Role of Si in the anodizing behavior of Al-Si alloys: additive manufactured and cast Al-Si10-Mg

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ABSTRACT:
In this work, the role of the Si phase microstructure in the anodizing behavior of Al-Si alloys is studied. Experiments were conducted using an additive manufactured (AM) Al-Si10-Mg specimen and a cast alloy of approximately the same chemical composition. A systematic characterization of the anodic oxide film was conducted using a variety of surface analysis techniques. Clear evidence is provided through X-ray photoelectron spectroscopy analysis for the almost entire oxidation of Si during the anodizing of the additive manufactured specimens, which can explain the lower anodizing efficiency observed in the AM material compared to the cast alloy. Additionally, a more detailed characterization of the oxide layer revealed that a slightly thinner anodic oxide film is formed at the borders of the characteristic melting tracks resulting from the metal additive manufacturing process. Furthermore, the features observed in the voltage–time response during the anodizing of the AM specimens seem to be closely associated with the dimensions of the Al/Si cells present in the plane parallel to the direction of the oxide front growth.
1. Introduction

Metal additive manufacturing (MAM) is a technique that allows the production of complex and multifunctional metal parts in a layer-by-layer fashion [1–5]. Among the MAM processes, the powder-based systems are the most widely used due to their capability to fabricate fully dense parts. Nowadays, a great number of alloys can be processed by using this technique, depending mainly on the availability of the raw materials as metal powders [5]. Amongst these alloys, AlSiMg is of great interest for the automotive and aeronautic industry due to its relatively high strength and stiffness to weight ratio [6]. The special conditions during the MAM process promote the formation of unique microstructures with very fine internal phase distributions [7–11]. This fine microstructure has a considerable influence on the corrosion [12–14] and anodizing mechanism [15] of these materials. In a recent study on the galvanostatic anodizing of additive manufactured (AM) Al-Si10-Mg parts, we reported that the anodizing voltage–time characteristics as well as the resulting anodic film structure are highly affected by the fine distribution of the silicon network present in these specimens [15]. We showed that the anodic oxide growth efficiency is much lower in the additive manufactured samples than for conventional cast alloys (CA). The average oxide film thickness is significantly lower for the same anodic charge input; however, a more continuous layer is formed in the AM materials compared with the CA. Moreover, branched–like pores developed throughout the entire anodic oxide layer of the AM specimens as a result of the fine and relatively continuous silicon network, which encapsulates the aluminium phase in very small cells [15]. It was also shown that a continued increase in the potential is obtained in the voltage–time response of the AM samples for a larger period of time (compared with the CA) before reaching a stable value, even after the formation of the porous structure [15].

In our previous work, the galvanostatic anodizing behavior of AM Al-Si10-Mg alloy was studied through the analysis of the voltage–time response complemented with an initial characterization of the anodic oxide layer [15]. Nevertheless, based on the results obtained, a number of assumptions were made in that study. For instance, a higher oxidation of the silicon phase during anodizing was inferred for the AM materials compared to the CA in order to explain the higher voltages measured during the anodizing of the AM specimens with respect to the CA [15]. The confirmation of this conjecture is essential for a better comprehension of this phenomenon. Moreover, a further characterization of this anodic oxide layer is needed in order to gain a more complete understanding of the role of Si in the anodizing mechanism of additive manufactured Al-Si alloys. In this work, a characterization of the anodic oxide film grown galvanostatically in H₂SO₄ electrolyte was carried out. A cast Al alloy of approximately the same chemical composition as that of the AM specimens was used as a reference. Optical microscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS) were employed for the characterization of the samples.
2. Materials and methods

2.1. Sample preparation
Additive manufactured Al-Si10-Mg samples were prepared by direct metal printing (DMP), using a ProX DMP 320 machine (3D Systems Leuven) equipped with a 500 W laser in an argon atmosphere with resulting oxygen content of < 50 ppm. LaserForm AlSi10Mg powder and standard 3D Systems processing parameters for 30 µm layer thickness were used to fabricate rectangular cuboids of 5×30 mm$^2$ and a height of 10 mm. A laser energy density of 51 J/mm$^3$ was used for the sample preparation. No post heat treatment was applied on the AM specimens. Additionally, a cast aluminium alloy (AA4420 – from Aleris) with approximately the same chemical composition as that of the AM specimens, was used as a reference material. The chemical composition of the samples is shown in Table 1. All the samples were mechanically ground and polished, finishing with 0.04 µm standard colloidal silica suspension (OP–S). The samples were anodized in a stirred 3M H$_2$SO$_4$ electrolyte at room temperature and a constant current density of 10 mA/cm$^2$ using an ES 0300-0.45 power supply (Delta Elektronika). The anodic potential was monitored 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 and further characterization of the AM samples was conducted on the surface oriented in the direction parallel to the building platform (referred to as AM_XY), as well as on the surface oriented in the direction perpendicular to the building platform (referred to as AM_XZ) separately. In order to image the microstructure of the samples, the surfaces were etched with Keller’s reagent.

