Effects of Silicium in aluminum alloy anodizing

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The use of the aluminum alloys is experiencing new horizons, from the automotive to the building industries; one of the major treatments to which these alloys are submitted is anodizing, an electrolytic process mainly aimed at providing corrosion protection. The surface oxide layer, which develops during this treatment, is noticeably affected by the alloy elements that cause secondary and tertiary phases. The aluminum alloys most commonly used for permanent mold casting and die casting processes have silicium as the main alloy component; other elements such as copper and iron [1] may be present as alloying elements or impurities. In particular, silicium increases liquid metal fluidity and has a refining action on the grains. This element is available in a solid solution with the aluminum in very low percentages (0.05%at. at 300 °C), consequently the microstructure of alloys having a high silicium content consists of an α-Al primary phase and an Al-Si secondary eutectic phase; tertiary phases may also be found, deriving from the presence of other alloy elements or impurities. In particular, this secondary phase involves considerable alterations of morphology, pore distribution and microhardness and generally affects the anodized layer growth.

Silicium influence

During the anodizing, the aluminum matrix is dissolved by the electrolyte and originates Al³⁺ ions which, binding with oxygen, produce Al₂O₃. In this way, eutectic silicium particles are discovered and, through ordinary process parameters, are subjected to very slow oxidizing and are absorbed by the anodic layer. Si oxidation in order to obtain the SiO₂ is feasible but involves the application of considerable voltage because the energy of the Si- O bond (466 kJmol⁻¹) is much higher than that of the Al-O bond (281 kJmol⁻¹); consequently phases containing silicium do not react and remain unchanged inside the anodic film. Moreover, their possible oxidizing, if it occurs, also involves the formation of gaseous oxygen, creating voids inside the layer, and modifying the anodic coating morphology, being SiO₂ not porous. When Si undergoes oxidation [2], voids generated by the oxygen are formed near the eutectic particles. Both eutectic particles and voids involve a decrease in the oxidation velocity of the surrounding matrix, with respect to the regions where only primary aluminum is present.
If the anodizing time increases, the silicium volumetric fraction inside the anodic layer increases, with consequent closing or deformation of the pores. This way, the electrolyte access at the pore base decreases and causes a rise in the applied voltage, involving the barrier layer growth.

The presence of secondary and tertiary phases, due to silicium, copper and iron, also affects the anodic layer microhardness [3]. The intermetallic particles are trapped in the ceramic layer, which, for this reason, becomes more brittle. The main component responsible for this behavior is copper, which forms intermetallic particles that may be attacked by oxidation during anodizing, thus creating voids and cracks. The anodic layer adjacent to the secondary and tertiary phase particles is not always associated to the presence of defects, but the defects are always present near the intermetallic particles containing copper, confirming that this element is detrimental even as a trace metal.

As it is impossible to act directly on the alloy composition, in order to obtain a corrosion resistant anodic film, one may decide to act in such a way so that the eutectic silicium does not involve oxide layer decay. In order to do so, the microstructure parameters to be taken into consideration are Si particles distribution and size [4]. In this case the presence of tertiary phases, due to copper and iron impurities, may be neglected. Composition being equal, size and shape of grains and dendrites change according to the cooling velocity of the cast piece and therefore it is possible to find inside the same piece different microstructures with a different anodizing response. In fact, examining the section of a cast part it can be seen that the grain size is small near the surface zone due to the high overcooling, while it increases toward the central zone. Analogously, at the $\alpha$
border, the eutectic phase solidifies: the Si particles are smaller in the cortical zone with respect to the central zone of the piece, and this has an impact on the anodic layer growth. In fact, oxide film development occurs according to the base metal morphology, as the primary aluminum dissolution occurs at different velocities according to the grain size and to the presence of eutectic silicium. If the grains are small, the eutectic particles will also be small; if the grains have a diameter below 5 μm, the secondary phase particles are absorbed within the anodic layer, which appears continuous. In particular, in presence of the eutectic phase, the interfaces between the oxide layer and the base metal assume an undulated trend; this phenomenon occurs as the presence of the eutectic silicium locally diminishes the quantity of dissolved aluminum, with consequent lowering of the oxide thickness. With regard to particles with diameters ranging from 5 to 20 μm, the anodic layer is still capable of absorbing the Si but only with significant modifications of the oxidized film. The thickness is greatly reduced, the speed of growth diminished and the undulated trend of the oxide increases; in such conditions, the probability of silicium oxidation increases, with all due consequences, such as the formation of cracks and voids. For Si particle sizes greater than 20 μm, the velocity of dissolution of the primary aluminum around the particles decreases so greatly, that metallic aluminum may be found under the particle absorbed in the anodic layer. The influence of the silicium dimension on layer development is indicated in table 1.

