

Cathodic Protection -Based Solutions for Corrosion Prevention of “Green Aluminum” Alloys

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ABSTRACT

The manuscript investigates the use of cathodic protection -based strategies (e.g. sacrificial anodes) to prevent corrosion phenomena of two green (e.g. recycled) 43200 and 46400 Aluminum alloys. These materials are selected due to their high concentration of alloying elements (e.g. Si, Cu, Fe) that renders them as a representative example of the typical composition of secondary Aluminums. Voltammetry and zero resistance ammeter (ZRA) -based methods are used to: a) asses the protection capability of Zinc-based sacrificial anodes; and b) experimentally determine the amount of Zinc required to cathodically protect a certain surface area of each investigated material for a specific period of time. As a further level

of analysis, the manuscript investigates the protection capability of sacrificial anodes when coupled with an anodized secondary alloy. It is demonstrated that, in the case of highly alloyed Aluminums, cathodic protection can provide competing advantages with respect to conventional anodization treatments.

Key words: Aluminum alloys, sacrificial anodes, cathodic protection, anodization, zero resistance ammeter (ZRA).

INTRODUCTION

In the recent years, the reduction of the environmental footprint of industrial processes is gaining momentum, targeting the carbon neutrality.¹ This also involves Aluminum industry, in which the use of secondary (e.g. recycled) alloys is a possible solution in order to decrease the greenhouse gases (GHG) emissions.² Indeed, raw materials produced starting from secondary Aluminum show GHG emission values up to one order of magnitude lower with respect to their primary equivalents.³

When referring to corrosion resistance, Aluminums are usually unsuitable for most of the industrial applications and anodization is often required.^{4,5,6,7,8} Nevertheless, secondary alloys, which typically include a high concentration of Silicon, Copper, Magnesium and Iron, are particularly challenging to be anodized, especially using conventional processes.^{9,10} At a first approximation, this can be associated with the presence of intermetallic precipitates within the Al matrix which generate microgalvanic coupling events and associated inhomogeneous anodic layers.^{11,12,13} In this context, the use of cathodic-protection-based strategies (e.g. sacrificial anodes) appears as an interesting possibility in order to increase the corrosion resistance of green Al alloys.

It is demonstrated that the composition of each alloy can strongly modulate its corrosion resistance and, consequently, the sacrificial anode consumption rate.^{14,15} Indeed, a high concentration of noble elements such as Iron and/or Copper increases the quantity of intermetallic precipitates within the Aluminum matrix. The presence of these elements, which are typical of secondary alloys, could trigger several corrosive events and require a careful design of the selected sacrificial anode.¹⁶

As already mentioned, considering the complex corrosion mechanism of highly alloyed Al, it appears clear that the sacrificial anode life cannot be fully predicted by only considering literature data.¹⁴ Therefore, a lab-scale study seems fundamental in order to calculate actual anode consumption rates, when applying CP to each investigated secondary Aluminum structure.

In this scenario, the manuscript aims at providing a preliminary experimental evaluation regarding the applicability of Zn-based sacrificial anodes for protection of 43200 and 46400 alloys. Results will allow the design of cathodic-protection-based systems for Aluminum structures, targeting a low environmental impact.

EXPERIMENTAL PROCEDURE

Materials and Sample Preparation

Two secondary (e.g. recycled) Aluminum alloys with a surface area equals to 1dm² are investigated, namely a: 1) EN-AC-43200; and 2) EN-AC-46400, as per EN 1706:2020.¹⁷ Compositions of these alloys are summarized in Table 1.

Table 1: Composition of the investigated EN-AC-43200 and EN-AC-46400 as per EN 1706:2020.¹⁷

	Si / % _{wt}	Cu / % _{wt}	Mg / % _{wt}	Fe / % _{wt}	Mn / % _{wt}	Al / % _{wt}
EN-AC-43200	11	0.3	0.5	0.6	0.6	bal.
EN-AC-46400	10	1.3	0.7	0.7	0.6	bal.

Sacrificial anodes are obtained through cold pressing of a Z4 Zinc powder (as per EN 12496:2013).¹⁸ The final surface area of the electrodes is 0.5cm². It is important to mention that the selected powder has a concentration of Zn≥99.3%_{wt}. Such a high purity electrode was selected to avoid eventual side-reactions during the electrochemical experiments.

Before each experiment, all specimens (both Aluminums and Zinc) are: 1) grinded with SiC sandpapers up to 1000 grit; and 2) carefully degreased by sonicating in absolute ethanol for 10min. Along the manuscript, samples are labelled in agreement with the following nomenclature: a) EN-AC-43200 alloys = “43200”; b) EN-AC-46400 = “46400”; and c) Z4 Zn sacrificial anode = “Z4”.

