O were also always detected in these areas (Spectrum 1), possibly due to the combined effect of the small size of these spots, their proximity to large Si particles, and the characteristic electron interaction volume during EDS analysis. However, as can be seen in Spectrum 2, some (a small amount of them) of these unanodized spots presented, together with the high content of Al, a relatively high percentage of Si. This indicates that these spots are composed of unanodized Al, and in few cases also partially unanodized Si. Spectrum 3 was acquired inside of an anodized Al cell. Therefore, here only Al oxide was detected. On the other hand, Spectrum 4 was obtained near oxidized Si phase. Here a high oxygen content and relatively high content of Si was measured. Nevertheless, some Al was also detected in Spectrum 4. This could also be related to the small size of this region, its proximity to large Al cells, and the characteristic electron interaction volume during EDS analysis. Additionally, the existence of Al in regions like the one from which Spectrum 4 was acquired, could be due to the presence of a lamellar microstructure of alternating layers of Al and Si phases where large Si particles exist [15,16]. Moreover, as can be seen in the micrographs of Figure 5, the interphase between the anodic oxide film and the metallic matrix seems to be much more uniform for the AlSi7Mg0.6 sample and more
irregular for the AlSi12 sample. Therefore, by increasing the amount of Si in the alloy, the uniformity of the oxide front decreases. 

The pores formed in the anodic oxide as a result of oxide dissolution by the acidic electrolyte can also be distinguished in the micrographs of Figures 5d-i. As also reported in previous studies, due to the fine distribution of the Si phase, branched pores developed throughout the entire anodic oxide layer [14,16,33]. This was the case for all the alloys analyzed (see Figure 5d-i). Nevertheless, a closer look at the micrographs revealed that the width of the pores and the separation between them is greatly affected by the content of Si in the alloy. In AM Al-Si samples with greater amounts of Si, larger pores with a greater separation between them are developed. The discontinuous green arrows in Figure 5 highlight two neighboring pores in each sample. Since higher anodizing voltages were reached for higher Si content, this relation seems to be in agreement with the high-field formation mechanism, in which the geometry of the porous structure is directly dependent on the voltages reached during anodizing. This mechanism predicts wider pores and larger interpore distances for higher anodizing voltages [37, 38]. 

Lower magnification backscattered electron images of some cross sections are shown in Figure 7. Clear irregularities can be observed in the thickness of the anodic oxide film. At the MPBs, where a coarser microstructure is present, a thinner oxide layer is formed compared to regions within the MPs. This phenomenon was also observed in previous works, and it seems to be caused by a slightly higher accumulation of Si at the MPBs in comparison with other areas of the MPs [16]. This was observed in all the samples anodized independently of the Si content in the alloy.

**Impact of porosity on the anodizing behavior**

The presence of internal porosity in AM metal parts is an area of interest in the MAM industry [39]. The amount of porosity is critical for high stress applications. Therefore, during this study the effect of subsurface porosity on the anodizing behavior was also analyzed. Figure 8 shows selected backscattered electron images of the cross section of anodized specimens in which internal pores intercepted by the anodizing front can be seen. In Figure 8a a large pore can be observed with a diameter around 12 µm. Figures 8b and 8c show medium-size pores with diameter around 3 µm. As in Figures 5, 6 and 7, the oxide layers in Figure 8 can be easily identified due to the darker appearance of the oxide in the backscattered electron micrographs. In Figure 8 can be seen that the periphery of the pores is surrounded entirely by an oxide film. This outer oxide layer encircling the pores was observed for all the pores that were reached by the anodic oxide front. That was the case for all the alloys analyzed. Additionally, cracks in the anodic oxide layer were always noticed in the side of the pores reached by the anodizing front. This is indicated by the red arrows in Figure 8. As it can be seen in this figure, these cracks have a similar appearance for all the cases and are generally found in a symmetric arrangement at both sides of the pores (considering the surface at the top).

