

Monitoring of Electrode Temperature in Exothermic Electrochemical Process

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Abstract – In this paper the features of temperature control of aluminum electrode during the anodization are discussed. Temperature monitoring in this exothermic process is a necessary condition for obtaining a high ordered nanoporous structure. A new electrochemical cell with a Peltier device working in cooling or heating mode was proposed. Time dependences of the electrolyte and Peltier element temperatures without and during anodizing process were presented. The results demonstrated that the cell construction allows precise control of the electrode temperature.

Keywords – anodization, monitoring, Peltier element, temperature control.

I. INTRODUCTION

In modern electronics, microelectronics, MEMS and so on, layers of anodic aluminum oxide (AAO) are widely applied. They are used both as functional elements and as structural protective layers in capacitors, sensors, micro-modules and others. In nanotechnology, the anodic aluminum oxide is also used as a template for the fabrication of one dimensional structures as nanotubes, nanowires and nanorods because of the possibility to obtain a nanoporous structure with well controlled self-ordered nanopores at defined conditions [1]. The quality of the obtained oxide depends on the purity of the aluminum substrate, the working temperature, the nature of electrolyte, and the current density.

The process for fabrication of AAO layer includes anodization in various acid electrolytes. On the one hand, this electrochemical process is highly exothermic and is associated with the emission of a significant amount of heat. On the other hand, it is necessary to maintain a fixed temperature to produce a highly ordered porous alumina. Usually, anodization at low temperatures (around and below 15 °C) is recommended in order to improve homogeneity of the nanoporous structure. Local elevation of the temperature results in acceleration of chemical dissolution and breakdown of the oxide layer [1, 2]. Different methods to investigate the effect of temperature on the electrochemical process are proposed. Most often, control of the electrolyte temperature is used. Recently, a few electrode temperature control studies have been reported [2, 3]. Various approaches for controlled temperature change of the electrode are proposed. Aerts et al. [2, 3] use a special electrode holder including a thermo-electronic component

based on the Peltier effect for controlled temperature decreasing and increasing. In this regard, Chowdhury et al. propose a new constructive solution for measuring the temperature of the aluminum substrate [4]. The authors put a thin palladium layer on the back side of the aluminum foil with a 12 or 50 um alumina layer. In this case the change in substrate temperature is achieved by different applied voltage value. However, this experiment does not allow control of the aluminum substrate temperature.

This work presents results from the electrode temperature monitoring during the anodizing process by a device, designed especially for this experiment. Thus it becomes possible to determine and control the temperature distribution during the anodization in different parts of the electrochemical cell, including the electrode.

II. EXPERIMENTAL PART

The anodizing of the aluminum foil was carried out in an electrochemical cell in which the anode was situated as a bottom of the cell. The dried aluminum sample was placed on the brass plate 3 mm thick with a temperature probe in the core. The underside of the brass plate was coated by a thermally conductive paste and placed on the Peltier element. On the top side of aluminum sample was placed a silicone washer seal and the electrochemical cell was being assembled by four studs and nuts. The working anode area was 2.54 cm² and the electrolyte volume was 250 mL. The anodization process was carried out in 0.4 mol/L oxalic acid at 40 V and an ambient temperature of the electrolyte (about 25 degrees). A glass heat-exchanger was used to maintain the temperature of the electrolyte when required.

The Peltier element used in the experiments (TEC1-1270TEC1-1270TEC1-1270) had a heat pumping capacity over 20 W. It was used for both cooling and heating of the electrode. The pumped heat by the Peltier element was controlled by the magnitude and direction of the supply current. Therefore, in the work the dynamic characteristics of the temperature change are presented at the corresponding test current values.

III. RESULTS AND DISCUSSION

A. Heat release during of anodization process

During the anodization a nonlinear heat was released from the electrode surface. Heat was being generated at the

aluminum/alumina interface and was transmitted to the layers with different thermal conductivity. It is well known that aluminum is a very good heat conductor with thermal conductivity of 237 W/m.K, while the anodic oxide one is characterized by low thermal conductivity of 1.32 W/m.K [5] which is close to that of water (0.6 W/m.K).

From the oxide side, the removal of the heat from the anode reaction site takes place through the AAO and the circulation of the electrolyte in the pores. The latter is a result of natural convection due to the large difference between the electrolyte temperature and the aluminum interface.

In the conventional construction of the electrochemical cell, the sample is completely immersed in the electrolyte and all the heat is transmitted to the electrolyte. The design of our cell allows separation of the heat flows. Part of the heat was passed to the electrolyte through a small contact area of 2.54 cm². The other part of the heat was absorbed by the aluminum substrate and was dissipated to the surrounding area. Thus, the removal of heat from the aluminum should be facilitated in order to prevent burning. In some specific cases, such as the theoretical study of the temperature effect on the kinetics and morphology of the anode layers, additional heating of the anode could be necessary. Thus, it can be more easily and quickly realized on the aluminum than by the electrolyte temperature changes.