2.2. Sample characterization
The optical characterization of the samples was conducted using a Leitz Metallovert optical microscope. Morphology and microstructure characterization was carried out by means of scanning electron microscopy in combination with energy dispersive X-ray spectroscopy. An FE–SEM JEOL JSM–7100F with 15 kV acceleration voltage, 5 nA probe current, and a working distance of 10 mm was used. AFM topography mapping was conducted using a commercial atomic force microscope (Park Systems XE–100). Rectangular 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 elemental composition of the anodic oxide layer was studied using X-ray photoelectron spectroscopy combined with Ar$^+$ depth profile sputtering. A PHI-5600ci XPS spectrometer (Physical Electronics) was used to acquire the spectra with the hemispherical analyzer detector tilted 45° with respect to the surface of the sample. A diameter aperture of 800 µm was used. The X-ray source was operating at 100 W with a bias voltage of 14.5 kV. The sputtering rate was calibrated using a SiO$_2$ sample as a reference, obtaining an approximate sputtering rate of 10 nm/min for Al$_2$O$_3$, which is the main constituent of our anodic oxide layers. This value was then taken for simplicity as an approximate sputtering rate for our samples. However, some differences might exist due to the Si/SiO$_2$ present in the anodic film.
Additionally, slight differences might also exist between the cast alloy and the additive manufactured specimens due to the great differences in the distribution of Si. The spectra before sputtering were calibrated using the C1s peak at 284.8 eV, while the spectra acquired after sputtering were calibrated using the Ar2p and the Ar2s peaks from the implanted Ar at 243 eV and 319 eV, respectively. For the XPS characterization, samples with a 2 µm anodic oxide layer thickness were prepared. In order to obtain the same average thickness of 2 µm on the cast alloy and the AM specimens an anodization time of 400 min and 538 min was used, respectively (estimated from the results obtained previously [15]).

3. Results
3.1. Initial characterization by optical microscopy and SEM/EDX

Figure 1 shows optical images of the surface of the cast alloy (Figure 1a), as well as the surface perpendicular to the building platform, AM_XZ (Figure 1b), and the surface parallel to the building platform, AM_XY (Figure 1c), of an AM Al-Si10-Mg specimen. In the right lower corner of each figure, a higher magnification secondary electron image of the corresponding sample surface is shown. The same magnification was used for the different samples in order to properly compare their microstructure. Large silicon crystals can be seen in the cast alloy, while a fine silicon network encloses the aluminium phase in small cells in the additive manufactured specimens (see insets of Figure 1). This difference is associated with differences in the cooling rate during the manufacturing process. A much faster cooling rate is achieved during the MAM procedure compared to the cooling rate present during traditional casting. Additionally, as reported by other researchers, a directional solidification regime takes place in the AM materials [9]. This is the result of the directional heat transfer, caused by the relatively high energy density of the laser during MAM. Because of that, elongated Al cells can be seen in the surface of AM_XZ (see inset of Figure 1b). These cells, as described in our previous work [15], have an average length ranging from 0.4 to 1 µm. On the other hand, in the surface of the AM_XY samples the Al cells have a more circular shape (see inset of Figure 1c), with an average diameter ranging from 0.3 to 0.6 µm.

In the optical images shown in Figures 1b and 1c, the laser tracks from the MAM process can be clearly seen. These tracks have a semicircular shape in the AM_XZ surface (see Figure 1b) and an elongated shape in the AM_XY surface (see Figure 1c). The reason why these melt pools (MPs) are visible at relatively low magnification is because the microstructure is much larger at their edges [9,14,15]. A coarser microstructure at the melt pool borders (MPBs) has been associated with a lower cooling rate compared to the cooling rate at the center of the MPs [9].

