Galvanostatic anodizing of additive manufactured Al-Si10-Mg alloy

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ABSTRACT:
The galvanostatic anodizing behavior of additive manufactured (AM) Al-Si10-Mg alloy was studied in H2SO4 electrolyte. The analysis of the voltage vs time response was complemented with a systematic characterization of the anodic oxide layer using a variety of techniques. In addition, a cast alloy of approximately the same chemical composition as that of the AM specimens was used as a reference in this study. Significant differences were found in the voltage–time characteristics of the samples analyzed. Besides, an anisotropic anodizing behavior was observed in the additive manufactured specimens. Due to the fine silicon microstructure present in the additive manufactured samples, the anodic oxide growth was much more obstructed than for the cast alloy. Nevertheless, even though the oxide layer was generally thinner in the AM samples for the same conditions and anodizing time, a much more continuous and uniform oxide layer was found in the additive manufactured specimens compared to the cast alloy. The porous structure was found to be greatly affected by the fine distribution of the silicon phase in the AM parts.
1. Introduction

Metal additive manufacturing (MAM), a rapidly growing industry, is based on the fabrication of complex metal parts by adding material layer by layer [1]. Among the various alloys used for additive manufacturing, Al-Si10-Mg is of great interest for automotive and aeronautic applications [2]. This material is relatively easy to process by direct metal printing (also known as selective laser melting; the most common metal additive manufacturing process [1]) due to its proximity to the eutectic composition (~12.5 wt.% Si) [3]. Additionally, minor additions of magnesium (0.3 – 0.5 wt.% Mg) are known to induce hardening by forming Mg2Si precipitates in cast Al–Si alloys [4].

Due to the uniqueness of the MAM process (namely that the metal powder used is already pre-alloyed, and the melting occurs in small pools that rapidly solidify), the formation of a very fine microstructure is observed. This microstructure has been widely studied in the past years [5–9]. A fine silicon network decorates the primary crystalline aluminium forming very small cells. The size of these cells varies over the melt pool due to the thermal gradient created by the moving heat source (finer cells can be found towards the middle of the melt pools, and larger cells are observed in the borders of the melt pool) [7,8]. It has been demonstrated that the microstructure has a considerable influence on the corrosion behavior of the additive manufactured (AM) Al-Si10-Mg specimens [10]. Corrosion initiates in the melt pool borders, where a coarser microstructure is generally found [7,8,10]. Anodizing is commonly used for corrosion protection of Al and its alloys. The anodizing behavior of AM Al-Si10-Mg has however, to the best of our knowledge, not been reported in literature. A recent study on the growth of anodic oxide films on cast Al–Si alloys demonstrated that the growth of the oxide layer is dependent on the microstructure of the bulk material [11]. The researchers also concluded that the concentration of Si and the alloy cooling rate can influence the thickness of the anodic oxide layer [11]. In this work, the anodizing behavior of AM Al-Si10-Mg alloy is presented. The anodizing was conducted galvanostatically in H2SO4 electrolyte. Additionally, a comparison with a cast Al alloy of approximately the same chemical composition was carried out. The samples’ anodic oxide layers were characterized by using optical microscopy, Field Emission Scanning Electron Microscopy (FE–SEM), Transmission Electron Microscopy (TEM), and Atomic Force Microscopy (AFM).
2. Materials and methods

2.1. Samples

Two types of samples were used during the experiments: An AM Al-Si10-Mg alloy prepared by direct metal printing (DMP), and a cast aluminium alloy (AA4420) from Aleris. Their chemical compositions are given in Table 1. The AM process was executed using a ProX DMP 320 machine (3D Systems) equipped with a 500 W laser in an argon atmosphere with resulting oxygen content of < 50 ppm. Samples of $5 \times 30 \text{ mm}^2$ and a total height of 10 mm were fabricated using LaserForm AlSi10Mg powder and standard 3D Systems processing parameters for 30 µm layer thickness. A laser energy density of 51 J/mm$^3$ was used for the sample preparation. This parameter indicates the laser energy input into the material and is equal to the laser power divided by the scanning speed, the layer thickness, and the hatch distance. 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). The AM samples were divided in two groups: 1 – samples in which the surface analyzed was oriented in the direction parallel to the building platform (AM Al-Si10-Mg $XY$), 2 – samples in which the surface analyzed was oriented in the direction perpendicular to the building platform (AM Al-Si10-Mg $XZ$).

