

Anodizing Al–Si Foundry Alloys: A Critical Review

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Compared with pure aluminum and wrought aluminum alloys, Al foundry alloys are more difficult to be anodized. The high content of alloying elements prevents the uniform growth of the Al oxide layer and enhances the embedding of defects in the anodic film. The microstructure of the substrate and the anodizing parameters play a key role in the final quality of the oxide layer. Variations in the chemical composition, casting process, and pre- and post-anodizing treatments can significantly affect the anodizing response. This work aims to critically review the main factors influencing the growth and morphology of the anodic layer in Al–Si foundry alloys. In particular, the effects on the oxide thickness, surface mechanical properties, and corrosion resistance are discussed in detail.

1. Introduction

Aluminum (Al) alloys are widely used in many application fields, especially transportation, packaging, construction, and electrical components. The widespread use of these alloys is mainly related to high specific mechanical properties and excellent processability.^[1] Low density (2.7 g cm⁻³), high strength-to-weight ratio, and good electrical and thermal conductivity make these alloys important for industrial design.^[1,2] In addition, the passivating behavior of aluminum ensures good corrosion resistance in natural oxidizing environments.^[3] When exposed to the atmosphere, the Al surface reacts with oxygen and forms an inert aluminum oxide film with a thickness of 4 nm, which prevents the further oxidation of the substrate.^[3]

It is well known how the surface properties of aluminum alloys change with the number, size, and distribution of alloying elements. In particular, the presence of liquid segregation zones and the precipitation of intermetallic particles negatively affect the corrosion resistance, due to the formation of an electrochemically heterogeneous substrate.^[2,4,5] The corrosion resistance of Al alloys is also influenced by the acidity or basicity of the environment, which is generally measured by pH index. Although the natural oxide film is stable when the pH is between 5 and 8, in extreme alkaline environments, e.g., caustic soda or potash,

the resistance of Al alloys is very low.^[3] To improve the corrosion resistance, durability, hardness, and decorative appearance of Al alloy surfaces, an anodizing treatment can be performed.^[6,7]

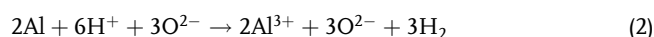
Anodizing is an electrochemical process where the aluminum surface is the anode of the electrolytic cell, and the growth of Al oxide on the metal substrate is artificially induced through the action of an electrical current. During the oxide growth process, the aluminum anode is continuously consumed, and the oxide front advances inside the substrate, forming new oxide at the metal/oxide interface. The growth

of the anodic layer is then strongly related to the microstructure of the substrate.^[2]

The anodizing process is based on ion exchange. Aluminum cations (Al³⁺) migrate from the metal substrate toward the electrolyte, going through the forming oxide, while the anions (O²⁻, OH⁻, and electrolyte anions) move in the opposite direction from the electrolyte to the metal substrate.^[2] The overall cell reaction which governs aluminum anodizing is presented in Equation (1).



which in ionic form results



By eliminating O²⁻ from both sides of Equation (2), it gives




where two half-cell reactions can be identified.



Equation (4) is an anodic reaction where aluminum cations are formed, while Equation (5) is a cathodic reaction which brings to hydrogen gas evolution (H₂).^[2]

The formation of the porous oxide layer during the anodizing process can be summarized in the following stages^[8]: 1) Aluminum cations (Al³⁺) are formed from the Al substrate at the anode, as described in Equation (4); 2) Under the influence of a high electric field, aluminum cations migrate toward the cathode, while the anions contained in the aqueous solution (O²⁻, OH⁻, and electrolyte anions) move in the opposite direction. At the metal/oxide and oxide/electrolyte interfaces, Al³⁺ cations react with the anions and form aluminum oxide (Al₂O₃); 3) At the oxide/electrolyte interface, the aluminum oxide

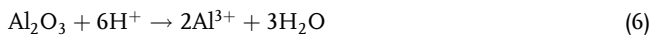
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can also dissolve inside the electrolyte allowing the formation of a porous structure. This reaction is governed by Equation (6).



A self-assembled, highly ordered hexagonal cell structure is thus formed, where each cell is closed at the base and has a central pore, extending from the base to the top of the cell itself. Two zones can be identified on the oxide structure: the barrier layer at the base and the porous layer (Figure 1). The thickness of the cell walls is the same as the base, which depends on the electrolysis parameters, i.e., the applied voltage and current density. Instead, the growth of the porous layer, especially the size of the hexagonal cell and the internal pore, depends on many anodizing parameters, e.g., type of electrolyte, current density, and anodizing time.^[9] Therefore, the performance of an anodized component is strongly affected by the selection of the anodizing parameters and the initial microstructure of the alloy, as well as treatments performed before and after anodizing.^[2,6]

These aspects have been thoroughly studied in commercial purity aluminum and wrought aluminum alloys. Many studies have been focused on the growth mechanism of Al oxide layer,^[9–13] the influence of chemical composition,^[14,15] and the effect of anodizing parameters.^[16–19] In particular, the improvement of the surface properties by hard-anodizing has been studied in detail.^[20] In addition, recent works concerned the corrosion protection of anodized wrought Al alloys for aerospace application and the re-use of anodizing waste.^[21,22] However, the anodizing response of Al–Si foundry alloys, which remain the most used and spread Al casting alloys, has not been studied in depth, due to the difficulty in obtaining a uniform oxide layer.

This review aims to describe and critically analyze the main factors that prevent the uniform growth of the oxide layer in Al–Si foundry alloys. The influence of the chemical composition of

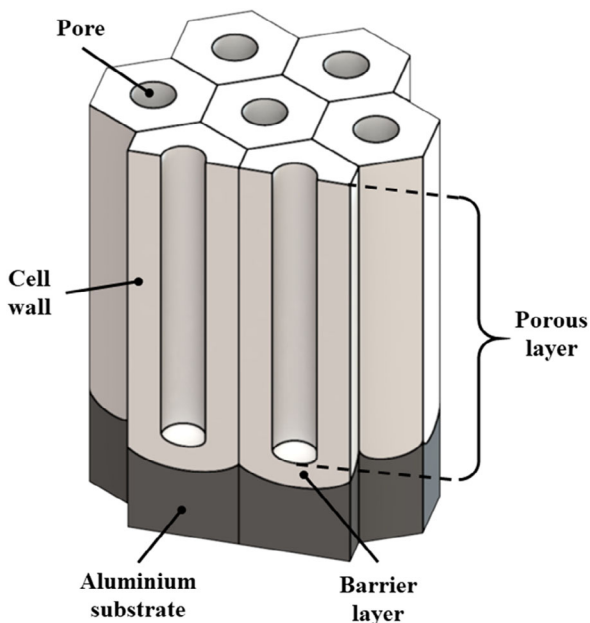


Figure 1. View of a hexagonal cell structure within an anodized substrate layer.

the alloy, the casting process, and the microstructure of the substrate was examined and discussed. Moreover, the effects of the anodizing parameters and pre- or post-anodizing treatments on the thickness and characteristics of the anodic film were analyzed.

2. Influence of the Chemical Composition and Microstructure of the Alloy

The growth of the oxide layer, as well as its final characteristics, is strongly affected by the chemical composition and the microstructure of the substrate. The presence of alloying elements in solid solution typically does not significantly alter the anodizing response of the Al alloys, while the formation of precipitates or intermetallic particles inside the α -Al matrix or along the grain boundaries compromises the integrity of the oxide layer.^[3,23–25] The oxidation rate of these compounds is often different from Al one, due to the different positions on the galvanostatic scale.^[2] Intermetallic phases with standard potentials higher than the α -Al matrix have slower oxidation rates and result in un-anodized particles at the end of the anodizing treatment. On the contrary, intermetallic compounds with higher oxidation energies are completely dissolved during the anodizing process, leading to the formation of porosities inside the oxide layer.