Figure 2 shows SEM micrographs of a region in the surface of an AM_XY specimen where a melt pool border is visible (It is important to notice that similar features can also be observed in the AM_XZ surface). In a higher magnification image of a zone within the MPB, large Al cells can be observed surrounded by a eutectic–like Al + Si structure (see yellow arrows in Figure 2b). This lamellar microstructure of alternating layers of Al and Si phases is commonly seen in cast alloys (see Figure 1a). The formation of these structures is only possible at relatively low cooling
rates. Clear similarities can be seen between the SEM images of the AM samples’ microstructure within the MPB (Figure 2b) and the optical images of the surface of the cast alloy (Figure 1a). On the other hand, a very fine silicon network (and an absence of the eutectic–like Al + Si structure) can be seen in higher magnification images within the melt pools (see Figure 2c). Several EDX mappings were obtained on the surface of the polished AM specimens. Figure 3 portrays an SEM image and the corresponding EDX mapping of the three main components present in the additive manufactured samples (Al, Si, Mg), taken in an area of an AM_XZ specimen (similar features can also be observed in the AM_XY surface). At this scale, an uniform dispersion of the different elements within the matrix can be detected. Except for the silicon, where (as also noticed in a previous work [14]) the melt pool borders can be generally discerned (see Figure 3c), depending on the magnification used. A further EDX analysis was conducted in order to have an estimation of the elemental composition around the MPBs and within the MPs. Multiple spectra (around 40) were taken in regions enclosing MPBs and in areas within the MPs. As an example to illustrate the analysis performed, Figure 4a shows in a Si map two zones from which the spectra were acquired (a spectrum at the MPB and a spectrum within the MP). From each spectrum, an approximate quantification of the different elements’ concentration was obtained. Except for Al and Si, no significant differences were observed between the concentrations of the other elements at the MPBs, the concentrations within the MPs, and the average concentration reported for the AM samples in Table 1. However, slight differences were noticed in the concentration of Si and Al depending on the region where the spectra were acquired. Figure 4b shows box plots obtained from the values of the concentration of Si and Al measured in zones containing MPBs and in regions within the MPs from the EDX analysis. These measurements were conducted in the AM_XY samples as well as in the AM_XZ samples. The continuous horizontal lines in the graphs of Figure 4b represent the concentration of Si (9.55 %) and the concentration of Al (89.99 %) reported for the AM samples in Table 1. At the left side of each graph (see Figure 4b) the value of Si and Al measured at the MPBs are shown, while at the right side are the values in the MPs. Despite the fact that EDX spectra are usually influenced by the underlying matrix (depending on the operating voltage, interaction volume/penetration depth), it can be clearly seen that at the MPBs the concentration of Si is in general slightly higher and the concentration of Al slightly lower than the values reported in Table 1. From the values measured using the spectra acquired (results shown in Figure 4b) a Si concentration of about 9.8 ± 0.3 % and about 89.7 ± 0.3 % of Al was estimated at the MPBs. The concentrations measured within the MPs are very close to the values reported in Table 1, 9.5 ± 0.1 % Si and 90.1 ± 0.1 % Al.

3.2. Anodizing

Representative voltage–time curves for each sample are shown in Figure 5. As previously observed [15], a fast increase of the potential in the first 6 s of anodizing is obtained for all the samples. This is then followed by a change in the slope of the voltage–time curve between 6 and 10 s (see inset of Figure 5). After approximately 10 s of anodizing, a stable regime can be seen in the voltage–time response of the cast alloy (black trace in Figure 5), while a prolonged increase
of the potential is obtained in the AM specimens before a relatively stable state is reached. A closer examination of the voltage vs time plots obtained during the anodizing of AM materials revealed that a gradual transition from the steep increase in potential to a reasonably steady regime is seen between 70 s and 225 s for the AM_XY samples. This time interval is marked with a red diagonal–line pattern in Figure 5. However, for the AM_XZ samples, this transition to a stable state is observed at shorter anodizing times, from approximately 40 s to 100 s of anodizing, which is marked with the blue diagonal–line pattern in Figure 5.

