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Citation for the original published paper (version of record):

Zhu, B., Seifeddine, S., Jarfors, A E., Leisner, P., Zanella, C. (2019)
A study of anodising behaviour of Al-Si components produced by rheocasting
Solid State Phenomena, 285: 39-44
<https://doi.org/10.4028/www.scientific.net/SSP.285.39>

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A Study of Anodising Behaviour of Al-Si Components Produced by Rheocasting

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Keywords: Rheocasting, anodising, oxide layer.

Abstract. This paper aims to investigate the anodising behaviour of Al-Si components produced by rheocasting, to understand the effect of the surface liquid segregation (SLS) on the anodising response. The material investigated was EN AC 42000 Al-alloy with an addition of 150 ppm Sr. The component was rheocast and conventionally liquid cast for benchmarking. The RheoMetal™ process was used to prepare slurry and subsequently cast using a vertical pressure die casting machine. Prior to anodising, mechanical grinding was used as pre-treatment method for selected samples as comparison with components in the as-cast state. Anodising was performed on the components using a constant controlled voltage at 25 V, in 1 M H₂SO₄, at room temperature. The duration of anodising was varied from 30 mins to 120 mins to examine the relationship between oxide layer thickness and the anodising time. The oxide layer was investigated and characterised. The results demonstrated that the presence of the SLS layer, which was enriched with alloying elements, had a significant influence on the anodising behaviour of the cast component. The oxide layer thickness of the components produced by rheocasting and fully liquid casting was measured and compared. The relations between the oxide layer thickness and anodising time, as well as the casting methods are presented and discussed in this paper.

Introduction

As an alternative to high pressure die casting (HPDC) method, semi-solid metal (SSM) processing such as rheocasting, is now widely applied to manufacture complex geometry components for automotive and electronics industries from Al-Si alloys. SSM processing offers the production of components with improved mechanical properties which is contributed by lower shrinkage and gas entrainment porosity defects[1].

Besides the complex geometry and strength, one of the vital criteria for outdoor applications is the corrosion resistance of Al-Si components. Anodising, which is an electrochemical process, is one of the most extensively used methods to improve the surface performance of aluminium alloys such as corrosion and wear resistance and aesthetic property. Previous studies have revealed that the anodised layer and its performance is strongly influenced by anodising process [2, 3], surface condition [4, 5], alloying elements [4, 6] and microstructure [7-10].

The surface liquid segregation (SLS) layer which is enriched in alloying elements is expected to be observed in the final component by SSM processing especially integrated with HPDC. Previous studies have evaluated the anodising behaviour of rheocast Al-Si components, but most of them were limited in the investigation without the consideration of the SLS layer. A limited number of research have reported that the presence of SLS layer has a significantly influence on the growth of oxide layer and its performance [7, 8]. Chauke et al. [7] reported that the rheocast 6082 and 6111 components with SLS layer

have a porous and thinner oxide layer than the components without SLS layer. Moreover, in another work by Chauke et al. [8], it was found that samples with SLS layer present more corrosion attack.

The present paper aims to investigate the anodising behaviour of Al-Si components produced by rheocasting and to understand the effect of the SLS layer on the anodising response. Moreover, the relationship between oxide layer thickness and anodising time, as well as the casting method, was examined in this study.

Experimental

Materials. In this study, one common Al-Si alloy, EN AC 42000 with addition of 150 ppm Sr, was used for benchmarking (Table 1). An addition of 150 ppm Sr aims to change the Si particle morphology from interconnected flake-like to disconnected fibrous. Previous studies revealed that the modification of Si particle morphology promotes the formation of the anodised layer with less defects, which also improves the corrosion resistance [9, 10].

Table 1: Chemical composition of EN AC 42000

Alloy	Si	Mg	Cu	Fe	Mn	Sr
Average value [wt-%]	7.00	0.38	0.074	0.40	0.26	0.015
Standard deviation	0.030	0.007	0.0010	0.003	0.002	0.0007

Casting. The RheoMetal™ process [11] was used to prepare the slurry with the stirring speed around 1000 rpm and melt temperature at 650 °C (around 35 °C of superheat). The solid fraction of primary α -Al particles in slurry was controlled by weight of enthalpy exchange material (EEM), and amount of EEM was set as 7 pct of the shot weight. The slurry was subsequently cast by 50 tons vertical pressure die casting (VPDC) machine to produce bars in 10 mm thick. The die temperature was controlled by a PolyTemp HTF 300 heater with temperature at 175 °C. Other machine parameters, plunger advance speed and intensification pressure, were kept constant, of 0.3 m/s and 160 bar, respectively. Moreover, to heat up the machine and maintain the thermal conditions in the shot sleeve and die cavity, first of 10 liquid shots were performed before fully liquid and semi-solid casting.