During the anodizing process, the electrochemical inhomogeneity of the substrate alters the distribution of current, which is focused on the less resistive zone of the substrate. This implies that the oxide front does not advance homogeneously at the metal/oxide interface, but it follows preferential growth directions according to the current distribution.^[26]

Among all the Al–Si foundry alloys, the anodizing response of hypoeutectic alloys (Si content <12.6 wt%) has been mainly investigated. The microstructure of these alloys consists of an α -Al primary phase and a eutectic mixture of silicon and aluminum. According to the chemical composition of the alloy and cooling rate during solidification, intermetallic compounds can also be present in the interdendritic regions and along the grain boundaries (Figure 2). The growth of the anodic layer in Al–Si alloys is mainly hindered by the presence of Si particles and

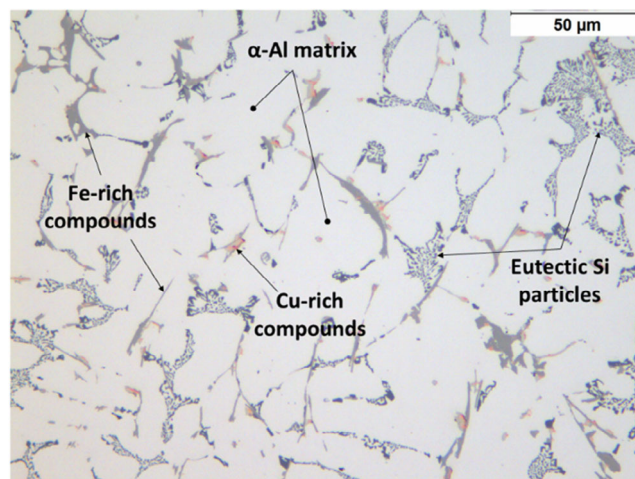


Figure 2. Typical microstructure of a gravity die-cast hypoeutectic AlSiCu(Fe) alloy.

Cu-, Mg-, and Fe-rich intermetallic compounds, which not only decreases the surface mechanical properties of the oxide layer but also promotes the formation of aesthetic defects on the casting surface.^[27,28]

To clarify the influence of the chemical composition and microstructure on the growth of the oxide layer, the effects of the main secondary phases on the anodizing response of Al–Si foundry alloys are further analyzed.

2.1. Si Particles

In Al–Si casting alloys, the silicon content varies generally from 4 to 25 wt%, and it is used to improve the castability of the alloys and reduce the volumetric shrinkage during solidification. The higher Si amounts with respect to wrought Al alloys lead to the formation of a large volume of Al–Si eutectic structure, which prevents the uniform growth of the anodic layer during the anodizing process.^[29,30] Eutectic Si particles have a slower oxidation rate than the surrounding matrix and promote the preferential growth of the oxide front in the α -Al phase.^[26]

When the oxidation front encounters a Si particle, it reacts with the particle surface, forming a thin anodic SiO_2 layer. The further oxidation of the Si particles would require higher energy than the oxidation of the adjacent Al-matrix, so the oxide front proceeds circumventing the particles, as shown in **Figure 3**.^[26,31,32]

According to the size of the Si eutectic particles, these can be partially or totally embedded within the oxide layer. In general, silicon particles smaller than 5 μm are not considered deleterious for the continuity of the oxide layer, because the oxidizing front can easily engulf them.^[26] On the contrary, coarser Si particles (>20 μm) can cause the formation of a discontinuous oxide layer with a locally scalloped oxide/metal interface.^[4,31]

Moreover, the amount of the eutectic structure can affect the growth of the anodic layer. In general, the average thickness and continuity of the oxide layer decrease by increasing the eutectic fraction in the Al alloys, due to greater electrochemical inhomogeneity of the substrate.^[26,31,33,34]

During the anodizing process, the presence of eutectic Si particles can also induce the formation of other defects within the anodic layer, such as (i) oxygen gas-filled voids, (ii) un-anodized zones, and (iii) cracks, as illustrated in **Figure 4**. 1) When the oxide front reacts with the silicon phase, both SiO_2 and gaseous oxygen are generated, due to the semiconducting nature of the Si–O bond. Oxygen gas-filled voids are therefore formed in the Al substrate close to Si particles.^[33,34] 2) Un-anodized zones are instead generated when the oxide front is not able to totally circumvent the Si phase, due to its shape or the reduced distance between particles. Thus, the eutectic silicon phase acts as a shield for the adjacent Al-matrix, which is not reached by the oxide front and remains un-anodized. Residual metallic Al phase is mainly

detected below or between coarse and interconnected Si eutectic particles.^[31] 3) Silicon particles can also prevent the volumetric expansion of the oxidizing matrix, generating localized intrinsic stress and film cracking.^[31,35]

The formation of these three types of defects has been reported in many studies^[26,33,34,36–39] and it strongly depends on the morphology of the silicon particles. Fratila-Apachitei et al.^[26] found how the surface roughness and cracking of the oxide layer increase when the eutectic Si structure is coarser. On the contrary, refined eutectic structures, obtained with higher cooling rates during solidification or the addition of modifying elements (e.g., Sr, Na, and Ca), facilitate the engulfment mechanism of Si particles and promote a more homogeneous growth of the oxide layer.

Zhu et al. studied the influence of the morphology of both unmodified and Sr-modified eutectic Si particles on the anodizing response of Al–Si alloys.^[31] Different levels of Si content were investigated (2.4–5.5 wt%). The unmodified alloys presented polygonal flake Si particles, which formed a continuous branched network.^[40] These compounds are visible in green in the energy-dispersive spectroscopy (EDS) element map, shown in **Figure 5a**. During the anodizing process, the anodic oxide front grew between the Si flakes, but, due to the narrow space between the particles, a large amount of Al-matrix was shielded from oxidation. Moreover, due to the Al_2O_3 volumetric expansion, great localized intrinsic stresses were generated, resulting in the formation of cracks and cavities, as indicated in **Figure 5a**. Similar results were found by Fratila-Apachitei et al.^[34] and Riddar et al.^[39]

In contrast, the refined microstructure showed disconnected eutectic Si fibers, which were easier embedded inside the oxide layer during anodizing (**Figure 5b**). The growth of the anodic layer was more homogeneous than in the unmodified alloys, and only a few cracks and cavities were detected.

The variation of the Si particles' morphology influenced the formation of the anodic SiO_2 layer too. In the alloys without Sr, the eutectic particles were covered by a thin Si–O film of about 40 nm, in agreement with the previous observations made by Fratila-Apachitei.^[34] Instead, in the refined alloys, the thickness of this layer increased up to 100 nm, demonstrating that higher fractions of anodized Si were formed when the size of the eutectic Si particles was reduced.

The interface between Al-matrix and eutectic Si particles is also a weak point for the corrosion resistance. Zhu et al.^[4] performed a corrosion attack by immersing anodized AlSi7Mg0.4 samples in 3 wt% NaCl solution for 72 h. Due to the formation of a micro-galvanic cell between Al and Si phases, the corrosion attack penetrated the anodic layer and formed corrosion pits on the Al–Si interface (**Figure 6**). Upon increasing the content of defects in the oxide layer, the galvanic corrosion beneath the oxide surface was enhanced. Similar results were found by Chaukea et al.^[41] and Menargues et al.^[42]

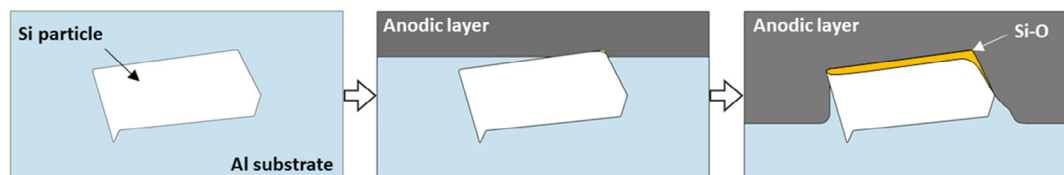


Figure 3. Sketch of the behavior of a Si particle during the growth of the anodic layer.