3.3. Optical microscopy and SEM characterization of the anodic oxide layer cross-sections

Following the anodization of all the specimens, characterization of the anodic oxide layer cross sections was carried out using optical microscopy and scanning electron microscopy. Figure 6 shows optical microscopy images of the cross section of an anodized CA and an anodized AM specimen. On average, the oxide film is thinner in the AM samples than in the CA for the same anodizing time. An anodic oxide growth rate of about 0.2 μm/min was calculated in a previous work for the AM samples using the same anodizing conditions, while the CA showed a rate of 0.4 μm/min [15]. Nonetheless, a more uniform layer is formed on the AM materials compared with the CA [15], as can be seen in Figure 6. The large Si particles present in the CA specimen obstruct the growth of the anodic oxide layer (red arrows in Figure 6a). This can be seen in more details in the SEM images presented in Figure 7. The same result has been shown in previous studies on the anodizing of cast Al-Si alloys [15-17]. A clear discontinuity of the anodic oxide layer is observed in the cast alloy at the positions where superficial and large Si particles are present (see Figure 6a and 7a). On the other hand, a relatively uniform oxide film thickness is obtained for the additive manufactured specimens (see Figure 6b and 7b).

Figure 8 shows a higher resolution SEM image of the cross section of an anodized cast alloy, in which a Si particle is present. It can be noticed, as also reported in previous works [15-17], that the anodic oxide front circumvents the large Si particles. In the proximity of the eutectic phase, the oxide layer is thinner than the oxide layer grown on areas that are free from Si particles. Moreover, the thinning of the oxide film from Si–particles free regions to areas near the eutectic structure is gradual. The yellow arrows in Figure 8 indicate this.

Furthermore, even though the anodic oxide layer formed in the additive manufactured specimens is relatively uniform compared to that of the cast alloy, a more detailed characterization revealed that a slightly thinner oxide film is formed at the melt pool borders of the AM samples. This can be seen in Figure 9 (black arrows), which shows optical microscopy images of the cross section of an anodized AM specimen. The MPBs are relatively easy to identify since a larger microstructure is present in those regions. It is important to mention that the same phenomenon was observed equally in both AM surfaces (AM_XY and AM_XZ) for different anodizing times.

3.4. AFM topography maps

In order to have an idea of the impact of the microstructure on the uniformity of the oxide layer, AFM topography images of the samples surface were acquired. Figure 10 shows an example of AFM maps obtained in the surface of an anodized CA and an anodized AM specimen together with the profile of a line scan from each sample. Great differences can be seen between the CA
and the AM specimen. Note that the color bar of the map of the cast alloy has a range of 800 nm while the color bar of the AM map has a range of 100 nm (8 times lower). A nanoscale surface roughness of 115.7 nm was calculated for the cast alloy, while a surface roughness of 15.9 nm was obtained for the AM sample after anodizing for 20 min. This represents a difference of more than 7 times. The exact value of the surface roughness could be influenced by parameters such as the anodizing time. However, the main purpose of these measurements is to illustrate the great influence that the microstructure can have on the final morphology of the anodized oxide layer. This observation is in good agreement with previously reported studies conducted on cast alloys with different aluminium cells’ morphologies [16]. A more uniform oxide layer can be obtained when there is a finer cell structure.

