Journal of Applied Electrochemistry (2006) 36:481–486
DOI 10.1007/s10800-005-9102-y

Thermal effects associated with hard anodizing of cast aluminum alloys

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Received 18 November 2005; accepted in revised form 21 November 2005

Key words: aluminum, convection, electrode temperature, hard anodizing, oxide layer

Abstract

Hard anodizing of three different cast aluminum substrates (i.e. Al99.8 wt%, Al-10 wt% Si, Al-10 wt% Si-3.5 wt% Cu) was performed in 2.25 M H_2SO_4 electrolyte at 0 °C. The effects of substrate composition, current density and convection regime on electrode temperature evolution were investigated. Temperature transients followed the voltage transients during anodizing. At a current density of 6.0 A dm^{-2}, the electrode temperatures increased with alloying whereas at 30 A dm^{-2} the temperature reached a steady value around 65 °C and severe oxide dissolution effects were visible on the surface of the anodized specimens. Further, at this current density and under forced convection regime, highest temperature values were recorded for the Al99.8 wt% substrate and were accompanied by fluctuations. Forced convection significantly reduced the electrode temperatures during the non-uniform oxide growth for all three compositions and increased the oxide layer thickness.

1. Introduction

Anodizing is one of the most used processes for surface treatment of aluminum and its alloys covering applications from microelectronics to building, automotive and aerospace industries [1]. The process involves anodic oxidation of aluminum, made anode in an electrolytic cell, under a high electric field. Amorphous Al_2O_3 layers with a porous or non-porous morphology, up to few tens of microns thickness can be produced under specific electrochemical conditions. Their hardness, wear resistance, corrosion resistance and appearance enhance the performance of aluminum alloys.

Controlling the temperature during anodizing is essential because of the Joule heating effects. In general, in industrial practice, electrolyte temperature is monitored during the process and forced convection or electrolyte cooling is used to control it [2, 3]. However, the temperature at the alloy/oxide/electrolyte interfaces may be significantly larger relative to the bulk electrolyte temperature [4]. The use of high current densities and low electrolyte temperatures, specific to hard anodizing, favor the breakdown events and can eventually determine 'burning' (local dissolution of the layer and substrate).

Previous studies on electrode temperature rise during anodizing [4–8] have shown that, under galvanostatic conditions, temperature evolution generally follows the voltage transients. Depending on the current densities used the increase in temperature of the anodizing specimen can reach a few tens of degrees Celsius [4, 7]. The oxide layer grows at the temperature at the alloy/oxide interface and not at the bulk electrolyte temperature. A change in local temperature of 5 °C under hard anodizing conditions may cause a deterioration of the layer properties by at least 20% [3]. The application of forced convection, e.g. by air agitation, can significantly reduce the temperature difference and also contribute to the growth of thicker oxide layers [2]. Studies of the local electrode temperature evolution during anodizing [8] revealed that, under non-uniform convection, provided by a wall-jet electrode reactor, non-uniform heat transfer occurs that determines a distribution of the electrode temperature and oxide film thickness with higher values at regions of lower convective heat transfer. Further, it was reported [9] that anodizing under extreme conditions of current density (i.e. the stage preceding burning) may favor nanopore self-ordering.

Most of the above results were obtained for anodizing pure aluminum at room temperature. It is of interest to extend these investigations to other multiphase commercial aluminum alloys such as castings, and to the hard anodizing processes where temperature control is essential for layer properties. Cast aluminum alloys contain relatively large concentrations of alloying elements and are mainly hard anodized to improve their hardness and wear resistance [1]. Information on the thermal effects associated with anodizing of such alloys would help in understanding to what extent the alloy composition, the anodizing conditions and other factors are responsible for oxide layer breakdown and burning problems frequently encountered in practice with some of these alloys.

In the present study, hard anodizing of three different cast aluminum substrates (i.e. Al99.8 wt%, Al-10 wt% Si, Al-10 wt% Si-3.5 wt% Cu) was performed and the electrode temperature evolution was recorded. The effects of substrate composition, current density and convection regime on temperature transients are presented.

2. Experimental

2.1. *Aluminum substrates*

Aluminum substrates (i.e. Al99.8 wt%, Al-10 wt% Si and Al-10.5 wt% Si-3.2 wt% Cu) were prepared by permanent mold casting in metallic molds. The specimens for anodizing originated from disk shaped samples cut from cast bars and having a thickness of 7 mm and a diameter of 45 mm. From each disk four specimens were prepared (surface area 0.1 dm^2) and were ground to 600-grade SiC paper. Ultrasonic cleaning in isopropanol was performed prior to anodizing. The elemental and phase composition analyses, as well as the microstructural investigations of the alloys were previously performed and described [10].