In Fig. 1 the temperature increase of 250 mL electrolyte during anodization of 2.54 cm² area at 40 V is presented. In this case a forced cooling or heating was not applied and therefore the temperature change was completely natural. In the potentiostatic mode, the current density was strongly dependent on the temperature. As a result of the temperature increase, there was a slight acceleration of the electrochemical reaction (current density). These changes were relatively weak (about a few milliamps). However, the high ratio (about 100) electrolyte volume:surface of the anode must be taken into account. At a ratio of about 100, the electrolyte temperature increased with 3 °C during the 90 min anodization. However, the temperature increase was less than expected, probably due to the presence of aluminum substrate that was outside the electrolyte and takes the heat out of the electrochemical cell.

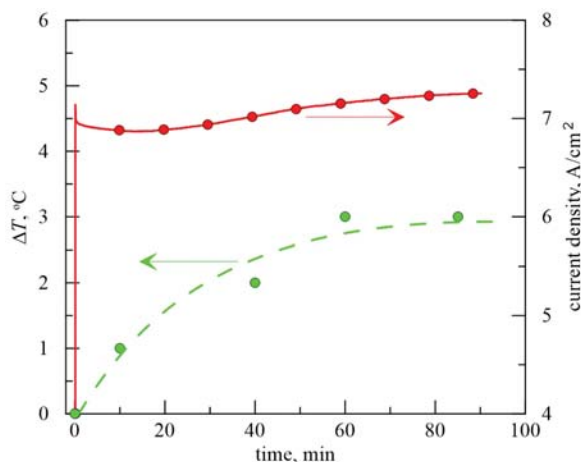


Fig. 1. Change of current density (solid line) and the electrolyte temperature (dotted line) during anodization process at 40 V in 0.4 mol/L oxalic acid.

Moreover, in an anodizing process the thickness of the oxide increases, resulting in a greater length of the electrolyte convection channel and increased thermal resistance of the oxide layer. Furthermore, the thickness of the aluminum substrate decreases and the thermal resistance in this direction decreases too.

B. Scheme of electrochemical cell with Peltier device for monitoring of the electrode temperature

For study and management of the anodization process, a new electrochemical cell construction containing two parts was developed (Fig. 2). The first part was the electrolyte cell with a heat exchanger and electrolyte temperature control (1+5). The aluminum sample (6) was located on the underside. The second part corresponded to heat/cooling module. The aluminum anode was pressed by a contact block (7) including an electrical connector to the positive pole of an external current source and a temperature probe. It was made of brass and we assumed that its temperature was the same as that of the aluminum electrode. The Peltier element (8) served to regulate the temperature of the aluminum substrate. The top plate of the element was called working side. A second brass plate was placed between the back side of the Peltier element and the aluminum radiator (9) completed with temperature probe and fan. That last one was provided to remove or supply heat to the Peltier element.

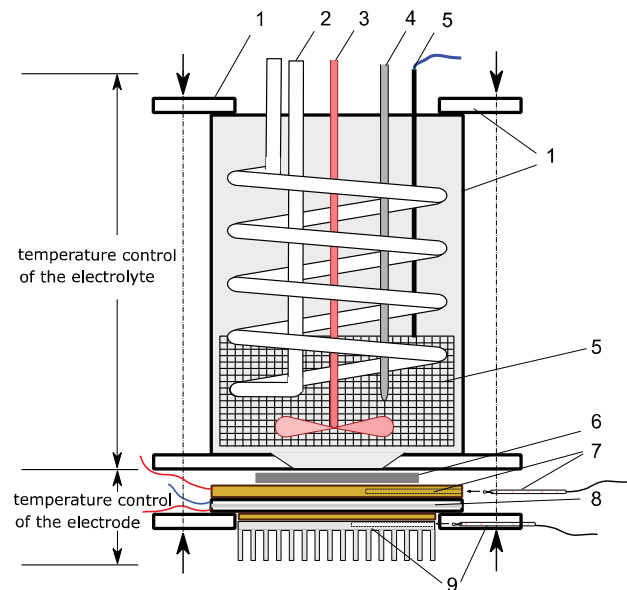


Fig. 2. Schematic representation of the electrode temperature control system.

1 - glass cell with Teflon holders; 2 - glass serpentine heat exchanger; 3 - stirrer; 4 - temperature probe I; 5 - Pt counter electrode; 6 - aluminum foil; 7 - brass plate with connector to (+) pole and temperature probe II; 8 - Peltier module; 9 - radiator with temperature probe III.