3.5. XPS characterization of the anodic oxide layer

An elemental characterization of the anodic oxide layers was conducted using X-ray photoelectron spectroscopy. Samples with the same oxide layer thickness of around 2 µm were prepared for this purpose. The chemical composition of the oxide films was analyzed by acquiring high resolution XPS spectra of the Si2p and Al2p peaks through depth profiles. Figure 11 shows the Si2p and Al2p spectra acquired in an anodized cast alloy as a function of sputtering time. As can be seen in Figure 11a, the only Si2p peak observed before sputtering (sputtering: 0 min) has a binding energy of approximately 103.5 eV, which corresponds to SiO$_2$. The Al2p peak observed in Figure 11b before sputtering has a binding energy of around 74.6 eV, corresponding to Al–O. This shows that at the surface of the anodic oxide layer the Si and Al are entirely in the oxide form. After sputtering for 5 min, only a peak around 99.4 eV is observed in the Si2p region. This peak corresponds to the Si element, which means that 50 nm from the surface (considering the sputtering rate from the experimental section) no silicon oxide can be found and, instead, elemental Si is present. On the other hand, only the oxide form of Al is detected in the Al2p region after 5 min of sputtering (see Figure 11b), which shows that the spectra were acquired in the anodic oxide film without any influence from the underlying metal matrix. Subsequent spectra acquired until around 130 min of sputtering showed comparable features as those taken after 5 min of sputtering (the elemental Si peak around 99.4 eV and the oxide Al peak at 74.6 eV). After 130 min of sputtering, the Al2p peak at around 74.6 eV presents a rather asymmetrical shape (see Figure 11b), which can be associated with the influence of metallic Al from the matrix beneath the oxide layer. This means that most of the anodic oxide film has been removed at this point. After having sputtered for 250 min, the main Al2p peak observed has a binding energy of about 72.6 eV. This peak corresponds to the metallic form of Al. However, a slight contribution from the oxide form of Al can still be seen (Figure 11b). On the other hand, together with the peak associated with elemental Si, another peak can be detected at around 104 eV in the Si2p region. This peak at 104 eV increases in intensity after relatively longer sputtering times (sputtering for 370 min or more), as can be seen in Figure 11a. Following a comparison between the acquired spectra and a reference Al spectrum from Physical Electronics [18], it can be seen that this slightly asymmetrical peak obtained at around 104 eV corresponds to a plasmon loss feature of the aluminium metal. This can be clearly seen in Figure
12, where the spectrum obtained in the cast alloy after 490 min of sputtering is compared with the spectrum from a reference Al metal. The plasmon loss structures of Al [19] are known to interfere with the assignment and quantification of other spectral peaks such as Si2p and Si2s. Summarizing, at the surface of the anodic oxide layer (< 50 nm from the surface), most of the Si is in the oxide form, while within the anodic oxide layer (from around 50 nm from the surface) the large Si particles present in the cast alloy are mostly in the elemental form. The evolution of the oxide and metallic form of Al in the Al2p region were used to identify if the measurements were conducted in the oxide layer or in the metal alloy matrix.

The same XPS analysis as the one described for the anodized cast alloy was conducted in anodized additive manufactured samples. Figure 13 shows the Si2p and Al2p spectra acquired as a function of sputtering time in these specimens (AM_XY and AM_XZ). As can be seen in Figure 13, the only peaks observed in the Si2p and Al2p regions before sputtering have binding energies of about 103.5 eV and 74.6 eV, respectively. These peaks detected before sputtering, as with the cast alloy, correspond to the oxide form of Si and Al respectively. On the other hand, unlike the cast alloy, the SiO$_2$ peak was detected in the spectra acquired after sputtering from 5 to 130 min (see Figures 13a and 13c). Moreover, this was the only peak observed in the Si2p spectra of the anodized AM samples obtained from 0 to 70 min of sputtering. In Figures 13b and 13d can be seen that from 0 to 130 min of sputtering the main Al2p peak acquired in the AM_XY and AM_XZ surface has binding energy of approximately 74.6 eV (corresponding to Al–O). This confirms that the main contribution in those spectra comes from the anodic oxide layer and not from the metal matrix. Additionally, this also demonstrates that unlike the cast alloy, the Si present in the anodic oxide layer seems to be almost entirely oxidized. For the AM_XY sample (Figure 13b), the Al2p spectrum acquired after sputtering for 130 min shows a peak at around 72.6 eV (Al metal) together with the peak from Al oxide (~74.6 eV). Therefore, this spectrum has clear contribution from the oxide layer as well as from the metal matrix beneath the oxide layer. For the same sputtering time, the elemental Si peak at approximately 99.4 eV together with the Si–O peak can be observed in the Si2p spectrum (see Figure 13b). The same features were observed in the spectra acquired in the AM_XZ specimens after sputtering for 190 min. This reveals that the spectra obtained after these sputtering times are acquired relatively close to the interface between the oxide layer and the metal matrix. For longer sputtering times (≥250 min) the Al metal peak was the main peak obtained in the Al2p spectra of the AM samples (see Figure 13b and 13d), confirming that after sputtering for 250 min the main contribution to the XPS spectra came from the metal alloy matrix. At the same time, the main Si2p peak obtained had binding energy around 99.4 eV (elemental Si), as can be seen in Figures 13a and 13c. Additionally, the plasmon loss features from the Al metal at around 104 eV can also be observed in the Si2p spectra acquired after sputtering for 250 min or more (see Figures 13a and 13c).

An estimation of the amount of Si/Al oxidized for the different samples as a function of sputtering time (taking into account the contribution from the (Si/Al)–element and (Si/Al)–oxide peaks in the Si2p/Al2p region) is presented in Figure 14. This represents a clear evidence that
contrary to the CA, where only the superficial Si is oxidized during anodizing, most of the Si in the anodic oxide film of the AM specimens is oxidized.