**Discussion**
The unanodized parts observed in the anodic oxide films (underneath of large Si particles) are mainly composed of unanodized Al, and in some cases also partially unanodized Si (see Figure 6). The larger Si particles could have a shielding effect over the Al positioned on the opposite side of the anodic oxide front growth, protecting it from being oxidized. A similar effect was described by Zhu et al. [36] for cast Al-Si alloys. The fact that to some extent more unanodized spots were noticed for higher Si content in the alloy could be the result of a greater connectivity and thickness of the Si network. When more Si is present in these AM alloys, larger and coarser Si particles form the Si network. Additionally, by increasing the Si content, the discontinuities of the Si network are greatly reduced [15]. This could partly hinder the progression of the anodic oxide front, especially at thicker regions of the Si network. Moreover, the greater connectivity and thickness of this network could also be responsible for the increased irregularity of the interphase between the anodic oxide film and the metallic matrix for higher contents of Si (see Figure 5).

On the other hand, even though slightly more unanodized spots were noticed for samples containing higher amounts of Si, in general, most of the Si phase encountered by the anodizing front was oxidized. This can be clearly seen in the backscattered electron images of the cross section of the anodized AM specimens in Figure 5, in which most of the Si network within the anodic oxide film has a much darker appearance. Additionally, the unanodized spots present in the anodic oxide are, generally, not very numerous. Consequently, by increasing the percentage of Si in the AM Al-Si samples, the total amount of oxidized Si in the oxide layer seems to be higher. Since relatively higher field strength is required for the anodic oxidation of Si compared to Al [40], this could explain the considerable increase in voltage seen for higher Si content.

As seen in Figure 7, the MPBs have a marked influence on the uniformity of the anodic oxide layer. Due to variations of the thermal gradient created by the moving heat source, which results in a lower cooling rate towards the MPBs [9], a coarser microstructure and a slight accumulation of Si is present at the MPBs [16]. Therefore, since the anodic oxidation of Si requires a relatively high field strength [40], a thinner oxide layer is grown at the MPBs. This local reduction of the oxide layer’s thickness at the MPBs could be the main factor influencing the uniformity of the anodic oxide film. Moreover, during the anodizing of the XY surface, the oxide front encounters the microstructure of the XZ plane, which presents a considerably high density of MPBs (see schematic of Figure 9). These structures have been described in a great number of studies [14-18]. On the other hand, during the anodizing of the XZ surface, the oxide front encounters the microstructure of the XY plane, which has a relatively lower density of MPBs. Therefore, since during the anodizing of XY surfaces a much higher number of MPBs is encountered by the oxide front compared to the anodizing on XZ, this could explain why the standard deviation of the oxide thickness was higher for anodized XY surfaces than for XZ surfaces (Figure 3b). Additionally, this effect could also be responsible for the noticeable differences in anodizing voltage between the XY and the XZ surface of the AM Al-Si specimens. While anodizing XY surfaces, more MPBs (with locally more Si than the rest of the MPs [16]) are encountered than during anodizing XZ surfaces. Therefore, anodizing XY surfaces would require higher anodizing voltages during galvanostatic anodizing than XZ surfaces.
From the results shown in Figure 3a it was seen that the amount of Si in the alloy does not seem to have a major influence on the anodic oxide growth rate. However, previous studies have shown considerable differences between the oxide growth rates of as-received AM AlSi10Mg, heat treated AM AlSi10Mg, and cast alloy of approximately the same chemical composition [14,33]. The main difference between those samples resided in the distribution and microstructure of the Si phase. Therefore, the outcomes of the experiments conducted within our combined studies reveal that the distribution/microstructure of the Si phase seems to have a much greater impact on the anodic oxide growth rate than the absolute amount of Si present in these Al-Si alloys.

This work analyses for the first time (to the best of our knowledge) the effect of internal porosity on the anodizing behavior of Al-Si alloys. Two main interesting features of subsurface pores reached by the anodic oxide front were revealed during this work (see Figure 8): 1 – The formation of an anodic oxide layer encircling the pores; 2 – The formation of cracks on the side of the pores reached by the anodizing front.