2.2. *Anodizing*

Anodic oxidation was carried-out in a double-wall glass cell with a volume of 700 ml. The electrolyte was 2.25 M H_2SO_4 solution cooled to 0 °C by water circulation through the cell jacket. The water was cooled by circulation through an external Tamson thermostat connected to a cooler type Lauda UKT3000. The forced convection regime was provided by magnetic stirring of the electrolyte at a speed of 500 rotations per minute (rpm) using a magnetic stirrer type Ika. The experiments were conducted under galvanostatic conditions using two different current densities, i.e. 6.0 and 30 A dm^{-2}. The latter was selected as an extreme condition to possibly determine burning. The current was applied using a dc power supply type PBX43300-10 (Xantrex Tech.) and the experiments were designed using the WinCapp system (TCD Teknology). The voltage was acquired every 0.5 s using a TiePie transient recorder connected to the computer. An aluminum rod was used as counter electrode. Both electrodes were immersed in the electrolyte vertically, facing each other.

For the local electrode (anode) temperature measurements, a thermocouple type TT was inserted in the specimen, about 1 mm from its surface. The temperatures were acquired each 1.4 s using the LabVIEW program. In addition, a temperature probe was immersed in the electrolyte for bulk temperature measurements.

2.3. *Oxide layer thickness*

The thickness of the oxide layers was estimated by the Eddy current method using a coating thickness gauge type Elcometer 456, calibrated for the specific non-anodized substrates. Average and standard deviations of 20 measurements are reported.

3. Results and discussion

3.1. *Temperature transients*

The evolution of electrode temperature during anodic oxidation of the three different substrates at 6.0 and 30 A dm^{-2} is presented in Figure 1. Regardless of the specimen composition, forced convection and current density significantly affected the electrode temperature evolution.

At a current density of 6.0 A dm^{-2} (Figure 1a, b), the initial surge in temperature, corresponding to the stage of non-uniform oxide growth, decreased from 15 to 20 °C under free convection to 3–5 °C under forced convection. Further, at the end of the 10 min experiments, the electrode temperatures did not exceed 10 °C under forced convection whereas under free convection the final temperatures ranged between 17 and 25 °C depending on the substrate composition. By comparison, electrolyte temperature (dotted line in Figure 1a, b) increased from 0 to 3 °C. The *in-situ* temperatures of the binary and ternary compositions were larger than those recorded for Al. When the current was switched-off, the temperature of the anodizing specimens decreased rapidly towards the temperature of the electrolyte.

The second current density of 30 A dm^{-2} (Figure 1c, d), although not applied in industrial practice, was selected to create extreme conditions with respect to temperature and voltage, as a result of the high oxide growth rates imposed. These conditions can lead to oxide layer breakdown or burning. At 30 A dm^{-2}, the effects of forced convection remained significant during the non-uniform growth stage. However, the final temperatures under the two regimes were comparable, at least for the binary and ternary compositions, and seemed to stabilize around 65 °C. Further, at this current density, the effects of substrate composition do not follow the trend observed at 6.0 A dm^{-2} during the 10 minute oxidation. Under forced convection (Figure 1d), the highest temperature values were recorded for Al. In addition, fluctuations in temperature were observed under these conditions. The corresponding voltage transients (Figure 2) showed a similar trend. In general, the temperature transients followed the voltage transients for a certain substrate composition. When comparing free and forced convection regimes (Figure 3), the anodizing voltage increased under forced convection.

