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The Influence of Surface Segregation on the Anodizing of AlSi11Cu2(Fe) Diecastings

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Abstract. A positive segregation is usually formed on the casting surfaces produced by high-pressure die casting (HPDC). In diecast Al-Si-Cu alloy components, this segregation shows a higher content of Si compared to the nominal composition of the alloy and it drastically affects the anodizing response of the casting surface. In the present work, HPDC components were produced by AlSi11Cu2(Fe) alloy, grit-blasted, and then anodized in a sulfuric acid electrolyte at the temperature of -4.5°C. Before the anodizing process, some regions of the casting were also milled, in order to completely remove the surface segregation. Microstructural investigations were carried out on grit-blasted and milled surfaces to characterize the initial substrates before anodizing, and to study their effect on the growth of the anodic layer. Scratch and wear tests were also performed to investigate the surface mechanical properties after anodizing. The results show that the surface segregation and the rough surface present on grit-blasted substrate leads to the formation of a thin and homogeneous anodic layer. On the contrary, a thicker and scalloped oxide film is formed on the milled surfaces. After anodizing, grit-blasted surfaces show lower wear and scratch resistance than milled substrates. The presence of surface segregation prevents the thickening of the anodic layer, negatively affecting the surface wear resistance due to the reduced oxide thickness.

Introduction

High-pressure die-casting (HPDC) is a widely used casting method in the automotive sector due to its ability to produce net-to-shape components at a high production rate. This method enables the production of light and high-performance aluminum (Al) castings with complex geometries and thin walls [1]. However, one of the main limitations of HPDC components is the formation of a heterogeneous microstructure, which can negatively affect the final performance of the castings [2]. There are various types of microstructural heterogeneities, such as defect bands, externally solidified crystals, cold flakes and casting defects. However, one of the most significant heterogeneities concerning the surface properties of castings is the formation of a surface segregation. It consists of a solute-enriched surface layer, formed by inverse segregation and exudation phenomena during the casting process [3]. A greater amount of eutectic structure and intermetallic compounds converge on the casting surface compared to the underlying material. This microstructural heterogeneity may severely affect the final result of finishing processes, such as anodizing.

Anodizing is an electrochemical treatment that aims to form a hard and high-resistance oxide layer on the casting surface. The aluminum component is immersed in an electrolytic bath and exposed to a current flow, which promotes the formation of a surface anodic layer. This process aims to increase the hardness, corrosion and wear resistance of Al castings [4].

The integrity, thickness and performance of the formed oxide layer are deeply influenced by the anodizing parameters and the microstructure of the Al substrate. The greater is the heterogeneity of the substrate, the worse are the performance of the anodic layer [4–6].

The presence of surface segregation is a non-negligible factor in the anodizing response of Al castings. Indeed, the higher amount of solute may negatively influence the growth of a thick and homogeneous anodic layer. Therefore, this study aims to analyze the impact of surface macrosegregation on the growth and properties of the oxide layer formed on castings in AlSi11Cu2(Fe) alloy.

Experimental Procedure

Due to the widespread use of AlSi11Cu2(Fe) alloy in HPDC, grit-blasted castings produced with this alloy were selected for the study. Some regions of the castings were milled to remove the surface segregation, and then the components were anodized at -4.5 ± 2°C in a sulfuric acid electrolyte with a concentration of 168 g/L H_2SO_4. The current density was first linearly increased from 0 to 0.88 A/dm^2 in 20 minutes, and then kept constant for 25 minutes. Cold sealing in a NiF_2 solution was performed at the end of the anodizing process.

Microstructural and mechanical investigations were performed in two regions of the castings, corresponding to the grit-blasted and milled areas, respectively. The cross-sections of samples drawn from these two regions were polished with 0.3 µm diamond paste and SiO_2 colloidal suspension. Firstly, the microstructure of the substrate was characterized in the two regions of the casting. The fraction of the eutectic structure was semi-quantified at the optical microscope according to ASTM E562-19e1 standard after a chemical etching in Murakami solution (60 mL H_2O, 5 g $K_3Fe(CN)_6$, and 10 g NaOH). Moreover, secondary dendrite arms spacing (SDAS) measurements were performed according to the according to the line intercept method (EN ISO 1463:2004).

A field-emission gun scanning electron microscope (FEG-SEM) was used to characterize the thickness and morphology of the anodic layer. Due to the heterogenous morphology of the oxide layer, at least 50 measurements of its thickness were acquired in each investigated region to ensure statistically reliable results. Finally, the average surface roughness (Ra) of the anodized surfaces was measured with a stylus profilometer.

The scratch resistance of the anodized surfaces was quantified with an Erichsen Hardness Test Pencil according to EN ISO 22557:2020, by ranging the applied load from 0 to 20 N.