The anodizing conducted in acidic electrolytes is characterized by the formation of thin and elongated pores that progress inwards with anodizing time. Through these elongated pores formed during anodizing, the electrolyte advances to further anodize the metal part (see Figure 10a). When the anodic oxide front reaches an internal pore like those shown in Figure 8, these pre-existing pores are filled with the electrolyte that flows through the thin pores formed during anodizing (Figure 10b). Once the pre-existing pores get filled with the electrolyte, the anodizing continues perpendicular to the walls of these round pores, forming a lining of oxide inside these pores (Figure 10c). Therefore, the local anodic oxide front becomes parallel to the walls of these internal pores. During anodizing, Al from the matrix is converted into $\text{Al}_2\text{O}_3$, which produces a volume expansion of the anodic oxide layer. This volume expansion could be the cause of the cracks formed at the side of the internal pores reached by the anodizing front. The cracks form as a result of the encounter of oxide layers growing in opposite directions (the initial anodic oxide layer and the oxide layer growing in the direction perpendicular to the pores wall – Figure 10d). One might think that these cracks could be the result of the polishing of the cross section. However, the fact that they are always present at the same location (at the side of the pores reached by the anodizing front), symmetrically arranged at both sides of the pore, and with approximately the same shape (see Figure 8), suggest that they are formed during the anodizing process. The size of the cracks observed in this work range from 1 to 2 µm. Even though they are relatively small, they could compromise the integrity of the final piece. Additionally, these cracks could facilitate the access of corrosive media to the metal matrix.

Conclusions
In this work, the influence of Si content on the galvanostatic anodizing behavior of additive manufactured Al-Si alloys in $\text{H}_2\text{SO}_4$ electrolyte was studied. The main results can be summarized as follow:

1. Due to the fine distribution of the Si phase in additive manufactured Al-Si alloys, most of the Si encountered by the moving anodic oxide front is oxidized. This significant oxidation
of Si increases the voltage measured during anodizing. Additionally, the fine distribution of Si in these alloys also prompts the development of branched pores throughout the entire anodic oxide film.

2. Independent of the amount of Si in the alloy, an asymmetric anodizing behavior is always observed: A lower voltage response is obtained during the anodizing of the XZ plane of the samples compared to the XY plane, due to the great difference in the number of MPBs encountered during the anodization of these surfaces.

3. The melt pool borders have a considerable influence on the uniformity of the anodic oxide film. A locally thinner anodic oxide layer is grown at the MPBs of all the specimens independently of the Si content in the AM Al-Si alloys.

4. The Si content in the AM Al-Si alloys has a great impact on the porous structure of the anodic oxide layer. Increasing the amount of Si in the alloy greatly increases the voltage response during galvanostatic anodizing. Consequently, wider pores with a greater inter-pore distance are developed. Therefore, a lower density of pores is obtained.

5. The amount of Si in the alloy does not seem to have a major influence on the anodic oxide growth rate. Nevertheless, even though for the same anodizing time the average anodic oxide thickness is statistically the same for all the samples, a consistent tendency towards slightly thinner anodic oxide layers was seen by increasing the amount of Si in the alloys.

6. Increasing the amount of Si in the alloy increases the connectivity and thickness of the Si network, which, consequently, slightly increases the number of unanodized spots within the anodic oxide layer. These unanodized regions, usually located underneath of relatively large Si particles, are composed of unanodized Al, and in some cases also partially unanodized Si.

7. A less uniform interphase between the anodic oxide film and the metallic substrate is obtained for AM Al-Si alloys with higher contents of Si.

8. Internal pores resulting from the MAM process that are reached by the anodic oxide front are decorated by an outer anodic oxide layer. On the side reached by the anodizing front, cracks form due to the volume expansion of anodic oxide layers advancing in opposite directions.

Acknowledgements
The authors wish to thank Bart Lippens for his contribution with the sample polishing, and Marc Raes and Priya Laha for their contribution with the SEM imaging.

References
19. A. Leon, A. Shirizly, E. Aghion, Corrosion behaviour of AlSi10Mg alloy produced by additive manufacturing (AM) vs. its counterpart gravity cast alloy, Metals 6 (2016) 148.
Figures

Figure 1. Voltage vs. time response during anodizing in 3M H$_2$SO$_4$ at 10 mA/cm$^2$ of the additive manufactured AlSi7Mg0.6, AlSi10Mg, and AlSi12. Only voltage vs. time responses of the anodizing conducted in the XY plane is shown as an example. The same trend was obtained in the XZ plane.