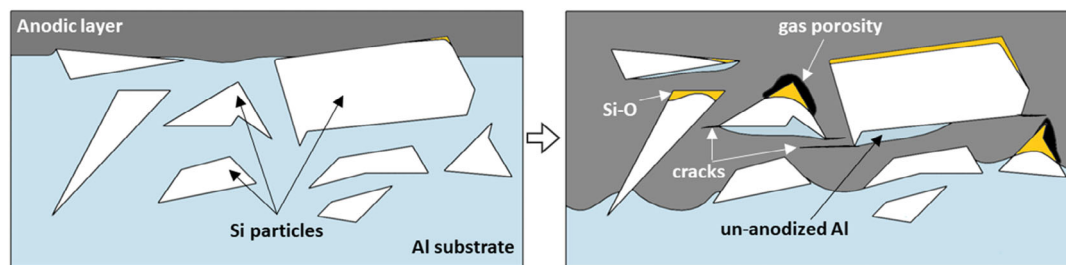


Figure 4. Sketch showing the formation of the principal defects, as indicated by arrows, during the growth of the anodic layer in the Al–Si eutectic region.

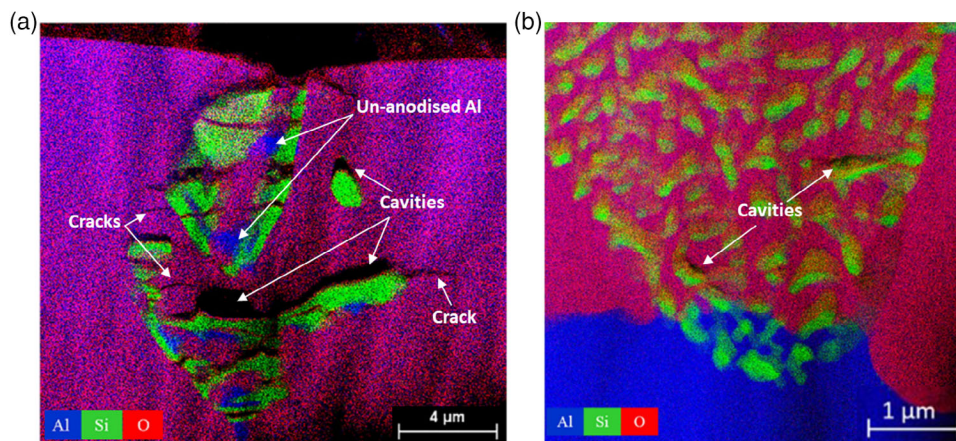


Figure 5. EDS elemental maps of the anodized layer in Al–Si foundry alloys containing a) Si flake-like and b) fibrous Si particles; the Al_2O_3 and SiO_2 layers are shown in red and orange, respectively. The presence of cracks and cavities is indicated by arrows. Reproduced with permission.^[31] Copyright 2021, Elsevier.

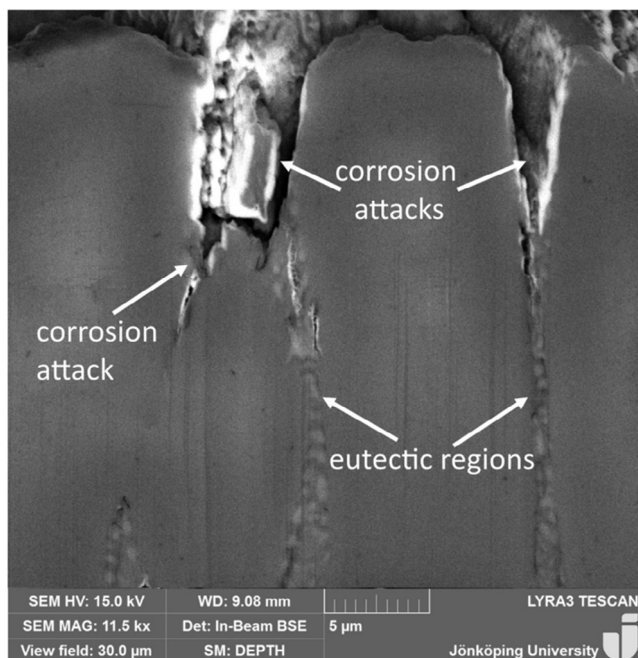


Figure 6. Focused-ion beam scanning-electron microscopy (FIB-SEM) micrograph of the corrosion attack at the Al/Si interface in an AlSi7Mg alloy. Reproduced with permission.^[60] Copyright 2021, Elsevier.

The anodizing of hypereutectic Al alloys has not been deeply investigated in the literature. Even without any anodizing treatment, this type of alloy ensures good wear resistance due to the Si content higher than 13 wt%.^[43] However, Chiang et al.^[44] analyzed the influence of primary Si crystals on the anodizing response of a die-casted AlSi17Cu4Mg alloy, where the thickness of the oxide layer decreased by increasing the size of the primary Si particles due to the increase of the electrical resistance at the substrate. The metal substrate resulted more electrochemically heterogeneous by increasing the dimensions of Si crystals. To obtain a better anodizing response, Chiang et al.^[44] suggested the application of a pre-anodizing heat treatment to homogenize the microstructure and reduce the size of the primary Si phase.

2.2. Cu-Rich Compounds

Copper (Cu) is often added to Al–Si alloys to increase the mechanical properties through solid-solution and precipitation strengthening.^[29] However, the beneficial effect of Cu addition is not preserved after anodizing^[28] due to the formation of defects inside the oxide layer, which decreases the surface hardness and quality of the anodic layer. The presence of Cu-rich compounds increases the electrochemical heterogeneity of the substrate, hindering the uniform growth of the oxide layer and increasing the content of defects embedded in it.^[5,26,37]

Even at low concentrations, Cu is detrimental for anodizing, and it greater affects the growth of the anodic layer than the eutectic Si particles.^[5] Caliarì et al.^[5] investigated the variation of oxide thickness in three different Cu-containing alloys, i.e., AlSi9Cu3(Fe), AlSi11Cu2(Fe), and AlSi12Cu1(Fe). The oxide thickness increased from $5 \pm 1 \mu\text{m}$ in the AlSi9Cu3(Fe) alloy to about $16 \pm 1 \mu\text{m}$ in the AlSi12Cu1(Fe) alloy, despite the greater Si content in the latter alloy.

In general, the behavior of Cu-rich compounds during anodizing depends on their chemical composition. Fratila-Apachitei et al.^[26] studied the anodizing response of Al₂Cu phase in an AlSi10Cu3 alloy. This phase was present in the form of large globular compounds or irregular particles (3–20 μm). Whenever the anodic front reached a Cu-rich particle, the current distribution changed in favor of the Cu phase, due to its lower oxidation energy with respect to the surrounding Al-matrix. A preferential oxide growth path is generated inside the particle, and it endures until the total oxidation of the Cu-rich compound itself^[26] (Figure 7). Moreover, the Cu–O bond has a semiconducting nature, which causes the formation of gaseous oxygen during the oxidation reaction.^[34] Film cracking can also occur if the gas pressure is sufficient.^[34,45] Another Cu-rich phase that shows an anodic behavior with respect to the Al-matrix is the S-phase (Al₂CuMg), as reported by Meng et al.^[46]

On the contrary, Al–Cu–Fe intermetallic phases, such as Al₇Cu₂Fe, show a cathodic behavior, which promotes the oxidation of the surrounding Al-matrix, as illustrated in Figure 7. Moreover, these compounds efficiently support oxygen reduction reactions, causing the dissolution of the adjacent Al-phase matrix, known as “trenching.”^[23,47]

Whether the behavior of a Cu-rich compound with respect to the Al-matrix is anodic or cathodic, the mechanical properties of the anodic layer decrease due to the heterogeneity created on the substrate by these compounds. Fratila-Apachitei et al.^[28] reported a decrease in local microhardness inside the anodic layer by adding 3 wt% Cu in an AlSi10 alloy. The Cu addition reinforces the substrate, but promotes the formation of voids and cracks during the anodizing process, which drastically influences the final strength of the surface. Similar results were also found by Caliarì et al.,^[5] who evidenced a decrease of the oxide microhardness and wear resistance by increasing the Cu amounts.