Anodising. Prior to anodising, the surfaces of the selected samples were ground mechanically by 500-grade SiC paper with the removal of 40-90 μ m and then ultrasonically cleaned in ethanol for 5 mins. The anodising was performed at a controlled voltage of 25 V in 1.0 M H₂SO₄ at room temperature. The duration of anodising was varied from 15 mins to 120 mins. After anodising, samples were ultrasonically rinsed in distilled water for 3 mins and oven dried at 50 °C for 30 mins. Colouring and sealing are not employed in this study.

Microstructural characterisation. Prior to microstructural characterisation, anodised samples were cut by a diamond saw with low speed and low load to avoid damaging the oxide layer. Microstructural features of substrates and anodised layer were investigated by optical microscopy (OM, Olympus GX71F) and scanning electron microscopy (SEM, JEOL JSM-7001F) equipped with energy dispersive X-ray spectroscopy (EDXS). Measurements of the oxide layer thickness in the cross-section was also performed by OM. 5 areas with the similar interval were selected in each cross-sectional sample, and at least 8 measurements with the constant interval were performed on each area. A Tescan focus-ion-beam (FIB)-SEM was used to cut and examine the anodised layer in the cross section without introducing extra defects.

Results and discussion

Microstructural characterisation of Al-Si substrates. The rheocast substrates (Fig. 1) show the presence of SLS layer which contains high amount of Al-Si eutectic regions and intermetallics both in locations near to the gate and near to the vent. Previous studies indicated that the presence of SLS layer is due to the skin effect [12] and migration of solid particles to the core of the component [13]. Fig. 2 presents an EDXS elemental mapping of an area inside the SLS layer. The mapping identifies the partly fibrous Si particles as well as relatively large Si plates, the relatively large Si plates could be due to the insufficient modification by 150 ppm Sr. Judging by the results of EDXS elemental mapping in Fig. 2, intermetallics identified in EN AC 42000 castings were mostly α -Al₁₅(FeMn)₃Si₂ phases and π -Al₈FeMg₃Si₆ phases due to the presence of 0.38 wt-% Mg and 0.26 wt-% Mn. Moreover, certain number of Mg₂Si particles were observed in the microstructure.

Figure 1: Micrographs of rheocast ENAC 42000 samples: (a) near to the gate; (b) near to the vent.

Figure 2: EDXS elemental mapping of area inside the SLS layer.

Oxide layer thickness. The anodising process generated an oxide layer on Al-Si substrates. Fig. 3 summaries the measured average thickness of the oxide layer of all samples with anodising time from 15 to 120 mins, and error bar in Fig. 3 represents the standard deviation. Moreover, the minimum value of oxide layer thickness measurements was marked in Fig.3. As shown in Fig. 3, the average thickness, as well as the minimum thickness, of all samples increases with an increase of anodising time. Moreover, all as-cast samples with anodising 15 to 45 mins show the similar value of average and minimum thickness. A comparison of the results with fully liquid casting and rheocasting in the as-cast condition shows that fully liquid cast samples obtains a thicker anodised layer than rheocast samples when anodising time is above 45 mins. Fig. 4a-b show the microstructure of oxide layer on as-cast samples by fully liquid casting and rheocasting methods, respectively. As shown in Fig. 4a-b, visually, the SLS layer on rheocast samples contains higher amount of Al-Si eutectic regions than in fully liquid cast samples. The eutectic

