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The influence of pre-anodization voltage on pore arrangement in anodic alumina produced by hard anodization

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ABSTRACT

The influence of various pre-anodization voltage (V_s) on pore self-ordering process in anodic alumina (AAO) produced by hard anodization (HA) was investigated. It was demonstrated that the V_s has substantial effect on the pore arrangement in the AAO. Moreover, the results revealed that the pre-anodization under the mild condition is not necessary to form a long-range ordered AAO. When the HA process starts at relatively high V_s, only a small change of voltage and current during the second anodization stage is sufficient to rearrange the pores into the close-packed hexagonal structure. Excellent pore ordering was achieved when the samples were pre-anodized at 120 V.

1. Introduction

Long-range ordered anodic aluminum oxide (AAO) can be fabricated by mild anodization (MA) in various aqueous electrolyte solutions or by hard anodization (HA) [1–3]. The HA is a high current process that usually consists of three stages [4,5]. In the first stage the sample is pre-anodized under MA voltage in order to form a protective oxide layer. This layer prevents local catastrophic flow of high electrical current and the resulting burning phenomena. In the second stage the voltage is gradually raised to a target value (V_t), and finally, at the third stage, the sample is anodized under stable V_t.

It was observed before that the change of voltage during anodization has a strong impact on final pore ordering in AAO [6–8]. Upon reducing the anodizing voltage a branching of original pores occurs. The ordered pore arrangement can be obtained only when the voltage is reduced by factors of $\sqrt{3}$, $\sqrt{4}$ and their common multiples. Furthermore, branched channels should maintain the original area of the template, their geometric arrangement should be hexagonal close-packed, and the barrier layer has to be sufficiently thin to allow for smooth migration of anions.

When the voltage is raised during the transition from MA to HA regime also an intensive pore rearrangement takes place [9]. This process is even more complicated than the above mentioned branching phenomena in terms that it additionally involves the change from low to high current anodization conditions. Santos et al. investigated the transition process upon a continuous voltage change from 40 V to different V_t at various voltage sweep rate [10]. However, no investigation on the impact of the pre-anodization voltage (V_s) on the geometrical parameters and pore arrangement in AAO was done before.

In this letter the effect of various V_s on the pore arrangement in AAO produced by HA is analyzed. The results demonstrate that the starting voltage has tremendous effect on pore ordering occurring during HA process. Moreover, it is not necessary to pre-anodize the samples under MA condition in order to obtain regular array of pores. The results shed a new light on the pore ordering phenomena occurring during hard anodization.

2. Experimental

Electropolished high purity Al foil (99.9995% Al, Puratronic, Alfa Aesar) was cut into rectangular specimens of size 2 cm × 1 cm. The Al samples were insulated at the back and the edges with acid resistant paint and served as the anode. A Pt grid was used as the cathode and the distance between both electrodes was kept constant (ca. 5 cm). The samples were anodized in 0.3 M oxalic acid solution at 0 °C according to the procedure presented in details in ref. [11]. The starting/pre-anodization voltage (V_s) was changing from 40 to 120 V, and the target voltage (V_t) was chosen to be 120–160 V. The samples were first anodized at V_s for 10 min. Then the voltage was raised to a given V_t and the samples were anodized for

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1 h. Various combination of V_s and V_t was applied and the respective samples were denoted as $S_{Vs\text{-}Vt}$. Morphology of PAAs was studied using field-emission scanning electron microscope FE-SEM (FEI, Quanta). The SEM images were taken from the bottom part of the produced AAO after Al removal and subsequent etching in 5 wt% H_3PO_4 solution. The interpore distance (D_c) was calculated based on the Fast Fourier transforms (FFTs) analysis [12].

3. Results and discussion

In Fig. 1 the current density (i_a) and voltage (V) vs. time transients are presented. The samples were divided into two groups. In the first group the pre-anodization voltage (V_s) was changed between 40 and 100 V and the target voltage was kept stable (V_t=120 V) (Fig. 1a and b). In the second group the V_s voltage was always set at 120 V and the V_t was ranging between 130 and 160 V (Fig. 1a and b). In both groups the curve for the sample anodized directly at 120 V (S_{120}) is also shown as a reference. In the first group the higher the V_s, the voltage ramp initiates from the larger i_a values. At the same time, the higher the i_a from which the voltage is raised to V_t the lower the resulted i_a reached at the respective V_t. In the group two the voltage increase begins always from $i_a \sim 30$ mA/cm^2. For the samples $S_{120–150}$ and $S_{120–160}$ the voltage ramp was slightly slowed down in order to avoid the undesirable heat evolution while approaching the higher V_t [9]. When the voltage is increasing only a small rise of i_a can be observed for all samples except the $S_{120–160}$ sample, for which a more pronounced current boost is detected when voltage was close to the V_t =160 V. Generally, the higher the i_a at the beginning of the voltage ramp the lower the current increase with the increasing voltage and the lower the i_a reached at a given V_t. This is due to the thicker barrier layer which is formed under the higher anodization voltage/higher current [4]. The migration of anions across the thicker barrier layer is slower resulting in smaller current flow.