2.3. Fe-Rich Compounds

In general, Fe-rich compounds are undesirable particles inside the anodic layer, due to their inert or cathodic behavior with respect to the Al-matrix. According to the chemical composition of these compounds, they can be partially or totally oxidized during the anodizing process.^[24] In particular, the Al₁₂(FeMn)₃Si and Al₆Fe phases hinder the growth of the anodic layer due to their higher oxidation energy.^[48] These particles are partially oxidized and embedded in the oxide layer, generating a scalloped interface with the un-anodized aluminum substrate.^[26] On the contrary, the Al₃Fe particles have an oxidation rate comparable with that of the Al-matrix, and they are not incorporated inside the oxide layer.^[26,49] The partial or total dissolution of Fe-rich intermetallics during anodizing causes the formation of voids and defects in the oxide layer (Figure 8), decreasing its mechanical performance.^[4,36,50,51]

Zhu et al.^[4,36,52] investigated the anodizing response of Fe-rich particles in a rheocast AlSi7Mg0.4 alloy. It was observed how the π-Al₈FeMg₃Si₆ phase, with respect to the α-Al₁₅(FeMn)₃Si₂ phase, is easier dissolved during anodizing due to a higher oxidation rate.^[52] In different areas of Fe-rich compounds precipitated in the interdendritic eutectic regions, the Fe and Mg contents decrease after anodizing, proving the dissolution of these particles.^[4,36] However, some vacancies and defects are formed on the oxide layer, and they negatively affect the hardness of the oxide layer. Moreover, the Fe-rich phases beneath the anodic layer are electrochemically nobler than the Al–Si eutectic structure and decrease the corrosion resistance of the alloy; these compounds form a galvanic couple with the surrounding Al–Si eutectic, promoting and increasing the pit corrosion below the oxide layer.^[4,36]

3. Influence of the Casting Process

As discussed in Section 2, the microstructure of the substrate strongly influences the anodizing response because the oxide growth is affected by the morphology and distribution of the secondary phases. Different casting processes result in different microstructures of the substrate that can positively or negatively influence the formation of the anodic layer. Riddar et al.^[39] investigated the response to natural anodizing of an AlSi7Mg alloy

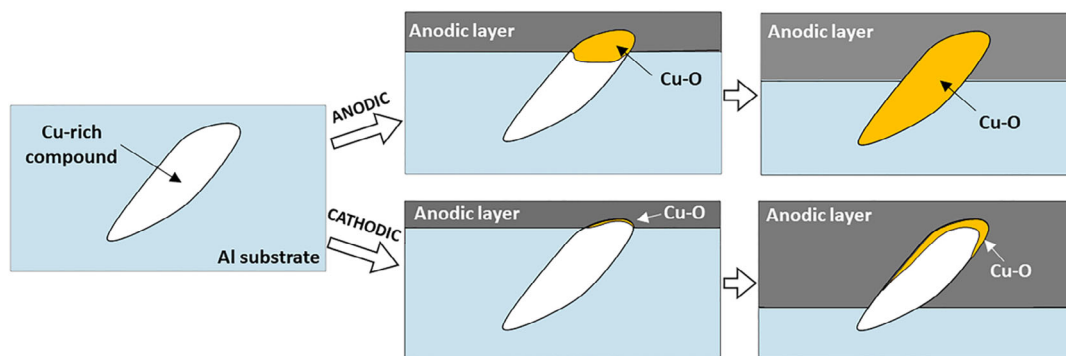


Figure 7. Sketch of the anodic and cathodic behaviors of Cu-rich compounds during the growth of the anodic layer.

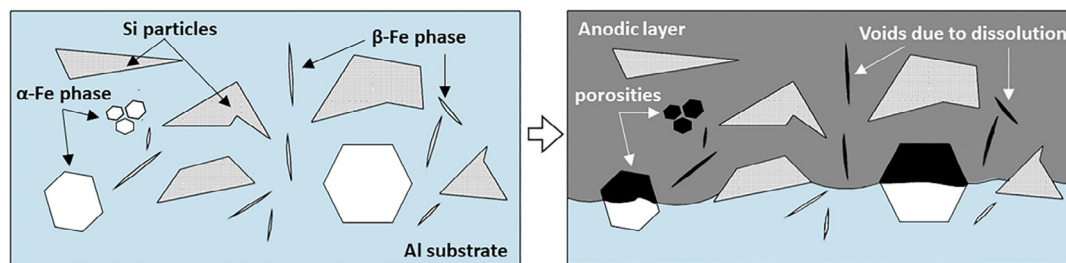


Figure 8. Formation of voids inside the anodic layer due to the dissolution of Fe-rich intermetallic compounds.

produced by sand casting and permanent mold casting. Before anodizing, both substrates were machined until the R_a value of surface roughness was in the order of 0.2–0.3 μm . After anodizing, some differences in the surface topography appeared clear, and the sand cast surface showed higher surface roughness (0.9 μm) than the permanent mold cast alloy (0.5 μm). Furthermore, the thickness variation of the anodic layer was greater in the sand casting than in the permanent mold one. These observations lead to the conclusion that the cooling rate during solidification significantly affects the final microstructure, and thus the subsequent anodizing response of the material.

In hypoeutectic Al–Si foundry alloys, high cooling rates promote the formation of the Al–Si eutectic structure and the refinement of the primary α -Al phase.^[31] This affects the growth of the oxide layer, which results scalloped and nonuniform due to the electrochemical heterogeneity of the substrate. Upon decreasing the cooling rate, the growth of the anodic layer is facilitated and its thickness increases; the eutectic fraction formed in the substrate decreases as well as the concentration of alloying elements in the α -Al phase decreases.^[31,53,54]

Among all the casting processes, the high-pressure diecasting (HPDC) is one of the foundry processes that allows to obtain very high cooling rates (up to $\approx 10^3 \text{ }^\circ\text{C s}^{-1}$ ^[55,56]). This technology is widespread in the foundry world due to the possibility to realize complex shape castings with thin wall thicknesses, good tolerances, and high production rates. However, the HPDC presents some technical and structural limitations, mainly related to the monitoring and optimization of the process parameters, which influence the final casting quality.^[57] Many types of casting defects and microstructure heterogeneities can be formed during HPDC, which can negatively affect the anodizing response. In hypoeutectic AlSi alloys, the quality of HPDC components is mainly affected by the presence of (i) defects bands, (ii) externally solidified crystals, (iii) surface oxide layers, (iv) sludge segregations, and (v) filling-related defects, which differently influences the growth of the oxide layer.^[27,58]

The “defects band”, or “segregation band”, is a region of the material containing a higher solute content than the average alloy composition (positive segregation) and it follows the contour of the casting surface.^[58] Due to the short freezing range, it generally does not contain a significant level of porosity, but it is enriched with a higher volume fraction of eutectic and

intermetallic compounds than the surrounding material.^[5,37] Thus, during the anodizing process, the high content of secondary phases makes the surface electrochemically heterogeneous, preventing the uniform growth of the oxide layer and decreasing the mechanical properties of the surface.^[5,59] The analogous phenomenon affects rheocast components, where the hardness and corrosion protection of the anodic layer are reduced due to the formation of a surface segregation layer enriched with solute elements.^[41,52,60,61]

The “externally solidified crystals” are large bright α -Al crystals solidified during the melt transfer from the holding furnace to the shot sleeve of a cold chamber diecasting machine, or inside the shot sleeve, and injected into the die cavity during the filling phase.^[59,62,63] Due to the greater dimensions with respect to the grains of the Al-matrix, these defects increase the heterogeneity of the surface and can create preferential areas for the growth of the oxide front with respect to the surrounding material.

In the HPDC, due to the extraction of the casting from the die at relatively high temperatures (200 ÷ 300 $^\circ\text{C}$ ^[64]), a “skin oxide layer” is formed. This oxide film is thicker than that naturally formed at room temperature, and it can negatively affect the growth of the anodic layer during the anodizing process due to its passivating effect.^[5,65,66]

The “sludge segregations” consist of the accumulation of large blocky-like primary Fe-rich compounds ($\alpha\text{-Al}_x(\text{Fe},\text{Mn},\text{Cr})_y\text{Si}_z$) formed during the transport of the molten metal from the casting furnace to the shot sleeve or inside the cold chamber.^[58] Due to their huge size and chemical composition, sludge particles can reduce the anodizing response of the substrate, increasing its heterogeneity and hindering the growth of the oxide layer.