4. Discussion

4.1. Influence of microstructure on the anodizing behavior

As can be seen in Table 1, no significant differences were observed in the concentration of alloying elements between the cast alloy and the AM specimens. Additionally, it can be noted that the concentration of Cu, Fe, Mn, Zn, and Mg is much lower than the amount of Si in the materials. Therefore, even though their distribution within the alloys differs (a much finer distribution of the alloying elements is present in the AM materials compared to the cast alloy), we believe that their influence on the anodizing mechanism is negligible compared to the effect of Si on the anodic oxide layer formation.

The XPS analysis clearly showed that most of the Si encountered by the anodic oxide front in the AM specimens was being oxidized during anodizing. This confirmed the assumption made in our previous study [15], and explained the continuous increase of the potential in the voltage–time response during the anodization of the AM samples (see inset of Figure 5). As shown in earlier works, Si requires a relatively higher field strength to be oxidized than Al [20]. A larger amount of charge is consumed for the oxidation of Si in the AM specimens in comparison with the cast alloy, increasing as a consequence the potential during anodizing, and resulting in a reduced anodizing efficiency for the AM materials, being half of that of the cast alloy [15]. This considerable anodic oxidation of Si in the AM materials is the result of their fine microstructure. As shown in previous studies, the Si network (mainly composed of small Si nanocrystals [10,15]) that encloses the Al cells has a width of ~ 40 to 50 nm [10,15]. As presented by Zhu et al. [17], a greater fraction of Si is oxidized for smaller Si particles in Al-Si alloys. The XPS analysis also revealed that for the cast alloy mainly the superficial Si (< 50 nm from the surface) was oxidized during anodization. This is in perfect agreement with works previously published [17,21]. Zhu et al. reported the formation of a barrier type SiO$_2$ layer with a thickness between 30 nm and 100 nm depending on the size and interconnection of the Si particles [17]. This SiO$_2$ layer was mainly found on the side of the Si particle facing the oxide growth direction [17]. In addition, Fratila-Apachitei et al. confirmed the existence of a 40 nm thick SiO$_2$ rim decorating the Si particles in Al-Si alloys [21].

The transition to a stable regime in the voltage–time curves of the AM specimens was markedly different depending on the surface orientation (AM_XY/AM_XZ). As seen above, a gradual transition from a fast increase in potential to a relatively steady regime was observed in the AM_XZ samples from ~40 s to ~100 s, while in the AM_XY samples this was observed from ~70 s to ~225 s (blue and red regions in Figure 5). Considering the results presented previously [15] regarding the average growth of the anodic oxide layer thickness with time ($\text{thickness(\mu m)} = 0.19 \times \text{time(min)} + 0.28$) for the AM specimens, the thickness of the oxide film at those specific
times can be estimated. For the AM_XZ sample, this transition is seen for an anodic oxide layer with a thickness between 0.4 µm and 0.6 µm. This coincides with the diameter of the Al/Si cells in the AM_XY plane, which on average ranges from 0.3 to 0.6 µm. A schematic of the samples is shown in Figure 15. It can be easily noticed that during the anodizing of the AM_XZ samples the oxide front encounters the microstructure of the AM_XY surface (see left panel in Figure 15). On the other hand, for the AM_XY sample, the transition is observed for an oxide film with a thickness between 0.5 and 1 µm. This is in good agreement with the length of the Al/Si cells in the AM_XZ plane, which on average ranges from 0.4 to 1 µm. In the right panel of Figure 15 can be seen that during the anodizing of the AM_XY samples the oxide front encounters the microstructure of the AM_XZ surface. Therefore, in each case the transition from a steep increase to a relatively constant potential is closely related to the dimensions of the microstructures on the direction of the oxide front growth. Since most of the Si in the AM specimens seems to be oxidized during anodizing, the stabilization of the voltage is achieved when the oxide layer thickness equals the average size of the Si features in the direction of the oxide front growth.