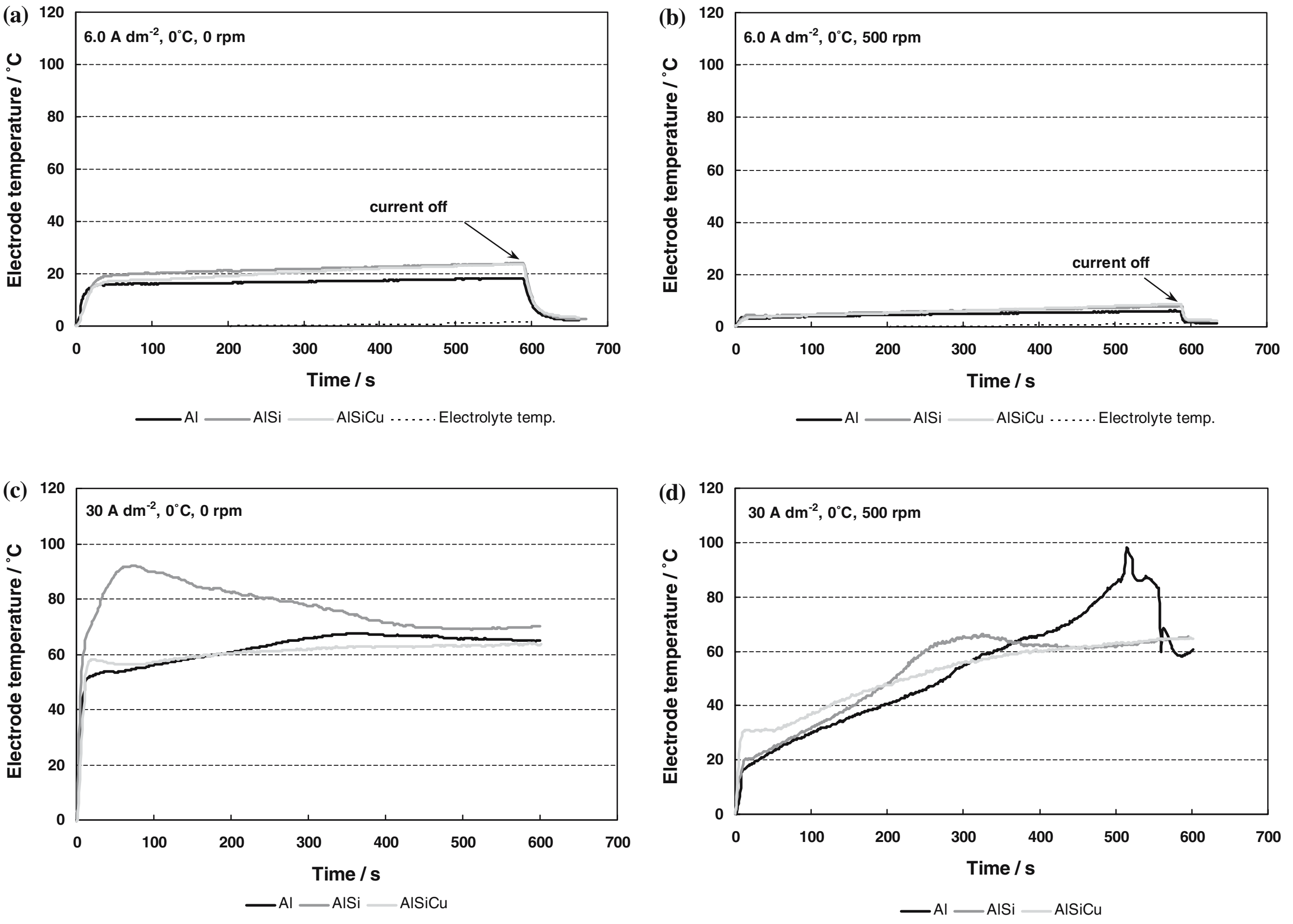

Fig. 1. Temperature transients during anodic oxidation of the aluminum substrates under galvanostatic conditions at two different current densities and two different convection regimes: (a) 6.0 A dm^{-2} and free convection; (b) 6.0 A dm^{-2} and forced convection; (c) 30 A dm^{-2} and free convection; (d) 30 A dm^{-2} and forced convection (2.25 M H_2SO_4, 0 °C, 10 min). Dotted lines indicate electrolyte temperature.

3.2. *Oxide layer thickness*

The values for the oxide layer thickness at a current density of 6.0 A dm^{-2}, estimated by the Eddy current method, are included in Figure 4. The trend indicates an increase in thickness under forced convection. The oxides produced at 30 A dm^{-2} under free convection revealed a patchy and non-uniform appearance due to enhanced dissolution, with areas having no visible oxide. Therefore, the thickness could not be accurately measured. Under these conditions, the electrode temperatures rapidly reached 60 °C during anodizing (Figure 1c), a temperature at which enhanced oxide dissolution seems to start.