2.2. Anodizing

Anodizing was carried out galvanostatically in a stirred 3M H$_2$SO$_4$ electrolyte at 10 mA/cm$^2$ and at room temperature. An ES 0300-0.45 power supply from Delta Elektronika was used. The anodic potential was measured as a function of the 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.

2.3. Sample characterization by FE–SEM, TEM, AFM and Optical microscopy

Morphology and microstructure characterization were carried out using a FE–SEM JEOL JSM–7100F with 15 kV acceleration voltage, 5 nA probe current, and a working distance of 10 mm. FE–SEM imaging was performed at different magnifications. The scale bar is indicated in every image. TEM images were obtained using a scanning transmission electron microscope Philips CM20 Ultra Twin operating at 200 kV. Cross-sectional TEM thin foils were prepared by focused
ion beam milling. AFM topography mapping was conducted using a commercial atomic force microscope (Park Systems XE–100). Rectangular conductive cantilevers (ANSCM–PT from AppNano) with a resonant frequency of 50 – 70 kHz, and a spring constant of 1 – 5 N/m were used for the measurements. The thickness of the anodic oxide layer was measured on polished cross sections of the samples using a Leica 125 optical microscope.

3. Results

3.1. Microstructure characterization

A microstructure characterization of the polished specimens was carried out prior to anodizing using optical microscopy and secondary electron microscopy. Figure 1 shows optical images of a region in the surface of the cast alloy and the surfaces parallel (XY) and perpendicular (XZ) to the building platform of an AM Al–Si10–Mg specimen. Large needle–like silicon crystals can be seen in the surface of the cast alloy sample even at low-to-medium magnification (see Figure 1a). This alloy has a hypoeutectic composition which leads to the formation of primary α–Al dendrites followed by the solidification of eutectic α–Al + Si. On the other hand, a very different morphology was observed in the optical images of the AM specimens (see Figures 1b and 1c). Figure 1b shows a surface parallel to the building platform (XY) and Figure 1c a surface perpendicular to the building platform (XZ). No silicon phase could be seen in the AM samples through the optical images; instead, the melt pools and melt pool borders (MPBs) are clearly visible. The reason why the MPBs are visible under the optical microscope is associated with the fact that the microstructure is coarser at the borders of the melt pool [7,8]. The elongated laser tracks can be clearly seen in the surfaces oriented in the XY (Figure 1b) plane while a scale–like feature was observed in the XZ plane (Figure 1c).

In order to study the microstructure in further detail the samples’ surfaces were observed using scanning electron microscopy after being etched with Keller’s reagent. Figure 2 shows secondary electron images of the surface of the specimens. The relatively large Si crystals can be easily observed in the surface of the cast alloy (Figure 2a), while the silicon phase in the AM samples is much finer and more dispersed within the matrix (Figures 2b and 2c). Figure 2b shows the microstructure of the surface of the AM specimen oriented in the XY plane and Figure 2c shows the microstructure of the surface oriented in the XZ plane. From Figures 2b and 2c can be seen that the fine silicon phase forms a 3–dimensional network that encloses the α–Al cellular cells.
These cells have an approximately circular shape in the XY plane (see inset of Figure 2b), while a more elongated shape is observed in the cells located in the XZ plane (see inset of Figure 2c). Other researchers in previous works [7] noticed a similar morphology. Due to the high energy density of the laser, a directional heat transfer and therefore a directional solidification regime takes place, resulting in elongated cells stretched along the direction perpendicular to the building platform [7]. The α–Al cells in the XY plane have an average diameter ranging from 0.3 to 0.6 µm, while the α–Al cells in the XZ plane have an average length ranging from 0.4 to 1 µm. Additionally, the microstructure at the melt pool borders is much coarser than that observed within the melt pools. As mentioned above, this has been previously associated with variations of the thermal gradient created by the moving heat source [7], resulting in a lower cooling rate towards the edges of the melt pool.