Figure 2. Comparison of the voltage vs time response between the XY and the XZ plane during anodizing in 3M H$_2$SO$_4$ at 10 mA/cm$^2$ of the additive manufactured AlSi7Mg0.6 (a), AlSi10Mg (b), and AlSi12 (c).
Figure 3. (a) Anodic oxide layer growth as a function of anodizing time for the XY and XZ plane of all the samples (AlSi7Mg0.6, AlSi10Mg, and AlSi12). (b) Comparison of oxide layer thicknesses obtained for the different specimens at the same anodizing time (Anodizing of the XY plane for 12 min, and the XZ plane for 20 min were taken as examples. The same trend was observed for all the other cases).

Figure 4. Standard deviation of the anodic oxide layer thickness as a function of anodizing time for the XY and XZ plane of all the samples (AlSi7Mg0.6, AlSi10Mg, and AlSi12).
Figure 5. Backscattered Electron images of the cross section of the AM AlSi7Mg0.6 (a, d, g), AM AlSi10Mg (b, e, h), and AM AlSi12 (c, f, i) after anodizing for 20 min in 3M H₂SO₄ at 10 mA/cm². In all of the cases, the anodizing was conducted in the XY plane.
Figure 6. Selected Backscattered Electron image of the cross section of an anodized AlSi12 specimen in which EDS spectra were acquired in different regions of the scanned area.

Figure 7. Backscattered Electron images of the cross section of selected anodized specimens highlighting the uneven thickness of the anodic oxide layer. Coarse and fine microstructure associated with the melt pool borders and the core of the melt pools respectively can be easily seen. MPB refers to melt pool border.
Figure 8. Backscattered Electron images of the cross section of selected anodized specimens highlighting pores in the material intercepted by the anodizing front. All images have a scale bar of 1 μm.

Figure 9. Schematic of the AM samples highlighting the melt pool borders (MPBs). XY is the plane parallel to the building platform, and XZ is the plane perpendicular to the building platform. A higher density of MPBs is seen in the XZ plane, while a relatively low density of MPBs exist in the XY plane.

Figure 10. Schematic showing the anodizing progress around internal pores reached by the anodizing front.
**Tables**

**Table 1.** Chemical composition (in wt%) of the metal powders used for the fabrication of the additive manufactured specimens as specified by the manufacturers.

<table>
<thead>
<tr>
<th>Element</th>
<th>AlSi7Mg0.6</th>
<th>AlSi10Mg</th>
<th>AlSi12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
</tr>
<tr>
<td>Si</td>
<td>6.50 – 7.50</td>
<td>9.00 – 11.00</td>
<td>11.00 – 13.00</td>
</tr>
<tr>
<td>Mg</td>
<td>0.45 – 0.70</td>
<td>0.20 – 0.45</td>
<td>–</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt; 0.19</td>
<td>&lt; 0.55</td>
<td>–</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt; 0.05</td>
<td>&lt; 0.10</td>
<td>–</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt; 0.10</td>
<td>&lt; 0.35</td>
<td>–</td>
</tr>
<tr>
<td>Ni</td>
<td>–</td>
<td>&lt; 0.05</td>
<td>–</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt; 0.07</td>
<td>&lt; 0.10</td>
<td>–</td>
</tr>
<tr>
<td>Pb</td>
<td>–</td>
<td>&lt; 0.05</td>
<td>–</td>
</tr>
<tr>
<td>Sn</td>
<td>–</td>
<td>&lt; 0.05</td>
<td>–</td>
</tr>
<tr>
<td>Ti</td>
<td>&lt; 0.25</td>
<td>&lt; 0.15</td>
<td>–</td>
</tr>
<tr>
<td>Residuals</td>
<td>–</td>
<td>–</td>
<td>&lt; 0.60</td>
</tr>
</tbody>
</table>

**Table 2.** Elemental composition calculated from the spectra acquired in the regions marked in Figure 6.

<table>
<thead>
<tr>
<th>Element</th>
<th>Spectrum 1</th>
<th>Spectrum 2</th>
<th>Spectrum 3</th>
<th>Spectrum 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>64.1</td>
<td>48.1</td>
<td>46.4</td>
<td>23.5</td>
</tr>
<tr>
<td>Si</td>
<td>15.4</td>
<td>31.4</td>
<td>–</td>
<td>24.0</td>
</tr>
<tr>
<td>O</td>
<td>20.5</td>
<td>20.5</td>
<td>53.6</td>
<td>52.5</td>
</tr>
</tbody>
</table>