4.2. Effect of the MPBs on the anodic oxide layer

Moreover, even though a rather uniform oxide film is grown in the AM materials during anodizing, a slightly thinner oxide layer was detected at the borders of the melt pools (as seen in Figure 9). This could be a direct consequence of the slightly higher concentration of Si found in those regions (as seen in Figure 4). As reported in previous studies, a relatively high field strength is required for the anodic oxidation of Si [20]. Additionally, Si oxidizes at a much lower rate compared to Al [20]. Therefore, a relatively lower oxide growth rate can be obtained at the MPBs compared to the growth rate within the MPs.

The slightly higher concentration of Si that seems to be present at the MPBs (as roughly estimated from the EDX analysis – Figure 4) compared to the average concentration measured in the AM samples could be associated with the directional solidification of the melting tracks. A lower cooling rate towards the borders of the melt pools is believed to exist due to the thermal gradient produced by the moving laser [9]. As a result of the fast cooling rate within the MPs, a supersaturated α–Al phase solidifies in these zones forming small cells that are decorated with a relatively fine Si network. The residual Si might segregate to the borders of the melting tracks, where a lower cooling rate is present.

Moreover, the formation of a eutectic–like Al + Si lamellar structure at the MPBs could also be the result of the relatively low cooling rate in these regions. This alloy is a hypoeutectic alloy (with eutectic composition ~ 12.5 wt%) [22]. Part of the Al-Si phase diagram [22] can be seen in Figure 16. When this material is cooled from a fully liquid phase, crossing the liquidus line (point (a) in Figure 16), the primary α–Al phase starts to solidify as dendrites at favorable nucleation sites. By further cooling the alloy within the α–Al + liquid region of the phase diagram (between point (a) and point (b) in Figure 16), other nucleation sites will form within the liquid part of the mixture. At the eutectic temperature (point (b) in Figure 16), the primary α–Al phase stops forming and the remaining liquid starts to solidify into alternating layers of α–Al
+ Si of eutectic composition. This type of structure can be clearly seen in the optical image of the cast alloy (Figure 1a), which is also very similar to the features present in the MPBs of the AM specimens (Figure 2b). Diffusion between the phases can occur as the alloy cools down to produce the equilibrium composition at a given temperature [22]. The possible diffusion of Si in the α–Al grains could be the reason for the gradual thinning of the anodic oxide film from the α–Al dendrites to areas near the eutectic structure of the cast alloy (as shown in Figure 8). Therefore, the formation of a eutectic–like Al + Si structure at the MPBs could also be accompanied with a gradual diffusion of Si into the Al cells (which are larger at the MPBs). This could reduce the growth rate and consequently form a slightly thinner oxide layer at the border of the melt pools.

5. Conclusions
In this work, the role of Si during the anodizing of Al-Si alloys was analyzed. Great differences were observed in the anodizing behavior of different specimens depending on the distribution of the Si phase within the alloy matrix. A comparison between an additive manufactured Al-Si10-Mg alloy and its counterpart cast alloy was executed. The main results can be summarized as follow:

- An eutectic–like Al + Si structure with a lamellar feature of alternating layers of Al and Si phases can be seen at the border of the melt pools in the additive manufactured specimens, due to the relatively lower cooling rate with respect to the center of the melt pools.
- At the borders of the melt pools, the content of Si was slightly higher while the concentration of Al was slightly lower than the average quantities measured in the entire AM samples.
- A relatively thinner oxide layer was detected after anodizing at the positions of the melt pool borders in the AM specimens, due to the slightly higher concentration of Si in those regions or the formation of a eutectic–like Al + Si lamellar structure.
- XPS analysis revealed that unlike the cast alloy, where only the superficial Si is oxidized during anodizing, most of the Si in the anodic oxide film of the AM specimens is oxidized. This great oxidation of Si in the AM materials results in a reduced anodizing efficiency compared to the cast alloy, where relatively large Si crystals exist.
- Due to the differences in the Al cells size between the CA and the AM materials, great dissimilarities in the uniformity and nanoscale roughness of the anodic oxide layer can be detected between these samples. A smoother oxide layer is obtained with a finer cell structure for the AM samples compared to the cast alloy.
- The differences obtained in the voltage–time response (namely the transition region from a steep voltage increase to a relatively steady state) of the AM surfaces (AM_XY / AM_XZ) seem to be related to the dimensions of the Al/Si cells in the direction of the oxide front growth.
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References


**Figure 1.** Optical images of a region in the surface of the cast alloy AA4420 (a), the surface perpendicular to the building platform (AM_XZ) (b), and the surface parallel to the building platform (AM_XY) (c) of an AM Al-Si10-Mg specimen. In the right lower corner of each figure a secondary electron image of the corresponding sample surface is displayed.
Figure 2. Secondary electron image of a region in the surface of an additive manufactured specimen (The surface of sample AM_XY was chosen as an example. Nevertheless, similar features can be observed in the AM_XZ surface). b) Higher magnification image of a zone in the melt pool border. c) Higher magnification image of a zone within the melt pool. MPB refers to melt pool border.