“Filling-related defects” are formed during the die-filling step due to the turbulent flow of the molten metal or its interaction with the die wall. During the filling phase, air/gas bubbles, bifilms, or external particles can be entrained inside the liquid metal due to the action of turbulence. Moreover, the metal front can interact with the lubricant covering the die wall and form surface defects or die soldering. When this occurs, the casting regions in contact with the die wall show different microstructures with respect to the surrounding material; this influences the subsequent thickness and morphology of the oxide layer.^[27] During the anodizing process, preexisting casting

defects, such as laminations,^[67] can lead to aesthetic defects on the anodized surface and prevent the growth of a compact oxide layer (Figure 9).

4. Influence of Pre-Anodizing Machining Operations

Post-casting machining operations are very common in industrial reality. These operations are needed to obtain the final geometry and dimensional tolerances of the component.

Some studies on rheocast and diecast hypoeutectic Al–Si alloys were carried out to investigate the influence of machining operations on the subsequent anodizing treatment.^[5,52,59,61] Regardless of anodizing parameters and investigated alloys, machined substrates show generally a thicker anodic layer after anodizing than the as-cast ones^[5,37] (Figure 10a). Caliarì et al.^[5,37,59] explained this result considering the effects of milling operation on the diecast substrate before anodizing. The removal of material from the diecast surface results in the partial or total elimination of the surface casting defects mentioned in Section 3. In particular, the passivating skin and the segregation

band are removed, and the microstructure of the substrate results more propitious for the growth of the anodic layer due to a greater amount of α -Al phase and less eutectic fraction. Moreover, the Si interparticle spacing is greater, favoring the propagation of the anodic front among the eutectic Si particles. Similar results were found in the machined rheocast substrates studied by Zhu et al.^[4,36,52]

The machining operations remove the surface liquid segregation enriched with Fe-rich compounds that are formed during the casting process. Due to the low amount of Fe-rich intermetallics embedded in the oxide layer, the machined substrate results slightly thicker, harder, and more resistant to corrosion after anodizing.^[4] However, it must be considered that a thicker oxide layer is not always even wear resistant. Caliarì et al.^[5,37] found a decrease in the abrasion resistance of the preliminary machined substrate with respect to the as-diecast surface (Figure 10b). Different features explain this behavior: (i) the thickness of the anodic layer and (ii) the size of the embedded Si particles. (i) The thickness of the oxide layer can affect its final mechanical properties, especially when the heterogeneity of the substrate involves the formation of voids and cracks during the growth of the oxide itself. Thicker oxide layer may entrap a

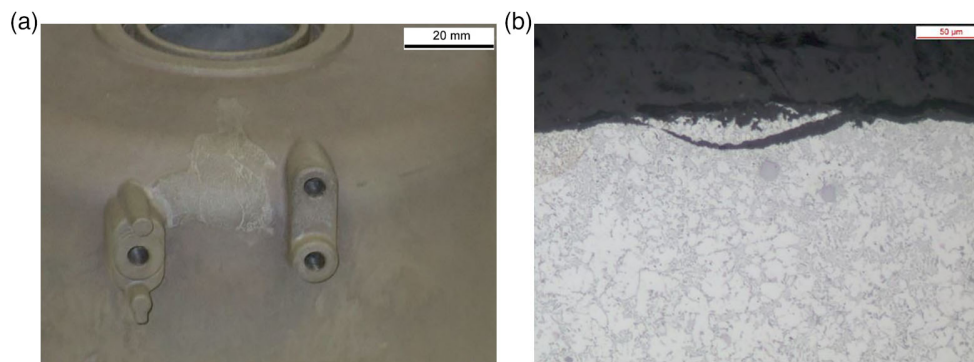


Figure 9. a) Aesthetic defect observed after anodizing on the surface of a diecast AlSi9Cu3(Fe) alloy component and caused by the presence of b) a preexisting casting defect identified as lamination.

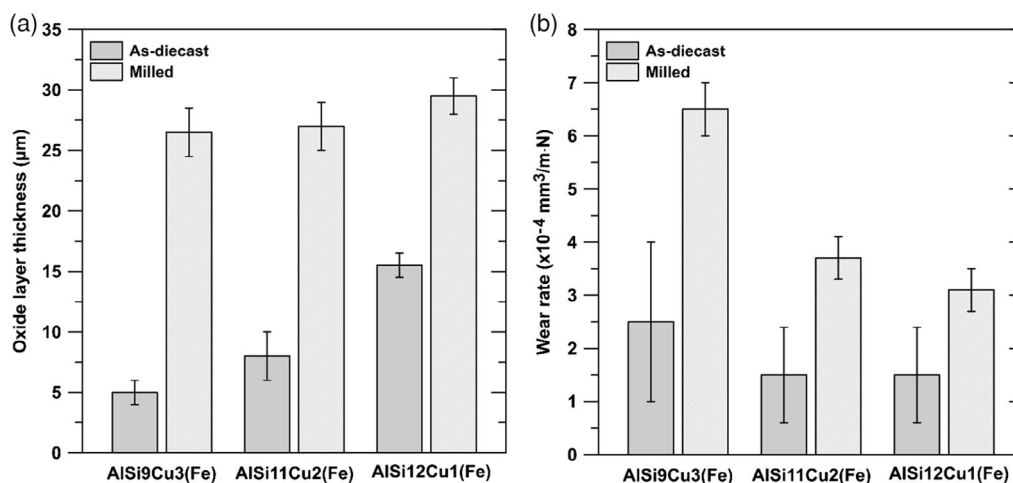


Figure 10. a) Thickness of the oxide layer and b) corresponding wear rate in milled and as-diecast substrates of different diecast AlSiCu alloys. Data are reproduced and re-elaborated with permission.^[5] Copyright 2021, Elsevier.

greater content of porosities and defects that decrease the integrity and the abrasion resistance of the surface.^[7] Shin et al.^[65] demonstrated how a thick oxide layer results less effective in terms of friction reduction, and it easily collapses under contact pressure. (ii) Moreover, the silicon particles embedded in the oxide layer may act like reinforced and increase the surface mechanical properties. It is known that a fine reinforce is more effective in increasing the wear resistance.^[68] A machined surface shows generally coarser Si particles with respect to the as-cast substrate, resulting in a less efficient post-anodizing reinforce.^[5]

The effect of sandblasting operations on the anodizing of die-cast surfaces was also investigated in a previous study.^[37] In general, this process has a beneficial effect on the anodizing response because it removes the passivating skin layer formed at 200 ÷ 300 °C during the extraction of the casting from the die (see Section 3). However, the growth of the oxide layer is strongly affected by the microstructure of the surface exposed after sandblasting. According to the chemical composition of the alloy and the morphology of the compounds, sandblasting operations can positively or negatively affect the growth of the anodic layer. In high Cu-containing Al–Si alloys, such as AlSi9Cu3(Fe) alloys, the microstructure of the sandblasted surface is similar to the as-diecast one due to the high Cu content, which promotes the refinement of Si particles. Therefore, the sandblasting operations positively affect the anodizing response, removing the skin layer and promoting the growth of a thicker anodic layer. On the contrary, in lower Cu-containing Al–Si alloys, such as AlSi11Cu2(Fe) and AlSi12Cu1(Fe) alloys, the sandblasted substrates present a more heterogeneous microstructure with coarser Si particles with respect to the as-diecast surface. The anodizing response of the sandblasted substrate is, therefore, poor, and it prevails over the positive effect of the removal of the anodic layer.^[37]