C. Dependence of the temperature of Peltier element on the supply current without anodizing process

To ensure normal operation of the Peltier device, it was necessary to provide a temperature difference between the two plates of element of less than 15 °C. Therefore, the

investigation of Peltier device behavior was started by measuring the temperature on the two sides of the element. In absence of anodization process, it was assumed that the temperature on the top of the element was equal to that of the electrolyte. Fig. 3 shows the change of temperature of the back side of Peltier element at current supply of 0.5, 0.75 and 1.0 A. In cooling mode of the working plate, the temperature of the back side increases by a logarithmic law. After some time, the temperature remains constant as indication of reaching a heat balance between the heat entering the plate and the cooling by the air. It seems that the stationary values do not increase linearly with increasing current. For example, when the current was increased from 0.5 to 0.75 A, the stationary temperature rises only about 6 degrees. At the same current augmentation of 0.25 A, the rise in temperature was twice greater in the range from 0.75 to 1.0 A.

For 12 minutes at 1.0 A, the back side temperature increased by about 28 °C, whereas the electrolyte one decreased by only 3 (Fig. 3, dotted line). At lower currents of Peltier element, lowering of the electrolyte temperature was below 2 degrees for the entire operating period. This result demonstrated that the main heat flux in operation of the Peltier element in contact with the electrolyte was directed to the radiator side.

In heating mode, the Peltier device was more effective. The stationary temperature values were reached with smaller deviations in the negative direction.

D. Time dependences of the electrolyte and Peltier element temperature during anodizing process

Fig. 4 shows the temperatures of the electrolyte, the anode and the radiator sides of Peltier element when switching on the element in cooling mode with current 2 A. In the same figure the time dependence of the current density of anodization process during anodization at 40 V in oxalic acid electrolyte is also presented. During measurement, the radiator side of the Peltier device was blown with air using a fan.

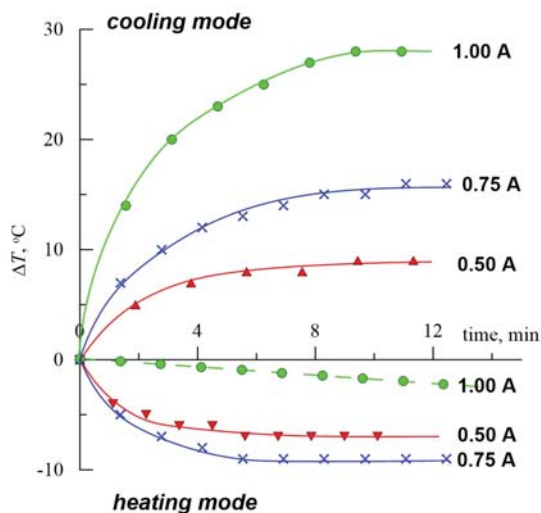


Fig. 3. The change of temperature of radiator side of Peltier element in cooling and heating modes (solid lines) and of 250 mL electrolyte at 1.00 A of Peltier element in cooling mode (dotted line)

After an initial sharp decreasing, the electrode temperature (equal to that of working side) slightly increases to equalize the heat flows between the two sides of the Peltier element. The stationary state occurred at 23 °C of electrolyte temperature and 45 °C of the radiator at 3.6 mA/cm² of anodization current density.

To determine the accuracy of the temperature control, a series of experiments were performed while maintaining the electrolyte temperature at 20 °C and the electrode temperature from 10 to 70 °C. It was found that after reaching and stabilizing the operating temperature of the electrode, the temperature control allows maintaining to an accuracy of 0.1 °C and 0.25 °C at 20 °C and 40 °C electrode/electrolyte temperature difference respectively.

Temperature regulation is related to knowing the dynamics of heat exchange in a working process. Fig. 5 shows a linear increase of the anode temperature (working side of Peltier) and of the current density of anodization process in cooling mode with 1.5 A and without using a fan. Obviously, transfer of heat from the radiator side to the electrode was registered. The observed effect was a result of the absence of forced heat removal from the radiator and is an indicator of its heat output.

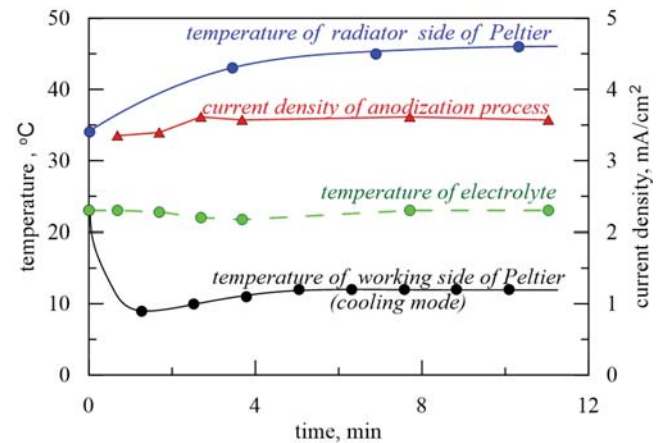


Fig. 4. Time dependences of current density and of the temperatures of electrolyte (dotted line) as well as of two side of Peltier element at 2A during anodization process at 40V and forced heat removal.