The above results indicate that, at a current density of 6.0 A dm^{-2}, the three different substrates can undergo anodic oxidation for at least 10 min duration with no effects of severe oxide dissolution or burning. The temperature transients followed the voltage evolution for each composition and revealed higher values for AlSi and AlSiCu relative to Al. Forced convection ensured enhanced convective heat transfer at the oxide/electrolyte interface during anodizing thus decreasing the actual electrode temperature and therefore reducing the thermally enhanced oxide dissolution [2]. As a result, the oxide layer thickness increased. Nevertheless, for the substrates under investigation and the anodizing conditions used, the positive effects of forced convection on the detachment of O_2 gas bubbles from the oxide surface could also play a role in the increase in oxide layer thickness. The orientation of samples relative to the electrolyte flow in the bath to favor escape of the gas and heat transfer is very important under both natural and forced convection [11, 12]. Forced convection allows a uniform surface coverage by the oxide film during initial oxidation and ensures continuous access of cooled and fresh electrolyte at the electrode surface and inside the pores during the process.

Under extreme current density (i.e. 30 A dm^{-2}), the effects of substrate composition on temperature and voltage transients do not follow the trend at lower current density (i.e. 6.0 A dm^{-2}) although severe oxide layer dissolution was visible on all three specimens anodized at 30 A dm^{-2}. This change in the anodic behavior under extreme conditions suggests that, additional factors may influence the oxide growth/breakdown mechanism. Among them, heat transfer and stresses associated with the growth of oxide at high

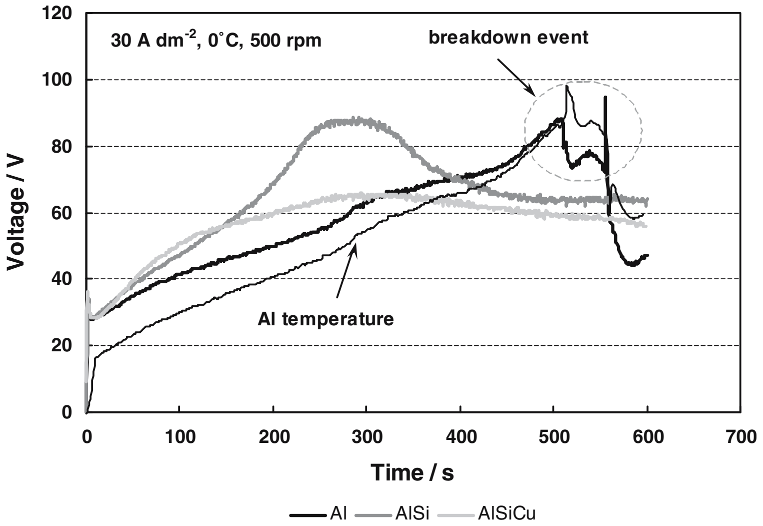

Fig. 2. Voltage transients during anodic oxidation at 30 A dm^{-2} under forced convection regime (2.25 M H_2SO_4, 0 °C, 10 min).

rates are important. With respect to heat transfer, a better thermal conductivity may determine a more efficient conductive heat transfer and also a more rapid heating-up of the specimen during anodizing under high current densities. This may be associated with a higher propensity for burning, especially in the case of thin specimens (all the other conditions being similar, including thickness of the specimens) [5]. Among the three substrates investigated in this study, Al has the highest thermal conductivity at 25 °C (230 W m^{-1} K^{-1}) as compared to AlSi (120 W m^{-1} K^{-1}) and AlSiCu (100 W m^{-1} K^{-1}) alloys [13]. This aspect was further investigated using the wall-jet electrode reactor [14]. With regard to stresses associated with anodic oxide layer growth and their effect on the layer breakdown mechanism, separate research is required for the specific compositions. A preliminary indication of the level of stress that can be generated in the three different anodized substrates was obtained by determining the residual stresses using X-ray diffraction. The analyses were performed on specimens previously anodized at 6.0 A dm^{-2} for 50 min under forced convection regime and the findings suggest higher absolute values for Al relative to AlSi and AlSiCu substrates (results not shown). Stresses during the growth of anodic oxide layers can be developed due to the lower coefficient of thermal expansion of the oxide relative to the substrate (usually tensile stresses) and due to the volume expansion associated with oxidation (usually compressive stresses) [15–19]. The latter were found to play a role in the self-ordering of nanopores in anodic alumina [20–22]. Stresses increase with layer thickness (i.e. with anodizing duration or current density) and temperature, and may change from compressive to tensile depending on the specific or local oxidation conditions [15]. The relatively defect-free oxide layer growing at high rates and the higher electrode temperatures that may develop during anodizing of Al (e.g. at 30 A dm^{-2}) can contribute to the development of increased stresses in the oxide layer.