region slows down the oxide layer growth in Al-Si substrates[10], and therefore a thinner oxide layer was formed on as-cast surface in rheocast samples. Comparing the oxide layer thickness of ground and as-cast samples in the rheocasting condition, it was found that a more even and thinner oxide layer was obtained in the as-cast samples with the anodising time from 30 to 120 mins. Similar results were also reported by Chauke et al. [7] and Shin et al. [14]. Fig. 4b-c shows the microstructure of oxide layer of ground and as-cast samples (rheocasting, near to the gate) in the cross-section. In the ground sample, the SLS layer was partly removed by mechanical grinding process, and therefore relatively large primary α -Al phases enclosed by Al-Si eutectic regions were displayed on the surface. Due to the relatively high oxidation rate in the primary α -Al phases [10], a thicker oxide layer was formed in the primary α -Al phase, resulting in a non-uniform distribution but high mean value of the oxide layer thickness on ground samples. In SSM processing, the separation of solid and liquid parts in the gating system leads to the longitudinal macrosegregation [15], and therefore higher fraction of liquid part containing most of alloying elements will be injected to the near-to-vent part. As shown in Fig. 3, comparing results of near-to-gate and near-to-vent samples, it seems that the longitudinal macrosegregation does not have an evident influence on the formation of oxide layer. In rheocasting, SLS layer were existed on parts both near to the gate and near to the vent region, and the oxide layer grows with a similar rate due to the similar microstructure in the SLS layer.

Figure 3: Thickness of the oxide layer

Figure 4: Micrograph of the oxide layer (anodising 60 mins) on (a) fully liquid cast sample; (b) as-cast sample, rheocasting, near to gate; (c) ground sample, rheocasting, near to gate.

Microstructural characterisation of anodised layer. FIB-SEM was performed to characterise the anodised layer without introducing extra defects. The embedded Si particles and a limited number of partial residual Fe-intermetallic particles (Fe-IMPs) in the oxide layer were shown in Fig. 5. Being difficult to be dissolved, Si particles remains in the oxide layer after anodising. Cracks were evident above or near the relatively large

Si particles due to the localised intrinsic stress, which have also been highlighted with the explanation in the previous study [10]. The EDXS elemental mapping reveals a limited number of partial residual Fe-IMPs containing Mn in the oxide layer. Previous studies indicated that Fe-IMPs can be partly dissolved and anodised during anodising, and it depends on the chemical composition and density of Fe-IMPs [6, 16]. In the present study, the residual Fe-IMPs in the oxide layer represented as partial $\alpha\text{-Al}_{15}(\text{FeMn})_3\text{Si}_2$ phases, as detected residual Fe-IMPs contain certain amount of Mn; while no $\pi\text{-Al}_8\text{FeMg}_3\text{Si}_6$ phase in the oxide layer was observed. It seems that $\pi\text{-Al}_8\text{FeMg}_3\text{Si}_6$ phases are easier to be anodised and dissolved during anodising than $\alpha\text{-Al}_{15}(\text{FeMn})_3\text{Si}_2$ phases. As shown in Fig. 5, voids which are enclosed by residual Fe-IMPs and have the similar geometry of Fe-IMPs were evident. Judging from Fig. 5, it appears as though the observed voids could probably be a result of partly dissolved Fe-IMPs during anodising. Nevertheless, a more detailed characterisation regards to the behaviour of Fe-IMPs during anodising, is needed in further studies.

Figure 5: FIB-SEM micrographs and EDXS mapping of the oxide layer.

Conclusion

In this study, the relations between the oxide layer thickness and anodising time, as well as the casting methods in EN AC 42000 are presented. The oxide layer thickness increases with an increase of anodising time. The casting method also influences the oxide layer thickness, and a thicker oxide layer can be obtained on samples by fully liquid casting when anodising time is above 45 mins. Being different to most of previous studies, the as-cast surface with SLS layer was studied. It was found that the SLS layer has a significant effect of the formation of oxide layer. The presence of the SLS layer limits the growth of the oxide layer on rheocast samples, resulting in a thin oxide layer but with a more uniform distribution of thickness. For the requirement of thick anodised layer, a pre-treatment of removing the SLS layer is required before anodising.

In this study, residual Fe-IMPs, as well as voids which are enclosed by residual Fe-IMPs and have the similar geometry of Fe-IMPs, were observed in the oxide layer. And this could probably be a result of partly dissolved Fe-intermetallics during anodising. Nevertheless, a deeper understanding of the behaviour of Fe-IMPs during anodising, is needed for further studies.

Acknowledgements

This research was supported by the Knowledge Foundation (CompCast project no. 201000280, CompCast Plus project no. 20170066), who are gratefully acknowledged.

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