5. Influence of Anodizing Parameters

The selection of the correct anodizing parameters is one of the most critical phases of the whole process; several features can strongly affect the final quality of the anodized surface. To simplify the understanding of the high numbers of variables that can be changed during the anodizing process, the different types of anodizing were classified. First, the potentiostatic anodizing is distinguished from the galvanostatic one. In the first process, the electrical voltage is imposed and controlled during the whole treatment, while the current is free to adapt to the system. In contrast, in galvanostatic anodizing, the electrical current is set and monitored during the process, while the voltage varies accordingly to the inertial of the system.^[6] Moreover, according to the nature of the electrolyte and the temperature of the anodizing bath, the MIL-A8625 specification^[69] identifies three principal types of anodizing: 1) Type I—chromic acid anodizing, where the component is immersed in an aqueous solution containing from 3 to 10 wt% CrO₃, with a pH between 0.5 and 1.^[6] Due to the passivating ability, this anodizing process is mostly used in riveted or welded assemblies.^[70] The chromic acid oxide is thin and compact, composed of lamellar oxide fragments and interlamellar fine bubbles over a continuous oxide layer. The

average thickness of this oxide layer is 3–5 μm, and it shows good corrosion resistance.^[2] 2) Type II—sulfuric acid anodizing, where the concentration of the sulfuric acid in the solution ranges from 5 to 25 wt%.^[70] The operating temperature is about 20–25 °C, and the current density typically ranges from 0.8 to 1.8 A dm⁻². The oxide layer thickens from 8 to 20 μm, and it shows a fine, columnar, unidirectional porous nanostructure. This treatment is widely used in the decorative metal finishing industry.^[2] 3) Type III—hard anodizing, which differs from sulfuric acid anodizing due to the processing temperature lower than 10 °C, the eventual use of an addition agent, and the different voltage and current density at which the process is accomplished. The oxide layer results less-porous, heavier, harder (>600 HV), and thicker (>25 μm) than those of Types I and II.^[6,70] Although the hard-anodic oxide layer is composed of columnar unidirectional pores as that of Type II, the oxide structure is coarser.^[2] For all the engineering applications requiring high wear resistance, hard anodizing is the most suitable treatment because it maximizes the hardness and abrasion resistance of the anodic layer.^[70] This treatment is widely used to produce pistons, cylinders, and hydraulic gears.

Due to their great corrosion resistance, Types II and III are widespread in industrial applications, and they are also known as natural and hard anodizing, respectively. Therefore, most of the studies regarding the anodizing of Al–Si foundry alloys were carried out with a sulfuric acid electrolyte at room temperature or temperatures lower than 10 °C.

In general, the morphology and growth rate of the oxide layer are based on a balance between the formation process of alumina and its field-assisted dissolution in the electrolyte.^[12,13] Low temperatures and concentrations of the electrolyte allow to reduce the field-assisted dissolution rate, promoting a thicker layer. On the contrary, high current densities or anodizing voltages increase the thermally enhanced dissolution of the outer oxide surface, promoting the formation of porosities inside the anodic layer. Therefore, a good balance of the anodizing parameters is necessary to form a high-performance oxide layer. Excessively high current densities, times, or anodizing temperatures cause the formation of a rough, cracked, and powdery oxide, which can be easily detached from the substrate.^[45] To allow a better understanding of this topic, the main anodizing parameters are set out in more detail in the following section.

5.1. Nature of the Electrolyte

The electrolyte is the main conductor during the anodizing process because it allows the ion motion between the anode and cathode and across the oxide layer. To maintain a high process efficiency, it is important to control the accumulation of reaction products generated during the substrate oxidation; a great accumulation can increase the resistance inside the electrolyte, decreasing its conductivity.^[2]

The chemical composition of the electrolyte strongly influences the growth of the oxide layer. A strongly adherent barrier-type film is formed when the products of the anodic reaction are insoluble in the electrolyte. Therefore, at relatively high voltage, a thin and dielectric compact film is formed in neutral pH salt solution (e.g., borate or tartrate electrolyte).^[70] On the contrary, a porous

oxide layer is formed in generally acidic electrolytes, such as sulfuric, phosphoric, chromic, and oxalic acids.^[70] According to the chemistry and the concentration of the acid in the electrolyte, a porous structure with various porous sizes can be formed.^[71] Konieczny et al.^[72] investigated the morphological variation of the porous oxide layer in an AlSi12 alloy by changing the type of electrolyte. Solutions with the addition of oxalic, phosphoric, sulfuric acids or chromium trioxide were analyzed. It was observed how the type of electrolyte influences the pores' diameter and their mutual arrangement. The pores' size results coarser by using phosphoric acid and oxalic acid, whereas chromium trioxide and sulfuric acid produce a more refined structure (**Figure 11**). Moreover, the structures produced in an electrolyte containing $\text{H}_2\text{C}_2\text{O}_4$, H_3PO_4 , or H_2SO_4 result ordered and regular, while the porous structure generated with CrO_3 is more disordered (Figure 11).^[72]

A variation in the mechanical properties of the oxide layer can be detected by changing the chemistry of the electrolyte. In particular, the addition of additives to the electrolytic bath affects the final performance of the anodic layer. Chiang et al.^[44] studied the hardness and abrasion resistance of a hypereutectic Al–Si alloy after pulse anodizing at 0 °C. Three different types of electrolytes were selected: a sulfuric acid electrolyte, a combination of sulfuric and oxalic acids, and a mixed solution of sulfuric and oxalic acids with dissolved aluminum sulfate. The results showed a progressive increase of oxide thickness and mechanical properties by adding oxalic acid and dissolved aluminum sulfate into the sulfuric acid electrolyte. During the anodizing process, the aluminum ions in the aluminum sulfate are dissociated from the electrolyte, increasing the conduction efficiency. Thus, a thick and refined oxide layer can be formed, which leads to better hardness and abrasion resistance.^[44] Romdhane et al.^[73] analyzed the influence of various alkaline media on the anodizing response of AlSi12 alloys. They performed micro-arc oxidation in four different electrolytic solutions, i.e., KOH, KOH + Na_2SiO_3 , KOH + KF, and KOH + Na_2SiO_3 + KF. In general, the addition of fluorides and/or silicates to the electrolyte reduces the current density required to reach the micro-arc regime, thus increasing the efficiency of the anodizing process. Under galvanostatic anodizing with the same anodizing time, a thicker oxide layer is obtained with the addition KF, because the fluorides present in the electrolyte accelerate the initiation of the micro-arc regime. A slight improvement in corrosion resistance was also observed by adding silicates in the electrolytic solution because they acted as sealing/healing agents.^[73]

The concentration of the electrolytic solution is another feature that can affect the anodizing response. Shang et al.^[74] demonstrated how adding an excessively high concentration of additives to the electrolyte would have a negative impact on the quality of the oxide layer. The weight and corrosion resistance of the anodic layer are significantly reduced by exceeding the addition of organic acids to the sulfuric acid electrolyte. On the contrary, a balanced mixing of additives improves the surface properties of the oxide film.^[74]

Gastón-García et al.^[45] studied the effects of the electrolyte concentration on the mechanical properties of the oxide layer. An AlSi9Cu3(Fe)(Zn) alloy was anodized at 0 °C in a sulfuric acid electrolyte at 5 and 15 vol%. Regardless of the current density, no evident differences were detected in the oxide thickness by varying the acid concentration. However, the anodic layer formed at a lower concentration presented less cracks and defects, which resulted in slightly higher microhardness and abrasion resistance. The comparable thickness of the two oxide layers indicated that the electrolytic efficiency of the anodizing process was comparable in both electrolytes.

In the same study,^[45] the influence of the electrolytic temperature was also investigated. It is well known how, decreasing the electrolyte temperature, the thickness and the mechanical properties of the anodic layer increase.^[16] At lower electrolyte temperatures, the reactivity of the electrolyte decreases, and the dissolution rate of the anodic layer becomes lower. Furthermore, the local heating effects on the oxide surface are reduced, and the oxide layer shows less porosity and greater mechanical properties.^[16] This was demonstrated by Gastón-García et al.^[45] after anodizing an AlSi9Cu3(Fe)(Zn) alloy at –5, 0, and 20 °C in a 15 vol% H_2SO_4 electrolyte. The increase of the oxidation rate by decreasing the electrolyte temperature can be more easily appreciated at a long anodizing time, when the variation in the oxide layer thickness becomes more evident. In Gastón-García's work, after 120 min at 5 A dm⁻², the thickness of the anodic layers formed at 0 and 5 °C exceeded 100 μm, while at 25 °C, it was lower than 60 μm (**Figure 12**).