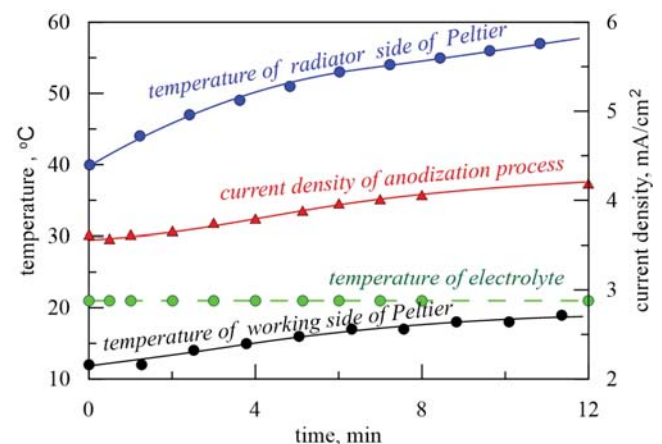


Fig. 5. Time dependences of current density and of the temperatures of electrolyte (dotted line) as well as of two side of Peltier element at 1.5A without forced heat removal, anodization process at 40 V.

Fig. 6 shows the internal heat exchange between the working (electrode) and back sides of Peltier element after its switch-off. A redistribution of heat was observed, which equalizes the temperatures of the electrode and the electrolyte.

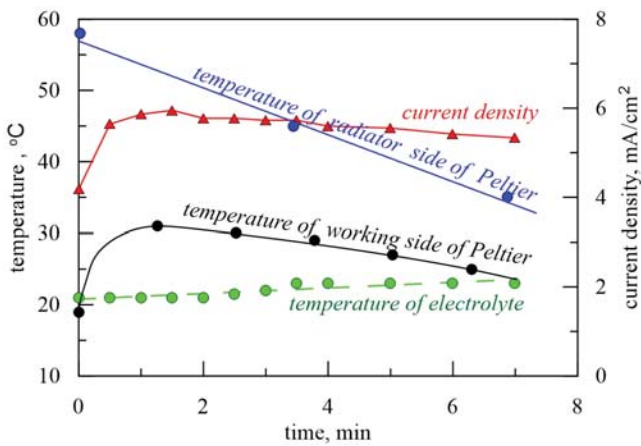


Fig. 6. Time dependences of current density and of the temperatures of electrolyte (dotted line) as well as of two side of Peltier element during anodization process after switch off of Peltier.

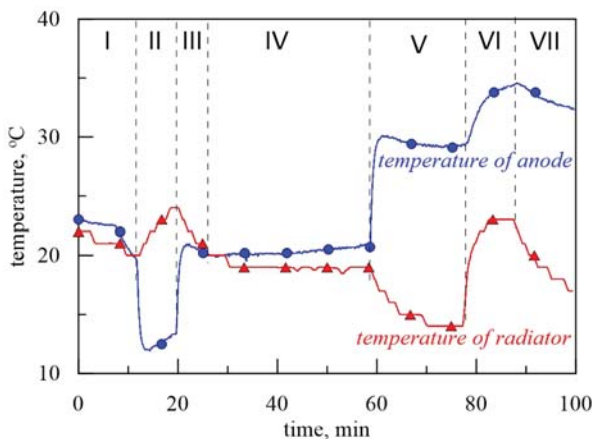


Fig. 7. Control process modes:

- I – indirect cooling of the anode and the radiator side by lowering the electrolyte temperature;
- II – switching on the Peltier in cooling mode;
- III – switching off the Peltier element;
- IV – start of anodization at 40 V without of cooling;
- V – switching on the Peltier at 0.6 A in heating mode;
- VI – switching on the fan of radiator;
- VII – switching off the fan of radiator.

In the first minute after the Peltier element switch-off, part of the heat accumulated in the radiator plate passed into the electrode side resulting in augmentation of the anode and electrolyte temperatures. The current density curve correlates with that of the electrode (working side of element). These results indicate an effective control of the anode temperature by the temperature of the working side of Peltier element in cooling mode.

Fig. 7 shows the complex behavior of the system under different control process modes. From the figure all the time parameters of the process can be deduced, which is intended to be described in detail in a subsequent work.

IV. CONCLUSION

The Peltier device for monitoring and regulation of electrode temperature during an anodization process was proposed. The main heat flows in the exothermic electrochemical reaction were discussed. The results demonstrated that the Peltier element disposed adjacent to the aluminum foil allows precise control of the electrode temperature.

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