The small Al cells are decorated with a very fine Si network. A more detailed characterization of this network was conducted by TEM (see Figure 3). In Figure 3a can be seen that the Si layer surrounding the Al cells has a thickness from 40 to 50 nm. Additionally, the electron diffraction pattern taken in different points of Figure 3a revealed that the silicon network has a poly–crystalline nature. This is confirmed by the existence of rings around the bright spot in the diffraction pattern (Figure 3b). While the pattern obtained in the Al cell (Figure 3c) revealed a single crystal structure. These results are in perfect agreement with previous works. Yan et al. [8] reported that the silicon network formed in AM AlSi10Mg specimens is predominantly composed of Si nanocrystals of approximately 20 nm in diameter. These nanocrystals aggregate to form the boundaries of the Al cells with a thickness of about 40 nm [8].

Furthermore, a statistical analysis was carried out using the image processing program ImageJ in order to estimate the average surface area of the Al cells in the AM specimens. For this, several SEM images (~18 images) taken in different areas of each surface were analyzed. The results of this analysis are shown in Figure 4. It was observed that the sections of the α–Al cells are generally larger in the XZ surface than in the XY surface. The area of the Al cells in the AM XZ specimens is on average 1.5 times larger than the area of the cells in the AM XY samples. Nevertheless, it is important to notice that the total active area of the aluminium phase was found to be approximately the same in both surface planes analyzed (XY and XZ).

3.2. Voltage vs time response
The samples were galvanostatically anodized using the conditions explained in Section 2.2. The behavior of the anodic potential with time is shown in Figure 5. Large differences in the voltage vs time response were observed between the samples. Figure 5a shows the voltage–time response for 20 min and Figure 5b zooms into the first 75 s of anodizing. Replications of each condition are plotted to indicate the repeatability of the data. As can be seen in Figure 5, a steep increase of the potential in the first 5 to 7 s (interval 0B in Figure 5b) was obtained for all the samples in the given conditions. In this region, the rise of the voltage with time is initially approximately linear (in the interval from 0 to 3 s – region 0A in Figure 5b). Moreover, all the specimens presented nearly the same slope in the voltage vs time plots in the first 3 s of anodizing (region 0A in Figure 5b). According to the well-known anodizing film formation mechanism [12,13], this initial linear increase in potential is associated with the formation of a barrier-type layer, followed by the generation of incipient pores. At 6 to 10 s (BC) a drastic change in slope was noticed for all the samples (see Figure 5b). Generally, in this region the porous structure is known to develop, with initiated pores reorganizing spatially and gradually covering the entire surface. After 10 s of anodizing (point C in Figure 5b) a relatively steady state can be observed in the voltage–time response of the cast alloy sample (black traces in Figure 5). In this stage, typically characterized by an approximately constant potential, the final columnar porous structure further propagates in a steady state regime. However, a continued increase of the potential was observed during the anodizing of the AM specimens from 10 s to approximately 1.5 min (region CD). A drastic change in the slope of the curves towards a relatively steady state was then observed in the AM specimens after 1.5 to 2 min as can be seen in Figure 5a. As can be noticed in Figure 5, the voltage–time behavior of the AM samples oriented in the XY direction is comparable to that of the AM specimens oriented in the XZ direction for the first ~1.5 min of anodizing (region 0D in Figure 5). However, even considering the spread observed in the measurements of each AM sample, a clear divergence was found in the voltage vs time plots for anodizing times greater than 1.5 to 2 min (point D in Figure 5a) between the AM sample’s surfaces oriented in the XY plane and those oriented in the XZ plane. During the anodizing of the XY surface of the AM specimens significantly higher potentials were obtained compared to those measured during the anodizing of the surface oriented in the XZ direction. For relatively long anodizing times (> ~6 min) a difference of about 5 V was obtained between the two surface orientations. Additionally, the potential measured for the AM specimens increased up to voltages
from 1.6 to 2.3 times larger than those obtained during the anodizing of the cast alloy for the given anodizing conditions.