<table>
<thead>
<tr>
<th>Secondary phase sizes</th>
<th>x &lt; 5 μm</th>
<th>5 μm &lt; x &lt; 20 μm</th>
<th>x &gt; 20 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>How the anodic layer appears</td>
<td>Continuous and well bound layer; particles are engulfed in the film and make its trend undulatory</td>
<td>Continuous layer, with irregular trend; particles are engulfed in the film</td>
<td>The layer may show discontinuities; particles cause clear damages on the film</td>
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</tbody>
</table>

Table 1 - Anodic layer trend in the presence of secondary phase

**Technological developments**

For these reasons, the first step to obtain an anodized layer with technologically promising characteristics, also in alloys with a non-oxidizable secondary phase, is achieving a microstructure characterized by small sized grains. Several methods [5] have been developed to obtain these microstructure characteristics; the most used is a chemical method, by adding elements such as sodium, strontium, antimony, potassium, calcium and barium, which are identified as modifiers, to the casting bath. The addition of these elements results in a Si fine microstructure that may also be obtained by modifying the cooling velocity, without the addition of any element. If some
magnesium is present, an analogous result is obtained at the foundry by superheating the bath over the liquidus temperature of the alloy, before pouring. One of the most advanced techniques produces quite fine Si particles, by combining casting bath superheating with ultrasounds applied after the die pouring so as to obtain a large spheroid primary aluminum phase, bordered by the eutectic phase, with Si particle size below 5 μm.

The last frontier in anodizing is represented by the PEO (Plasma Electrolytic Oxidizing) process, which is included among the electrolytic plasma-assisted treatments, in presence of a solution containing silicates as electrolytes. This avant-garde technique produces considerably thick and hard ceramic layers, characterized by very high adhesion. With regard to aluminum alloys with high silicium [6] content, the influence of the eutectic phase on the process has been studied and the chemical-physical mechanisms on which the process is based have been clarified. Keeping the current density fixed, the voltage applied has been changed so as to keep the same density throughout the entire layer growth. The anodizing process has been separated into four main phases: the first phase involves the formation of the conventional anodic layer, in the second phase there is an increase of the electric oxide potential to originate, in the third phase, the surface microarcs typical of the process; the last phase is the melting of the layer in the discharge points and the reaction with some elements making up the electrolyte. The first three phases are noticeably affected by the volumetric fraction of eutectic Al-Si; it seems that the micro-arcs start from the Al-Si interfaces when the critical voltage, which changes according to the alloy composition, is reached. Si-Al-O compounds with relatively low melting temperatures and a porous microstructure form in the zones where silicium is present. The roughness tests reveal that the roughness of the anodic layer increases with an increase of the Si content of the alloy. The anodic layer consists in γ-Al2O3 and a small portion of mullite, which is an aluminum silicate alumino, whose composition is Al[6-x]/3[Al2-xSiO5] with 0.6<x<0.8. From this study we may deduce that if high voltage values (600V) are applied, the surface morphology and layer roughness do not change when the silicium percentage is modified, and the effects are also insignificant if the oxide thicknesses exceeds 50 μm.

**Future perspectives**

The efforts of the industrial research are concentrated on the development of more and more advanced technologies, such as the PEO process, aimed at reducing the microstructure defects of the anodized layer, so as to control the parameters that determine mechanical strength and resistance to corrosion, in order to meet current market requirements. As shown by these studies, obtaining an optimum microstructure of the same layer is the first step toward guaranteeing anodic layers with a very high surface finish. With these aims, CALL in collaboration with the SMETEC Department of the Bologna University, has started an important experimentation activity, consisting in obtaining anodic layers on die-cast mechanical components, with a greater corrosion resistance during the storage and transport, characterized by a high-quality surface finish, pleasant to the eye and without the need to be painted.
Bibliography


CALL project

The CALL (Centre for innovation in the application of light alloys) project, co-ordinated by Cermet, aims to draw attention to the extent to which the increasingly vast use of products in light alloy is a key topic for the manufacturing industry and strategically important for maintaining competitiveness. Its main goals are:
- to gather and transfer information on the development of applications of light alloys in various contexts;
- to create professional profiles on light alloy technology;
- to sustain product and process innovation by means of suitable support to design and testing in order to create the ability to effect the autonomous assessment of the potential for using emerging technologies and materials;
- to set up a recipient body for the demand from companies for innovation in the field of light alloys. The body shall be authoritative and well referenced for access to national and community programmes for incentivating industrial innovation, thanks also to the recovery of the visibility of the ISML mark.
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