Although lowering the anodizing temperature reduces the dissolution rate of the oxide in the electrolyte, promoting the growth of the anodic layer, it also increases the resistance of the electrolyte to the current flow. At low temperatures, the electrical current flow inside the electrolyte decreases, reducing the anodizing efficiency. Therefore, the growth of the anodic layer is based on the balance between these two effects. By decreasing the anodizing temperature, the increase of the electrolytic

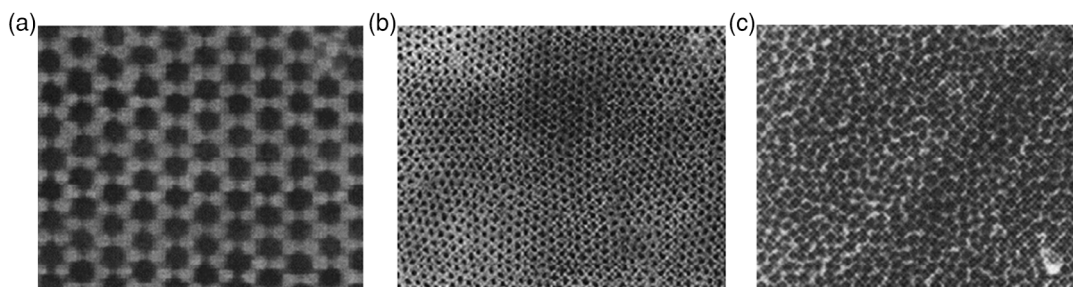


Figure 11. Porous structure formed in an AlSi12 alloy after anodizing with different electrolytes: a) $\text{H}_2\text{C}_2\text{O}_4$, b) H_2SO_4 , and c) CrO_3 . Reproduced with permission.^[72] Copyright 2021, Elsevier.

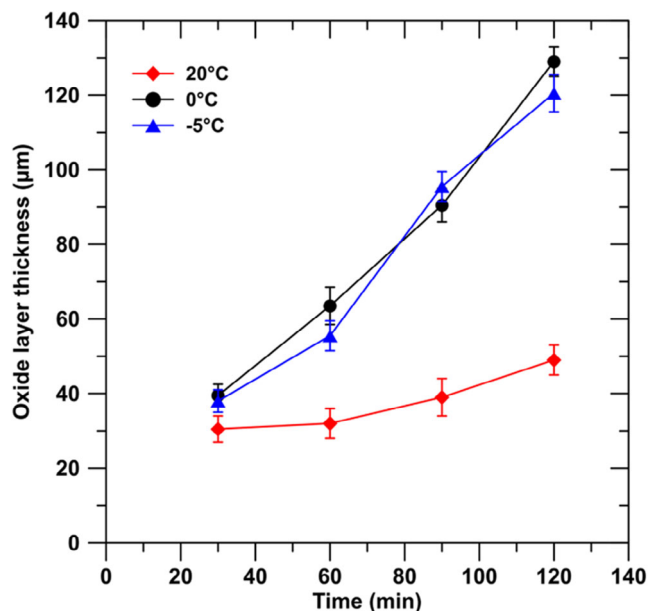


Figure 12. Influence of the anodizing time and electrolyte temperature on the thickness of the oxide layer. The data concerns an AlSi9Cu3(Fe)(Zn) alloy anodized in 15 vol% H₂SO₄ at 5.0 A dm⁻². Data are reproduced with permission.^[45] Copyright 2021, Taylor & Francis.

resistance to the current flow can prevail over the reduction of the oxide dissolution rate, decreasing the thickness of the anodic layer. Caliarì et al.^[37] studied the effect of an electrolytic temperature below 0 °C on the anodizing response of a machined AlSiCu(Fe) alloy substrate. Regardless of the chemical composition of the alloy, by reducing the anodizing temperature from 0 to -4 °C, a thinner anodic layer was formed. At -4 °C, under a current density of 2.5 A dm⁻², the increase of the current flow resistance prevented the thickening of the anodic layer, resulting in a poorer anodizing response.

5.2. Current Density

To study the influence of the electrical current on the anodizing response of the substrate, galvanostatic anodizing is generally used. In this technique, the electrical current is imposed, while the voltage can vary according to the system. It results particularly suitable to study the electrical response caused by the formation of cracks and voids in the oxide layer. By measuring the variation of voltage over time and comparing it with the electrical behavior of the anodized pure aluminum, it is possible to identify the formation of defects inside the oxide layer. Indeed, when oxygen gas-filled voids are formed, the ionic transport process is hindered, and the resistivity of the substrate increases.^[35,45] This growth of resistivity results in an increase in the recorded voltage. Therefore, in the voltage–time graph, when the Al alloy curve is higher than the reference pure Al curve, it indicates the formation of voids inside the anodic layer.^[35,45] In contrast, when the anodic layer cracks and re-anodizes due to the presence of high levels of intrinsic stresses, fluctuations in the voltage measurements are recorded.^[45,75,76] Therefore, in the voltage–time graph,

the voltage fluctuations in the steady-state region correspond to the formation of cracks in the anodic layer.

This technique was used by Fratila-Apachitei et al.^[35,76,77] and Gastón-García et al.^[45] to analyze the growth evolution of the oxide under different anodizing parameters. In particular, they studied the influence of the applied current density on the formation of the anodic layer. They found how, increasing the current density, the oxidation rate increases, forming a thicker anodic layer.^[35] However, the local heating effects on the oxide surface increase too, forming porosities due to a higher thermal enhanced dissolution rate.^[16,45] Therefore, the anodic layer results thicker but less hard as shown in Figure 13.^[26,45,76]

Finally, the influence of the current waveform on the hard anodizing of AlSi10 and AlSi10Cu3 casting alloys was also investigated.^[77] No significant variations in the oxide thickness and microhardness were detected by applying direct current with respect to pulse current in different waveforms.

5.3. Applied Voltage

The anodizing voltage is one of the most important parameters during the early growth of the anodic layer because it is mainly responsible for the barrier layer formation. Indeed, the thickness of the barrier layer is proportional to the applied voltage.^[70] In potentiostatic anodizing, the applied voltage does not only affect the barrier layer but also influences the growth of the porous layer. When the applied voltage increases, the oxide thickens because the electrical current flowing in the anodizing system becomes greater.^[60] Therefore, a voltage increase corresponds to an exponential growth of the current density, resulting in an increase in the oxide growth rate.^[78] However, it is important to consider that excessively high current densities will lead to the formation of heating effects on the outer oxide surface, decreasing its quality and mechanical properties (see Section 5.2).

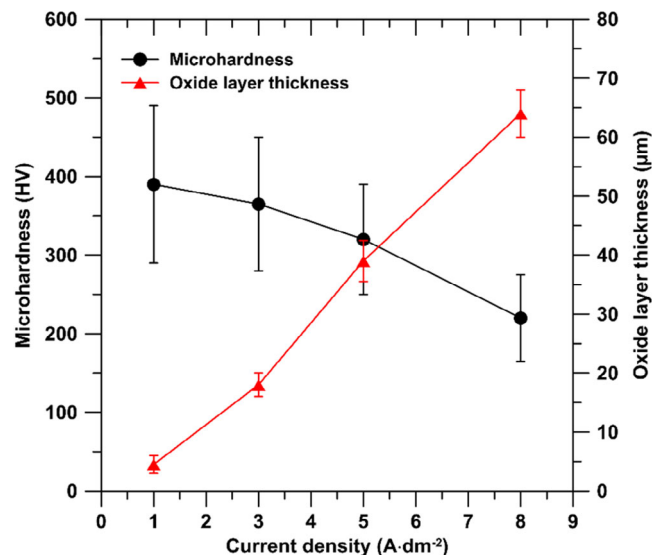


Figure 13. Variation of the thickness and microhardness of the oxide layer with the current density. Data concerns an AlSi9Cu3(Fe)(Zn) anodized in 15 vol% H₂SO₄. Data are reproduced with permission.^[45] Copyright 2021, Taylor & Francis.