A high level of stresses in the layer can lead to cracking [15, 16]. As a result, the substrate may be exposed to the electrolyte under high current density. The bare metal is rapidly anodized and the process continues. Under these conditions, sharp fluctuations in voltage and temperature may occur, as was recorded for Al in this study. Due to the local surge in temperature at these locations, the specimen is heated-up rapidly (especially in the case of Al) and, under extremely high temperatures (e.g. >100 °C), intense stresses are induced in the substrate that may lead to plastic deformation beneath the cracking oxide [16]. This is more likely to occur in the case of the relatively soft Al substrate and the effect can become visible (e.g. bending of the anodized specimen) when a thin specimen is oxidized [14]. In the case of the other two compositions, spalling of the oxide at regions with defects or inclusions may be favored under conditions of severe dissolution. The most sensitive regions should correspond to the presence of second-phase material in the alloys, in this case Si particles from the eutectic structures (that become occluded in the oxide) and $CuAl_2$ particles. Their presence may generate cracks and voids at the substrate/oxide or particle/oxide interface during anodizing [10] making the layer locally discontinuous and, therefore, probably more prone to spalling. Further research is required to understand the anodizing response and thermal effects under extreme oxidation conditions for different aluminum alloys. The research should include the accumulation of stresses in the growing oxides and the possible effects of morphological changes of the oxides in the case of highly alloyed substrates (e.g. barrier layer thickness, type and amount of defects) on heat transfer during the process.

When comparing the effects of bulk electrolyte temperature (i.e. 25 and 0 °C) on the anodizing voltage

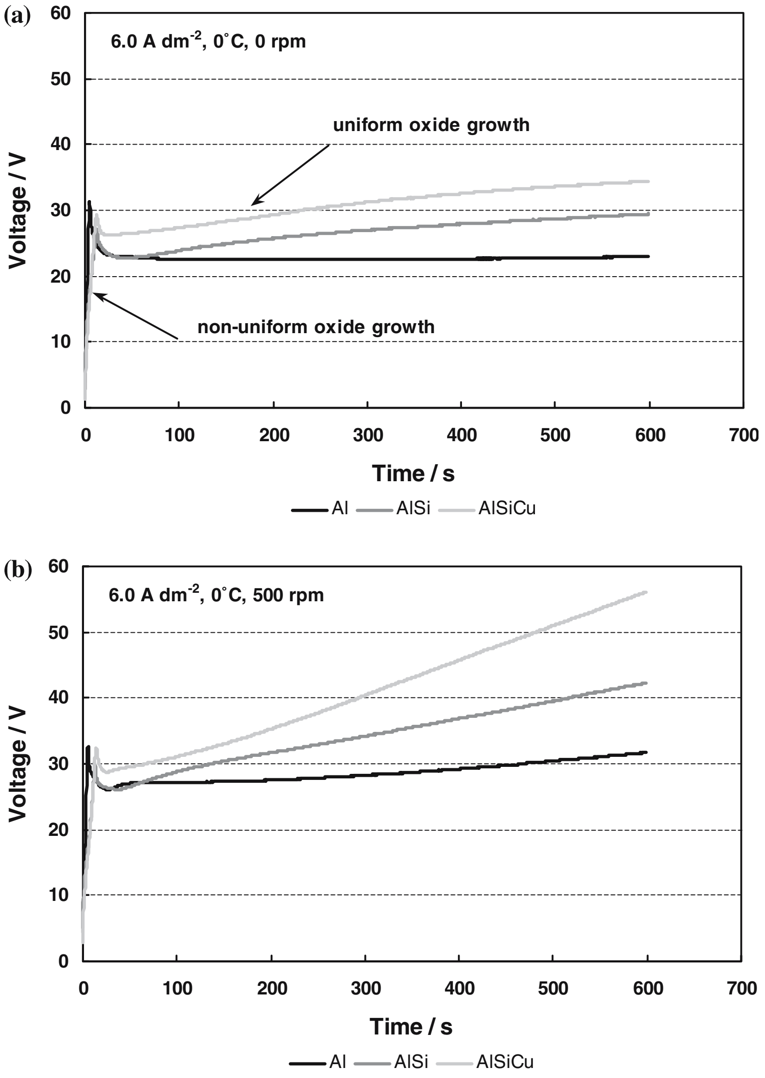

Fig. 3. Effect of forced convection on the voltage transients during anodic oxidation at 6.0 A dm^{-2} (2.25 M H_2SO_4, 0 °C, 10 min).