Ball-on-disc wear tests were performed to assess the wear resistance of the survey surfaces before and after the anodizing process. The counter body was an alumina sphere that slid for 400 m at a speed of 0.1 m/s on the sample surface. At least four repetitions for each condition were performed at room temperature, under dry conditions, and with an applied load of 2 N. The wear rate was calculated as the ratio of the wear volume (V) to the product of the sliding distance (L) and the applied load (N), as shown in Eq. 1. V was calculated as the average area of the wear track integrated over the track perimeter.

$$\text{Wear rate} = \frac{\text{V}}{\text{L x N}}. \tag{1}$$

Results and Discussion

During the HPDC process, high cooling rates and intense shear stresses are developed inside the die cavity, resulting in the precipitations of less-branched and equiaxed α-Al dendrites surrounded by a fine Al-Si eutectic mixture (Fig. 1). Blocky-like $\alpha\text{-Al}_x(\text{Fe,Mn,Cr})_y\text{Si}_z$ intermetallics and $\theta\text{-Al}_2\text{Cu}$ compounds also precipitate in the interdendritic regions.

From the casting surface to the center of the component, a gradient in the colling rate occurs. The regions close to the die solidify faster, leading to the formation of a fine microstructure, while the solidification time in the inner regions of the casting increases and the microstructure results coarser with higher SDAS values. The milling process exposes an inner region of the casting compared to the grit-blasted one, resulting in a coarser microstructure. Indeed, the secondary dendrite arms spacings in the grit-blasted and milled regions are 2.8 ± 0.6 µm and 5.6 ± 0.7 µm, respectively. The grit-blasted substrate shows an ultra-fine fibrous eutectic structure surrounding smaller cells of the primary α-Al phase (Fig. 1a). In contrast, the milled substrate exhibits a coarser microstructure characterized by plate-like Si particles and larger α-Al cells and intermetallic compounds (Fig. 1b).

Gourlay et al. [3] demonstrated that the HPDC process leads to the formation of a surface segregation on Al-Si casting surface, consisting of a solute-enriched layer with a thickness of approximately 250 ± 60 µm [2]. This surface macrosegregation shows a higher area fraction of eutectic and intermetallic compounds, as also reported in other studies [7,8]. In the present work, the milling operation removed the surface segregation formed on the casting surface, as evidenced by the decrease in the eutectic area fraction from 76±2% in the grit-blasted region to 61±3% in the milled substrate.

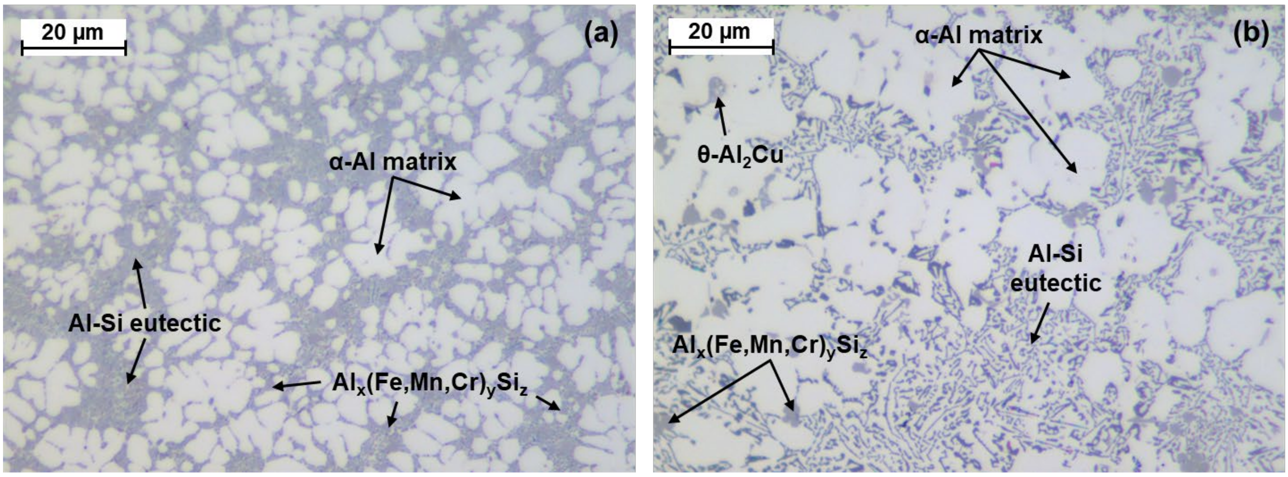

Fig. 1. Microstructure of the substrate in the **(a)** grit-blasted and **(b)** milled regions.