5.4. Anodizing Time

The growth of the oxide is a matter of time: higher is the anodizing time, greater will be the thickness of the anodic layer. However, this growth cannot be endless. When the growth rate of the oxide is balanced by its dissolution rate inside the electrolyte, the oxide layer is stabilized, and it cannot become thicker over time.^[45] Longer anodizing time can only decrease the quality of the layer. Indeed, greater heating effects are generated over the outer surface of the anodic layer, and they can increase the local temperature of the electrolyte, enhancing its reactivity. Thus, the consequent increase of the dissolution rate leads to the formation of defects and porosity on the external surface of the anodic layer, decreasing its hardness and wear resistance. This mechanism was confirmed in several studies.^[28,60,79] Zhu et al.^[60] analyzed the influence of the anodizing time during natural anodizing of a Sr-modified AlSi7Mg alloy. It was observed how, increasing the anodizing time, the thickness of the oxide layer became greater, but after 30 min the hardness decreased (**Figure 14**). For a long anodizing time, the heating effects formed on the oxide/electrolyte interface make the local porous structure coarser, reducing its mechanical properties. In general, the nanohardness of the anodic layer decreases from the oxide–metal interface to the electrolytic–oxide interface. Moreover, increasing the anodizing time produces a thicker, but more stressed, oxide layer; these intrinsic stresses are released during the growth of the anodic layer. As a consequence, a greater number of cracks and porosities are formed and embedded in the anodic layer, decreasing the corrosion resistance.^[60]

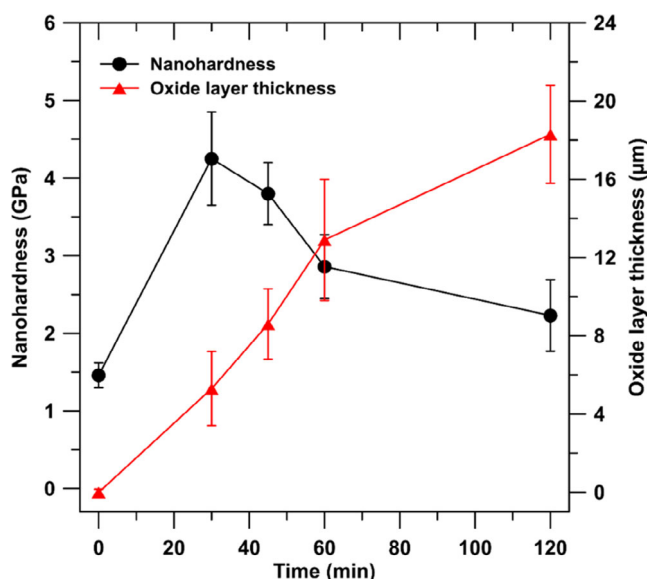


Figure 14. Variation of the thickness and nanohardness of the oxide layer with the anodizing time. Data concerns an AlSi7Mg alloy anodized at 25 V in 1.0 M H₂SO₄ at room temperature. Data are reproduced with permission.^[60] Copyright 2021, Elsevier.

6. Influence of the Post-Anodizing Processes

To improve the surface properties of an anodized component, a post-anodizing process is generally performed. In the industrial context, dyeing and sealing are the most common post-anodizing operations. Even though the first process is mainly used to change the surface color and improve the aesthetic properties of the anodized components, the second one is necessary to enhance the corrosion resistance and prevent the leaching of dyes.^[2,80]

Sealing is the final step of the anodizing process, and it is necessary to seal the microporosity of the oxide layer, avoiding the penetration of aggressive substances that may decrease the corrosion resistance.^[80] During the sealing process, the porous oxide structure reacts with the seal chemistry, creating reaction products that are adsorbed into the anodic surface, or precipitated throughout the seal; this will increase the corrosion resistance of the superficial oxide.^[2] Many types of seal chemistry can be used, according to the required surface properties. Hydrothermal, cold nickel fluoride, chromate, silicate, and nickel acetate sealing are among the most famous sealing processes investigated in literature.^[80] Different sealing processes affect not only the corrosion resistance of the oxide layer but also its hardness and wear resistance.^[80,81] For instance, conventional hydrothermal sealing (HTS) and steam sealing are sustainable processes that improve the surface corrosion resistance, but they also reduce the abrasion resistance of anodic coatings. In contrast, chromate and silicate sealing processes increase the corrosion resistance, keeping good surface mechanical properties, but they can present adverse effects during anodizing and disposal phases.^[80]

The positive effects of the sealing process on the corrosion resistance of wrought aluminum alloys have been widely investigated.^[82–84] However, the studies concerning the effect of sealing on anodized Al–Si foundry alloys are limited. Mohedano et al.^[85] investigated the effect of different sealing processes over an AlSi7Mg0.3 alloy. Sealing techniques based on salts of cerium, nickel, potassium permanganate, and phosphonic acid were investigated. It was evidenced how all the performed post-treatments showed a beneficial effect on improving the corrosion resistance, although the potassium permanganate and nickel acetate-based sealings showed the best results.^[85]

The influence of HTS on a rheocast AlSi5.5Mg alloy was investigated by Zhu in a previous study.^[36] The author observed that the corrosion resistance of the alloy decreased after HTS due to the formation of a great number of cracks, which promoted the initiation and propagation of corrosive phenomena throughout the anodic layer. During the HTS process, the volume expansion associated with the transformation of porous aluminum oxide into boehmite involves the formation of intrinsic stresses, especially around the Si particles. More cracks are therefore formed in the sealed oxide layer, especially in the regions adjacent to the eutectic structure.

7. Conclusions

In the present work, the main factors affecting the anodizing response of Al–Si foundry alloys have been critically reviewed.

The effects of alloy chemical composition, microstructure, casting process, pre-anodizing machining, anodizing parameters, and sealing processes have been reviewed over the growth and morphology of the oxide layer. The following conclusions can be drawn: 1) The microstructure of Al–Si alloys is heterogeneous, and it generally presents different phases, which hinder the growth of the anodic front. Depending on their chemical composition, secondary phases can oxidize faster or slower relative to the Al-matrix. In general, Si particles show higher oxidation energy than the Al-matrix and have a cathodic behavior during anodizing. In contrast, Cu- and Fe-rich compounds can exhibit both anodic and cathodic behaviors according to their stoichiometry; 2) The nonuniform growth of the anodic front results in a scalloped substrate/oxide interface and involves the formation of oxygen-gas porosities, intrinsic stresses, cracks, and un-anodized zones inside the anodic layer; 3) The presence of a segregation band or skin oxide layer on the casting surface reduces the anodizing response. Higher contents of eutectic and intermetallic compounds prevent the growth of the oxide front. By embedding filling-related defects in the anodic layer, the aesthetic and mechanical properties can be further compromised; 4) The machining operations performed before the anodizing process can promote the anodic oxide growth by removing the initial segregation band and oxide skin from the casting surface. However, the formation of a thick oxide layer does not ensure excellent surface mechanical properties. In fact, thicker coatings generally embed more defects than thinner layers, and their surface hardness and abrasion resistance are lower; 5) The anodizing parameters control the morphology and thickness of the anodic layer. Generally, higher applied voltage, current density, and anodizing time promote the growth of the oxide front. Lower temperatures of the anodizing bath and less aggressive electrolytes are also used to increase the thickness and the mechanical properties of the oxide layer. However, local heating effects on the outer surface of the anodic film can enhance the dissolution rate, increasing the formation of porosities and defects; 6) The sealing process usually improves the corrosion resistance of the anodic layer. However, HTS may be harmful for corrosion protection if it increases the formation of intrinsic stresses and cracks. These defects are generally related to the transformation of alumina in boehmite due to the volumetric expansion.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

Al–Si foundry alloy, anodizing, anodizing parameters, corrosion resistance, microstructure, pre- and post-anodizing processes, surface mechanical properties

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