Figure 3. Secondary electron microscopy image and energy dispersive X-ray spectroscopy maps of the polished surface of an additive manufactured specimen (The surface of sample AM_XZ was chosen as an example. Nevertheless, similar features can be observed in the AM_XY surface). a) Secondary electron image, b) Al map, c) Si map, d) Mg map. The melt pool borders are clearly visible in the Si maps. MPB refers to melt pool border.
Figure 4. a) Example of an EDX Si map showing two zones from which spectra were acquired (a spectrum at the MPB and a spectrum within the MP) to illustrate how the EDX analysis was conducted. b) Box plots obtained from the values of the concentration of Si and Al measured from the spectra obtained in zones containing MPBs (data shown at the left of the graphs) and in regions within the MPs (data shown at the right of the graphs). The continuous horizontal lines in the graphs represent the concentration of Si (9.55 %) and concentration of Al (89.99 %) measured for the AM samples (see Table 1).

Figure 5. Representative voltage-time response of the different specimens during anodizing in 3M H$_2$SO$_4$ solution at 10 mA/cm$^2$. The inset of the figure represents the first 60 s of the curve. The zone with the blue diagonal line pattern represents a time interval from ~ 40 s to 100 s; while the zone with the red diagonal line pattern represents a time interval from ~ 70 s to 225 s.
**Figure 6.** Optical microscopy images of the cross section of an anodized cast alloy (a), and an anodized additive manufactured specimen (b) after anodizing for 25 min.

**Figure 7.** Secondary electron microscopy image of the cross section of an anodized cast alloy (a), and an anodized additive manufactured specimen (b) after anodizing for 400 s.
**Figure 8.** Secondary electron microscopy image of the cross section of an anodized cast alloy using an anodizing time of 400 s.

**Figure 9.** a) Optical microscopy image of the cross section of an anodized additive manufactured specimen after anodizing for 20 min. A slightly thinner anodic oxide layer can be seen at the melt pool borders as indicated by the arrows. b) Higher magnification image of a section in (a). Discontinuous red lines are used to indicate some of the melt pool borders. MPB refers to melt pool border.
Figure 10. AFM topography images of the CA (a) and an AM sample (b) after anodizing for 20 min. c) Line scan showing the topography profile of the white line marked in (a) and (b). Scan size: 40 µm × 40 µm.

Figure 11. XPS spectra of the Si2p (a) and Al2p (b) acquired in an anodized cast alloy as a function of sputtering time.
Figure 12. Spectrum obtained in the cast alloy after 490 min of sputtering together with an Al reference spectrum from Physical Electronics. Plasmon loss peaks from aluminium metal can be clearly seen.
Figure 13. XPS spectra of the Si2p (a,c) and Al2p (b,d) acquired in an anodized AM_XY sample (a,b) and an anodized AM_XZ sample (c,d) as a function of sputtering time.
Figure 14. Estimation of the percentage of Si and Al oxidized for the different samples as a function of sputtering time. (The calculations were done taking into account the contribution from the (Si/Al)–element and (Si/Al)–oxide peaks in the Si2p/Al2p region). The grey zone in each figure was arbitrarily selected as a rough representation of the anodic oxide layer, considering a thickness of 2 µm and a sputtering rate of 10 nm/min.

Figure 15. Schematic of the samples’ microstructure. The top surface represents the anodized surface. While anodizing AM_XZ (left) the oxide front encounters the microstructure of the AM_XY surface. While anodizing AM_XY (right) the oxide front encounters the microstructure of the AM_XZ surface.

Figure 16. Phase diagram for the Al-10 wt.%Si alloy.
Table 1. Chemical composition of the AM specimens and the Al cast alloy acquired from Aleris calculated using EDX analysis.

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<thead>
<tr>
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<th>Chemical composition (wt%)</th>
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<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>AM samples</td>
<td>–</td>
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<tr>
<td>CA AA4420</td>
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