3.3. Anodic oxide layer thickness

The specimens’ cross sections were analyzed for different anodizing times. Optical microscopy images of the cross section of the samples after anodizing for 20 min are shown in Figure 6 as an example. In the image of the cast alloy (left panel in Figure 6) the large silicon crystals can be easily identified. These silicon particles interrupted the growth of the anodic oxide layer while a relatively regular anodic film developed in areas free from second–phase particles. After 20 min of anodizing using the conditions specified in Section 2.2, an anodic oxide layer with an average thickness of 7.7 ± 1.6 µm was obtained for the cast alloy. On the other hand, a globally thinner but more continuous oxide layer was found in the AM specimens for the same conditions and anodizing time (see middle and right panel in Figure 6). This is in agreement with the studies conducted on cast alloys by Fratila-Apachitei et al. [14], in which the authors reported that a fine Al cell structure is favorable for the growth of anodic oxide layers with minimum defects and uniform thickness. An average anodic oxide thickness of 4.4 ± 0.9 µm and 4.3 ± 0.8 µm was determined after 20 min of anodizing for the AM in the XY plane and the AM sample in the XZ plane, respectively.

The oxide layer thickness was also measured as a function of anodizing time for all the samples. The results are shown in Figure 7. An approximately linear oxide growth was obtained in all the specimens, as expected under galvanostatic anodizing conditions. However, a considerable difference was observed between the cast alloy and the AM samples as can be seen in Figure 7. From the slope of the lines in Figure 7, the growth rate of the anodic oxide film was calculated to be 0.4 µm/min for the cast alloy and 0.2 µm/min for the AM specimens. The oxide growth rate of the AM specimens was half of that obtained for the cast alloy. Even though great differences were observed in the voltage vs time behavior between the AM specimens oriented in the XY and the XZ plane for long anodizing times, the oxide growth rate was nearly the same regardless of the surface plane orientation (see Figure 7).

3.4. Characterization of the porous structure

The formation of the pores as well as their arrangement was studied by SEM, TEM, and AFM. By carrying out an SEM characterization of the anodized surfaces, it was found that the initial formation of the porous structure takes place at approximately the same time for all the samples
(cast alloy as well as AM specimens). Figure 8 shows secondary electron microscopy images of the surface of the cast alloy and an AM specimen after anodizing for 3 s and 30 s. It is important to notice that the same behavior was obtained in the XY as well as in the XZ surface of the AM samples. Therefore, only one representative image is presented for both AM samples surfaces. Figures 8a and 8b portray an area of the surface of the cast alloy and an AM sample, respectively, after 3 s of anodizing. This point is located right before the drastic change in slope in the voltage vs time plot (region BC in Figure 5b) noted between 6 s and 10 s. Figures 8c and 8d show a region in the surface of the cast alloy and an AM sample, respectively, after 30 s of anodizing. This point is situated after region BC in Figure 5b. As explained above, in region BC the porous structure develops further and gradually covers the entire surface. As can be seen in Figures 8a and 8b, after 3 s of anodizing isolated pores can be observed, while after 30 s of anodizing the pores were seen to cover the entire surface of all the samples (see Figures 8c and 8d). Therefore, the development and further propagation of the porous structure seem to occur at about the same time interval for all the samples (around the slope change observed in region BC – see Figure 5b) despite the fact that large differences were observed in the further voltage–time response of the AM specimens compared to the cast alloy.