Variations in the microstructure of the substrate strongly affect the anodizing response. Indeed, the greater is the electrochemical heterogeneity of the substrate, the more difficult it is to form a thick high-performance oxide layer. During anodizing, the oxidation front preferentially grows in the less-resistant regions of the substrate, which correspond to the microstructural phases with the lowest standard potentials on the galvanostatic scale [4]. Si particles show higher potentials compared to the α-Al matrix, resulting in a slower oxidation rate during anodizing. When the oxidation front comes across a Si eutectic particle, it reacts and forms a thin layer of SiO_2, but then it tends to grow in the surrounding aluminum matrix, circumnavigating and incorporating the un-anodized Si phase inside the andic layer [5].

Fig. 2a shows the oxide layer forms on the grit-blasted substrate. It is a thin and well-bounded film with a homogeneous and continuous morphology. The average thickness is 4.6 ± 1.4 µm (Fig. 3), due to the presence of the surface segregation which limits the growth of the anodic layer. Indeed, the greater eutectic fraction hinders the advancement of the oxidation front and prevents the thickening of the oxide layer.

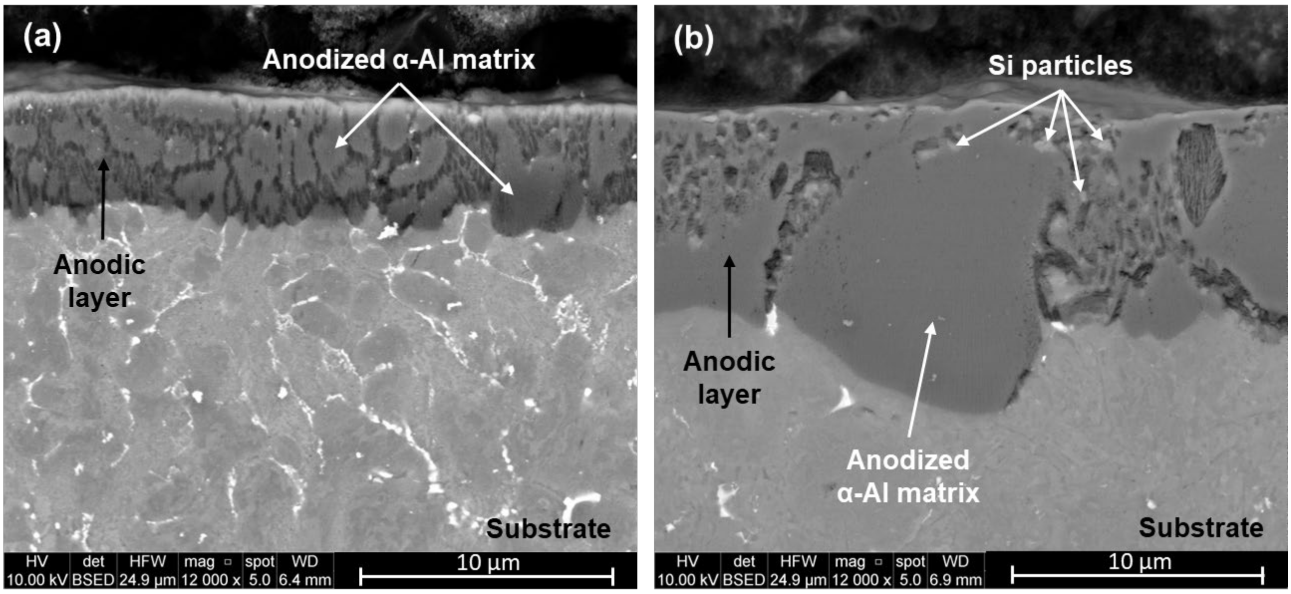

Fig. 2. FEG-SEM micrographs of the oxide layer grown on the **(a)** grit-blasted and **(b)** milled substrates.

The anodic layer formed on the milled surface is thicker and exhibits a scalloped oxide-metal interface, as shown in Fig. 2b. The morphology of the layer is not uniform and alternates between areas of limited thickness and areas where the oxide grew unrestrictedly. This is related to the distribution of α-Al and Si phases in the substrate prior to anodizing, which prevents the oxidation front from advancing evenly. Indeed, it grows freely within the α-Al dendrites, while it is hindered in the regions with local segregation of eutectic structure.

Compared to grit-blasted surface, the milled substrate has a higher amount of aluminum matrix in the form of larger, less-branched dendrites, resulting in the formation of a thicker anodic layer, with an average value of approximately 9 µm (Fig. 3). The higher standard deviation value (approximately 4 µm) is consistent with experimental observations and reflects the scalloped morphology of the anodic layer.