and electrode temperature at a current density of 6.0 A dm^{-2} (Table 1), it can be observed that, under otherwise similar conditions, the largest increase in electrode temperature and voltage is recorded when anodizing at 0 °C probably due to the larger temperature gradient at the substrate/oxide interface and lower

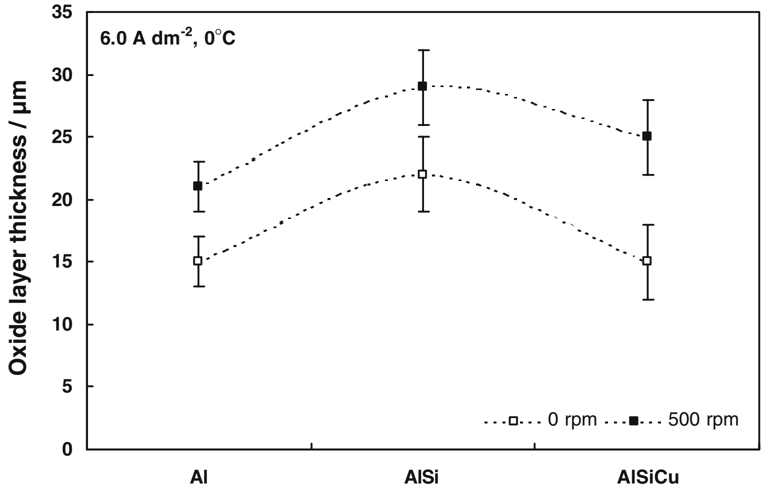

Fig. 4. Effect of forced convection on oxide layer thickness (6.0 A dm^{-2}, 2.25 M H_2SO_4, 0 °C, 10 min).

Table 1. The effects of bulk electrolyte temperature on the anodizing voltage and electrode temperature (6.0 A dm^{-2} for 10 min; 0 rpm = free convection; 500 rpm = forced convection; ΔV = surge in voltage during non-uniform oxide growth, V; ΔT = surge in electrode temperature during non-uniform oxide growth, °C)

Bulk electrolyte temperature	25 °C		0 °C	
Convection regime	0 rpm	500 rpm	0 rpm	500 rpm
ΔV/V	18–19	20–25	28–32	32–35
ΔT/°C	10–12	2–3	15–20	3–5
V_{final}/V				
Al	17	21	23	32
AlSi	22	28	29	42
AlSiCu	23	32	34	56
$T_{final}/\Delta T_{final}$/°C				
Al	39/14	28/3	18/18	5/5
AlSi	40/15	29/4	24/24	8/8
AlSiCu	42/17	30/5	24/24	9/9

electrolyte conductivity, respectively. Therefore, efficient heat transfer is very important during hard anodizing, especially when highly alloyed substrates are oxidized.

The extreme anodizing conditions (i.e. high temperatures close to the substrate/oxide interface) were generated in this study by the use of large current densities. However, in practice, factors such as insufficient cooling and convection of the electrolyte, non-uniform convection, increased bath load, unsuitable racking of the parts, microstructural heterogeneities of the alloys, complex geometry of the parts may lead to (local) critical temperatures (e.g. 65 °C) when enhanced oxide dissolution is promoted.

4. Conclusions

The electrode temperature evolution during hard anodizing of three aluminum substrates (i.e. Al, AlSi, and AlSiCu) under two different current densities and convection regimes was examined in this study. The results indicated that:

- The electrode temperature increased with current density and followed the voltage evolution.
- *In-situ* temperatures increased with alloying at 6.0 A dm^{-2} but at 30 A dm^{-2} under the free convection regime, a steady temperature around 65 °C was reached by all three compositions. At this temperature, severe dissolution effects were visible on the surface of the anodized specimens. Further, at 30 A dm^{-2} under forced convection, Al revealed the highest temperatures accompanied by fluctuations suggesting oxide layer breakdown.
- Forced convection produced a decrease in the electrode temperature, especially during non-uniform oxide growth, and an increase in the oxide layer thickness and anodizing voltage occurred regardless of substrate composition.

Acknowledgement

Financial support from Senter IOP-OT, The Netherlands, is acknowledged.

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