FE–SEM images of the specimens’ cross section are shown in Figure 9. The relatively large size of the silicon particles found in the cast alloy provokes a noticeable interruption of the anodic oxide film. This can be clearly seen in the secondary electron images of the cross section shown in Figure 9a. The anodic oxide front and the porous structure curve in the vicinity of the Si particles. This has also been shown in earlier studies [11,15]. On the other hand, a more uniform layer is formed on the AM specimens (see Figures 9b and 9c) due to the finer size of the silicon particles. In order to study in more detail the porous arrangement, TEM images of the oxide layer’s cross section were obtained for all the samples. In Figure 10 the cross sections of the cast alloy and an AM specimen are presented. In the cast alloy the pores grow perpendicular to the surface in areas free from second–phase particles (see Figure 10a). However, in the AM samples, due to the fine distribution of the silicon phase, branched–like pores developed throughout the entire anodic oxide layer. Previous studies on the anodization of Al–Si alloys have shown that the presence of Si particles influences the morphology of the enveloping porous anodic oxide film, provoking the branching and deflection of the pores around the particles [11,15].
A dimensional characterization of the porous structure is presented using AFM. AFM topography maps were acquired on the cross section of the oxide films. Figure 11 shows examples of AFM maps of areas on the surface’s cross section of the cast alloy and an AM Al-Si10-Mg XZ specimen. An example of a line profile of the cross section of a pore can be observed in Figures 11c and 11f. After mapping a great number of areas, an average value of the diameter of the pores was estimated for all the samples. Table 2 lists the values obtained per specimen. An increase was noted in the diameter of the pores following the same trend as that observed in the final anodization voltage ($d_{CA} < d_{AM,XZ} < d_{AM,XY}$). The pore diameter of the AM samples was found to be larger than the diameter of the pores grown in the anodic oxide layer of the cast alloy. Furthermore, the average diameter of the pores formed in the XY surface of the AM specimens was larger than that of the pores grown in the XZ surface. TEM results also confirmed this significant difference in pore diameter between the samples. Interesting to note, however, is that the ratio between these pore diameters and the corresponding steady–state anodizing voltages are in the same range for the three considered sample variants: between 1.3 and 1.7 nm/V. This is in good agreement with the ratio which can be deduced from literature [16], suggesting that the high–field ionic migration mechanism is the same for the three sample types.

4. Discussion

Obvious differences were found in the behavior of the voltage with time as well as in the anodic oxide layer of the specimens studied. The fine microstructure present in the AM samples as a result of the unique conditions of the MAM process, leads to an unusual anodizing behavior.

4.1. Influence of the microstructure on the voltage–time response

The fact that the silicon phase is finely distributed within the AM parts must somehow be the cause of the large voltage increase observed in the voltage–time response during the anodizing of the AM samples. From Figure 2 can be seen that the silicon phase encloses the small aluminium cells, forming what seems to be a three dimensional, almost continuous network. Every aluminium cell seems to be covered by a silicon shell–like structure. However, some local interruptions of this network can be seen where one aluminium cell connects to others. To form the anodic oxide layer, oxygen carrying anions migrate under the high electric field strength inward in the oxide to react with aluminium cations at the metal/oxide interface. The Si shell
decorating the Al cells could be limiting the high-field ionic migration, increasing as a result the potential difference needed to maintain a constant current. Nevertheless, other or additional explanations need to be considered since the anodization ratio between pore diameter and voltage seems to be in the same range for all the specimens. This suggests that the high-field mechanism is the same for the different samples. Moreover, considering the flow mechanism of pore formation proposed by S.J. Garcia-Vergara et al. [17], this also suggests that the flow ratio of the oxide from the barrier layer toward the cells wall could be the same for all the specimens analyzed.

During anodizing of Al–Si alloys, a partial oxidation of the silicon particles has been reported in previous studies [11,15]. The Si particles are anodized and a barrier type SiO$_2$ layer of 40 nm [15] or 30 to 100 nm [11] has been found decorating the large particles. In the AM samples the silicon network formed around the Al cells has a width of about 40 to 50 nm (see Figure 3a), which is comparable to the reported total thickness of the SiO$_2$ barrier layer generally formed around Si particles during anodizing of Al–Si alloys. Consequently, we need to consider that in the AM material a much higher percentage of this silicon phase could be oxidizing than in the conventional cast Al-Si alloys. As reported by Zhu et al. [11], the fraction of Si that is oxidized during the anodization of Al–Si alloys is determined by the size and the interconnection of the Si particles. For smaller particles, a larger fraction of Si is generally anodized [11]. Therefore, this could result in an increase of the anodizing voltage due to the relatively higher field strength required for the anodic oxidation of Si [18]. Nevertheless, a more detailed characterization of the oxide layer, and especially also the Si phase after anodization, is needed in further studies in order to confirm this assumption.