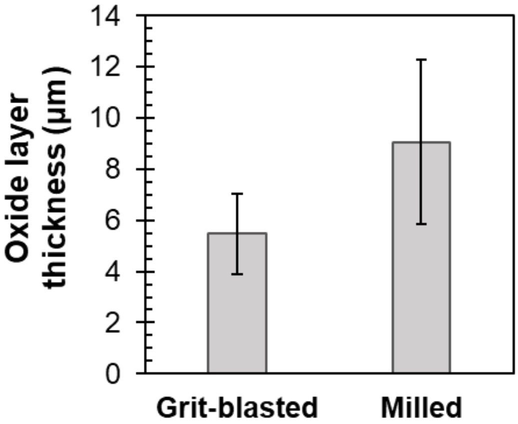

Fig. 3. Thickness of the anodic in the investigated substrates.

The limited thickness of the oxide layer formed on the grit-blasted substrate due to the presence of surface segregation negatively affects the surface mechanical properties, particularly the wear resistance. Fig. 4 shows the trend of the wear rate before and after anodizing. Both substrates exhibit a wear rate of approximately $28 \pm 4\cdot10^{-4}$ $mm^3/(Nm)$, which decreases after anodizing. Indeed, the electrochemical process leads to the formation of a hard surface layer of oxide, which decreases the wear rate, according to Archard's law (i.e. the wear volume is inversely proportional to the hardness of the material). With fixed tribology test conditions, a thicker anodic layer results in a lower wear of the softer aluminum substrate and therefore a lower wear rate. The wear rate values for the milled and grit-blasted anodized surfaces are 1.1 ± 0.9 $\cdot 10^{-4}$ $mm^3/(Nm)$ and 8.6 ± 0.9 $\cdot 10^{-4}$ $mm^3/(Nm)$, respectively. The milled surface shows greater wear resistance than the grit-blasted region due to the thicker anodic layer formed after the removal of the surface segregation.

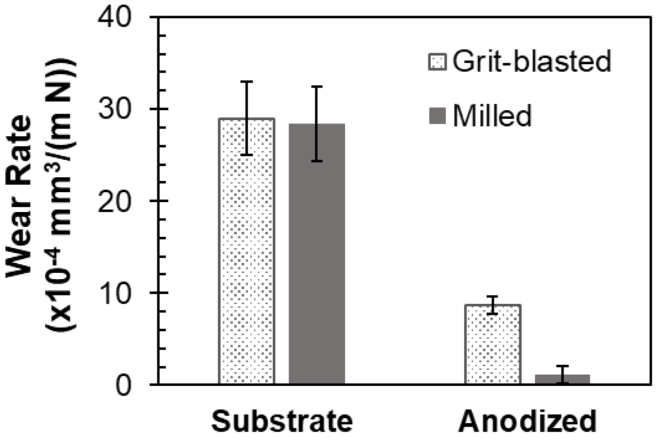

Fig. 4. Trend of the wear rate before and after anodizing in the investigated regions.

After anodizing, the grit-blasted surface shows lower scratch resistance than the milled region. The critical load, i.e. the load necessary to scratch the anodic layer and exhibit the substrate, is 5 ± 1 N for the grit-blasted surface and 19 ± 1 N for the milled region (Fig. 5).

The literature reports that smooth surfaces have higher scratch resistance than rougher ones. This is because the contact and residual stresses generated on a rough surface are significantly intensified, leading to increased plastic strain and reduced scratch resistance of the material [9]. In this study, the surface roughness of the milled anodized surface is 1.3 ± 0.1 μm, while for the grit-blasted region it values 5 ± 0.8 μm. As a result, the higher surface roughness of the grit-blasted surface reasonably leads to an increase in the local stresses during the scratch test, decreasing the critical load and the scratch resistance of the surface.

Fig. 5. Scratch resistance in the grit-blasted and milled surfaces after anodizing.

Conclusions

This research analyzes the effect of the surface segregation on the anodizing response of castings in AlSi11Cu2(Fe) diecast alloy. A grit-blasted industrial component was selected for the study, and some regions were milled to completely remove the surface segregation.

It was found that *the presence of the surface segregation creates an electrochemically heterogeneous surface, that negatively affects the growth of the anodic layer.* In fact, the higher fraction of Al-Si eutectic mixture hinders the propagation of the oxidation front during anodizing, leading to the formation of a thinner anodic layer. The *limited thickness of the anodic layer results in reduced wear resistance,* due to greater wear of the softer aluminum substrate. Moreover, the greater surface roughness of the grit-blasted surface compared to the milled one leads to lower scratch resistance. *After anodizing, scratch and wear resistance are maximized on the anodized milled surface due to its lower surface roughness and the removal of the surface segregation.*

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