Linear Sweep Voltammetry (LSV) and Tafel Evaluation

The corrosion resistance of each stand-alone material (43200, 46400 and Z4) is evaluated by performing linear sweep voltammetry measurements and Tafel fits.¹⁹ The analysis allows to calculate the values of corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel slopes of anodic and cathodic reactions (β_a and β_c). Polarization curves are obtained using a three electrodes configuration with the following setup: working electrode (WE): investigated sample, counter electrode (CE): graphite rod, reference electrode (RE): saturated calomel electrode (SCE). Electrodes are immersed in a 5%_{wt} NaCl aqueous solution at 30±0.1°C. Measurements are carried out when an open circuit potential (OCP) fluctuation ≤ 5mV/h is reached. The WE potential is scanned from -180mV vs. OCP to +300mV vs. OCP at a scan rate of 0.167mV/s.

Zero Resistance Ammetry (ZRA) Tests for Evaluation of Zinc Protection Capability

The performance of Z4 as sacrificial anode for secondary Aluminum alloys is tested by using a potentiostat/galvanostat as zero resistance ammeter (ZRA). This configuration allows to evaluate the: a) current flow between Zinc and Aluminum alloy; and b) potential of the couple.^{7,14,20,21,22} A three electrodes configuration is used in which the Aluminum alloy is used as working electrode (WE), the Zinc as counter electrode (CE) and a saturated calomel electrode (SCE) as reference electrode (RE). Following this, negative measured currents indicate oxidation phenomena at the CE (e.g. Zinc electrode) and reduction phenomena at the WE (e.g. Aluminum). On the other hand, positive currents demonstrate oxidation at the WE and reduction at the CE. A surface ratio equals to 200:1 between the WE and the CE is selected for all the experiments. Measurements are performed for 100h in a 5%_{wt} NaCl aqueous solution at 30±0.1°C without stirring. The adopted experimental setup in terms of concentration of the electrolyte, distances among electrodes and cell geometry allows to exclude the occurrence of voltage drop phenomena which are considered as negligible.

Anodization of the 46400 Specimen

A 46400 specimen is anodized using a lab-scale anodization setup. A vigorously stirred 200g/L H₂SO₄ solution at 17±0.5°C is used. The required current waveform is applied using a two electrodes configuration comprising the 46400 as working electrode (WE) and graphite rods as counter electrodes

(CEs). A standard set of anodization parameters is selected in order to obtain a maximum thickness of the oxide layer of about 20 μm .^{5,6,7} Finally, samples are cold-sealed using NiF_2 as described in the recent literature.^{5,6,7}

RESULTS

The applicability of sacrificial anodes for protection of green Aluminum alloys is studied using a multistep approach in agreement with the following points: 1) investigation of the corrosion resistance of stand-alone materials (both pristine Al alloys and Z4 anode); 2) calculation of the consumption rate of sacrificial anodes by using two methods; and 3) discussion of the efficacy of the anodization process with respect to the utilization of sacrificial anodes.

Corrosion Resistance of Stand-Alone Materials

Stand-alone corrodibility of materials (43200, 46400 and Z4) is evaluated by measuring their corrosion potentials (E_{corr}), corrosion currents (I_{corr}) and anodic/cathodic Tafel slopes (β_a , β_c).^{19,20,23} Measurements are performed as described in the experimental paragraph and results are reported in Table 2.

Table 2: Corrosion potentials (E_{corr}), corrosion currents (I_{corr}) and Tafel slopes (β_a , β_c) as obtained from LSV measurements.

	43200	46400	Z4
E_{corr} / mV vs. SCE	-735	-730	-1101
I_{corr} / $\mu\text{A}\cdot\text{cm}^{-2}$	0.5	0.8	20
β_a / mV	12	16	29
β_c / mV	330	217	410

43200 and 46400 show corrosion potentials equals to -735 and -730 mV vs. SCE, respectively. On the contrary, corrosion current values are significantly different, with 43200 showing a 30% I_{corr} reduction with respect to 46400. At a first approximation, these differences can be associated with their different composition and alloying elements content (See Table 1).^{4,20}

As expected, Z4 shows E_{corr} value in the order of -1100mV vs. SCE and a high I_{corr} (20 $\mu\text{A}\cdot\text{cm}^{-2}$). These values: a) suggest that Z4 can easily undergo oxidation with respect to both the Al alloys; and b) indicate an excellent tendency of Z4 to behave as a sacrificial anode to protect Aluminum.

Cathodic Protection of 43200 and 46400

The capability of Z4 to behave as sacrificial anode is investigated by measuring the current flow between Z4 and each investigated alloy. Measurements are performed using zero resistance ammeter -based methods as described in the experimental paragraph. Figure 1 reports the results in terms of: a) galvanic current flow between anode and alloy to be protected; b) potential of each couple (Z4-43200 and Z4-46400).^{7,14,20,21,22}