Furthermore, a clear voltage difference was observed between the voltage–time responses of the XY and the XZ surface of the AM samples (see Figure 5). The anodizing voltage of the AM_XY specimens was higher than the voltage measured for the AM_XZ samples. This could be associated with the fact that the active area of the Al cells in the XY plane is on average 1.5 times smaller than the active area of the Al cells in the XZ plane (see Figure 4). Nevertheless, it is important to remember that the total Al area estimated with the image-processing program ImageJ was the same for both AM surface orientations. The anodic aluminium oxide layer grows in the direction normal to the sample’s surface. However, at the interface between the Al matrix and the Si phase, the oxide front curves and circumvents the silicon particle [11,15]. At that
interface, a lower anodizing rate has been described in previous studies [11]. Due to the smaller size of the Al cells in the XY plane compared to the cells in the XZ plane, a greater amount of Al in the proximity of the Si phase is encountered by the oxide front in the AM_XY samples. This could, therefore, increase the anodizing voltage required to grow the oxide film. However, further research is necessary for a better understanding of this particular anodizing behavior observed in the AM specimens.

4.2. Influence of the microstructure on the anodic oxide layer

The thickness and the porous structure of the anodic oxide layer of the AM samples were markedly different from those of the cast alloy. As discussed above, due to the fine size of the silicon phase in the AM specimens, a greater fraction of this silicon might be oxidized during the anodization process. Therefore, a larger percentage of the charge would be consumed to anodize the silicon phase, resulting in a lower charge to form the anodic alumina, forming as a consequence a thinner oxide layer than for the cast alloy. Additionally, silicon anodizes at a much lower rate compared to the adjacent aluminium matrix [18]. The combination of these factors could be the reason why the oxide growth rate in the AM samples was much lower than in the cast alloy (see Figure 7).

Furthermore, as mentioned above, when the oxide front encounters a silicon particle, this front as well as the porous structure circumvents the particle [11,15]. Due to the fine distribution of silicon in the AM specimens (forming cells with average dimensions ranging from 0.3 to 1 µm – see section 3.1), a very high percentage of the pores meet a Si particle within 1 µm after being formed. The quite particular branched–like porous structure in each of the anodized Al cells is likely related to the fact that the encapsulating Si network is not fully continuous and that the progressing oxide front (when regressing into the metal) goes through these local network disruptions into the underlying aluminium cells. This can result in the pores continuing to grow deeper into the metal but with their growth direction perpendicular to the local entry point into the aluminium cell, and with the pores flaring out into a hemispherical pattern (see Figure 10).

5. Conclusions

In this work galvanostatic anodizing of AM Al-Si10-Mg alloy in H₂SO₄ electrolyte was studied. A cast alloy of approximately the same chemical composition was used as a reference. The main findings of our research can be summarized as follow:
• It is possible to anodize AM aluminium, but the anodizing voltage-time response and oxide film characteristics are significantly affected by the unique microstructure produced by MAM.

• The conventional steady state growth typically characterized by constant potential in the voltage–time response was clearly observed in the cast alloy, while a continued increase in the potential was seen in the AM specimens for a larger period of time before reaching a steady state value.

• In the cast alloy large dendritic eutectic silicon structures are present, while in the AM specimen the silicon is more finely distributed. Therefore, the oxide front during anodizing is more obstructed by the Si network in the AM samples, forming a thinner oxide film. The oxide growth rate in the AM samples was much lower than that measured in the cast alloy of approximately the same chemical composition.

• In the AM samples most probably a larger fraction of the anodic charge is consumed for the oxidation of the silicon than in the conventional cast alloy, explaining the lower film growth rate.

• Even though great differences were observed in the voltage–time response between the cast alloy and the AM specimens, the initial formation of the pores during galvanostatic anodizing in H₂SO₄ was observed at around the same time for the cast alloy as for the AM samples.

• The average diameter of the pores formed in the XY surface of the AM specimens was larger than that of the pores grown in the XZ surface; both were however larger than the pores formed in the cast alloy. This followed the same trend as the final anodization voltage in the voltage–time response, suggestion that the high-field migration mechanism was similar for the different sample variants.

• An anisotropic anodizing behavior was observed in the AM specimens. In the steady-state region of the porous film growth, the measured voltage was much higher during the anodizing of AM surfaces oriented in the XY direction than surfaces oriented in the XZ direction due to the differences found in the size of the aluminium cells.