In Fig. 2 SEM images of the bottom part of the analyzed AAO membranes along with their FFT images are shown. It is evident that the V_s has enormous effect on the AAO quality. In the first group, the pore ordering is maintained up to V_s=60 V. For higher V_s values the pore arrangement strongly deteriorates. In the sample S_{120} the hexagonal pore ordering is basically lost. In reference to the i_a/V curves it can be observed that as long as the initial current operating at the V_s is low, at the end of the HA process a very good pore ordering is obtained. For the samples $S_{80–120}$, $S_{100–120}$, where the initial currents from which the voltage ramp begins is relatively high, the pore ordering gets much worse. Direct HA at 120 V (the sample S_{120}) results in a very poor pore ordering due to extremely high and inhomogeneous current flow at the beginning of the process. In the second group where the V_s is set at relatively high value the pore ordering gets recovered. Already for the $S_{120–130}$ sample there are quite large domains with the close-packed hexagonal pore structure. For the samples $S_{120–140}$, $S_{120–150}$, $S_{120–160}$ the AAO is characterized by an excellent hexagonal pore arrangement. This is a completely new observation which reveals that it is not necessary to start the HA process under MA condition in order to obtain high quality AAO. Moreover, only a small change of voltage and current forces the pores to form the close-packed hexagonal cells. The pore ordering is also well reflected in the FFT rings which form distinct points at the corner of a hexagon for the highly ordered AAO.

In Fig. 3, D_c and the number of defects per given area in terms of stacking faults of hexagonal pores arrangement, are presented.

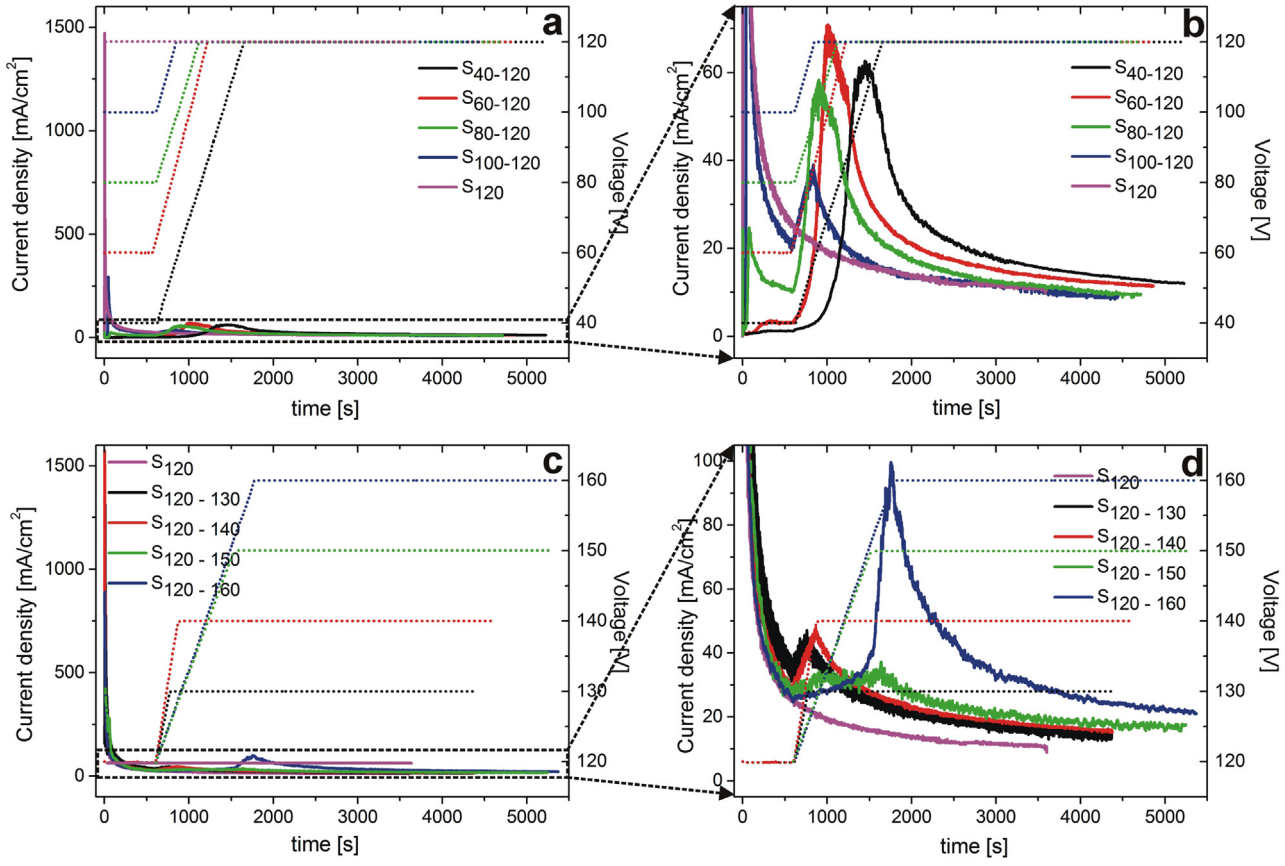

Fig. 1. The current density (solid lines) and voltage (dotted lines) vs. time curves for the studied samples. Fig. 1b and d are larger magnifications of the Fig. 1a and c, respectively.

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