• Due to the fine distribution of the silicon phase in an almost continuous network encapsulating the aluminium in small cells, branched–like pores developed throughout the entire anodic oxide layer of the AM specimens.
Acknowledgements
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References


Figure 1. Optical images of a region in the surface of the cast alloy AA4420 (a), the surface parallel to the building platform (XY) (b), and the surface perpendicular to the building platform (XZ) (c) of an AM Al-Si10-Mg specimen.
Figure 2. Secondary electron images of a region in the surface of the cast alloy AA4420 (a), the surface parallel to the building platform (XY) (b), and the surface perpendicular to the building platform (XZ) (c) of an AM Al-Si10-Mg specimen. MPB in (b) and (c) refers to melt pool
The insets in (b) and (c) are representative higher resolution images taken in the melt pools of surfaces XY and XZ respectively.

Figure 3. (a) Transmission electron microscopy image of the microstructure of the additive manufactured specimen. Electron diffraction pattern in point A (b) and point B (c) in the inset of the TEM image represented in (a). Point A was taken on the Si network while point B was chosen within the Al cell.
Figure 4. Relative frequency of the Al cells surface area in the surfaces XY and XZ as calculated by using the image processing program ImageJ. The inset of the figure represents an example of binary images of a region in the XY plane and a region in the XZ plane. The scale bar of the images in the inset of the figure is 1 µm.

Figure 5. (a) Voltage-time response of cast alloy (AA4420), AM Al-Si10-Mg XY, and AM Al-Si10-Mg XZ during anodizing in 3M H_2SO_4 solution at 10 mA/cm^2. (b) First 75 s of the voltage-time response represented in (a).
Figure 6. Optical microscopy images of the cross section of the cast alloy (indicated as “CA”), an AM Al-Si10-Mg XZ specimen (indicated as “AM XZ”), and an AM Al-Si10-Mg XY (indicated as “AM XY”) after anodizing for 20 min. The values shown in the figure inset refer to the oxide layer thickness at the positions indicated in the figure.

Figure 7. Oxide layer growth as a function of anodizing time for AA4420, AM Al-Si10-Mg XY, and AM Al-Si10-Mg XZ. The solid lines represent the linear fitting of the data points.
Figure 8. Secondary electron microscopy image of the surface of the cast alloy [(a) and (c)] and an additive manufactured specimen [(b) and (d)], after 3 s [(a) and (b)] and 30 s [(c) and (d)] of anodizing.

Figure 9. Secondary electron microscopy images of the cross section of the cast alloy (a), an AM Al-Si10-Mg XZ specimen (b), and an AM Al-Si10-Mg XY (c) after anodizing for 25 min.
Figure 10. Transmission electron microscopy images of the cross section of the cast alloy (a), and an AM Al-Si10-Mg specimen (b) after anodizing for 20 min. Scale bar (a) 200 nm, (b) 500 nm
Figure 11. Atomic force microscopy images of the cross section of the cast alloy (a, b), and an AM Al-Si10-Mg XZ specimen (d, e) after anodizing for 25 min. (c) Profile of the line represented in (b). (f) Profile of the line represented in (e). Color bar: (a) 20 nm, (b) 16 nm, (c) 30 nm, (d) 24 nm.
Tables

**Table 1.** Chemical composition of the AM specimens and the Al cast alloy acquired from Aleris. The values indicating the chemical composition of AA4420 represent the composition limits specified by the manufacturer. The chemical composition of the AM specimens was calculated using EDS analysis.

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<th>Fe</th>
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<th>Mn</th>
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<th>Zn</th>
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<td>0.09</td>
<td>9.48 – 9.89</td>
<td>0.18</td>
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**Table 2.** Average value of the pore diameter estimated by using the AFM topography maps of the anodic oxide layers’ cross section. The value of the final voltage reported in the table refers to the last voltage measured during the anodizing of the specimen used for the AFM characterization.

<table>
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<th>Pore diameter calculated from the AFM images (nm)</th>
<th>Final voltage (V)</th>
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<tr>
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