
Cu hydroxide deposition in aluminium anodic oxide template by selective ion extraction

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A new method of nanostructure formation in anodic aluminium template was proposed. Cu hydroxide was deposited into anodic film pores in CuSO_4 solution by extraction of H^+ ions through the barrier layer. For this purpose an electrode was designed where Al was substituted with Hg. Using this method, Cu hydroxide can be deposited through the whole length of the pores. The distribution of deposits in the pores can be varied by changing the current form and electrolyte concentration. It was found that the barrier layer of anodic oxide films is permeable for H^+ ions but impermeable for Cu^{2+} ions and gaseous H_2 .

Key words: aluminium, anodic oxide, deposition, electrolysis

INTRODUCTION

Porous anodic films (AOF) grown on aluminium in certain acidic electrolytes consist of a uniform array of hexagonal cells, each cell containing a cylindrical pore [1–3]. A cross-section of such a film is shown in Fig. 1. The size of cells, pores and the thickness of the barrier layer depend upon the anodizing voltage [2–5]. The length of the pores is determined by the amount of charge transferred during the anodizing. Methods for a precise control of structure uniformity have recently been developed [6–8]. All this enables to design films of a predetermined morphology and make them well-suited for use as templates for nanofabrication [8–18]. Usually metals [14–17], oxides [17–18] or semiconductors [13–14] are deposited in the pores electrochemically. In aqueous solutions, predominantly ac electrolysis has been used. Such method allows a rather limited range of chemical substances to be deposited into the pores. An other method of deposition has been developed, which explores the high absorptive power of anodic aluminium oxide. Anodized parts are dipped successively into two solutions which produce an insoluble compound [19]. However, this process is unsuitable for most applications except for coloring AOF, because in this case the precipitate concentrates only in the region adjacent to the pore openings [20]. For electronics and other technical use it is important to have deposits separated by the cell walls or situated at the bottom of the pores.

Therefore, new methods that can expand the possibilities of nanofabrication are required. In this pa-

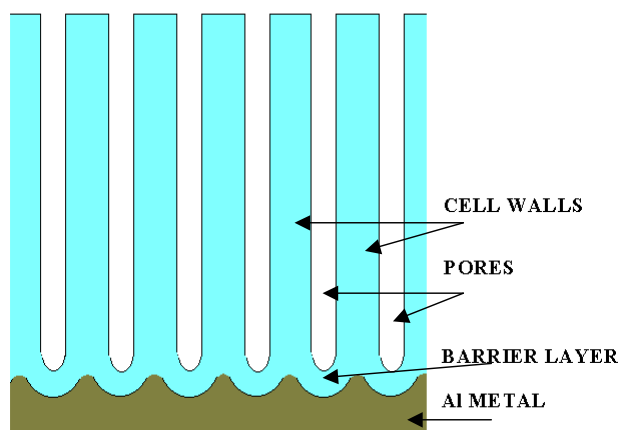


Fig. 1. Cross-sectional view of porous anodic film

per we describe a new method of metal hydroxide introduction into anodic oxide pores, where we make use of a barrier layer selective ionic conductivity.

EXPERIMENTAL

Anodic Al oxide was obtained by anodizing 99.95% pure Al in 1.5 M H_2SO_4 for 30 min at 2 A/dm² and a temperature of 20 °C. Electrodes were made from 0.3 mm thick plates. Before anodizing, they were etched in 5% Na OH solution at 50 °C and electro-polished in a solution containing 820 ml H_3PO_4 , 330 ml H_2SO_4 , 60 ml H_2O and 100 g CrO_3 at 10 V for 12 min at a temperature of 80–90 °C. Etching and polishing was repeated four times. This multiple polishing is essential, because the anodic film

is strong enough mechanically only if it is obtained on a sufficiently smooth surface. After anodizing, rinsing and drying the edges of the electrodes were coated with lacquer, and on one side of the electrode several drops of 30% NaOH were placed. When Al oxide on that side was dissolved, the electrodes were rinsed, dried and placed into 5% Br₂ solution in methanol. After dissolution of Al metal the oxide film was rinsed in methanol, distilled H₂O, dried and glued with acrylic glue to a glass pipe. Finally Hg was poured into the electrode. An AOF–Hg electrode produced in this way is shown in Fig. 2. Each time before electrolysis the AOF–Hg electrode was kept in the electrolyte for 10 min.

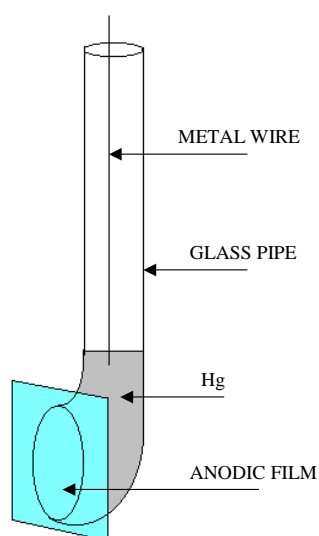


Fig. 2. Aluminium oxide–mercury electrode

The distribution of Cu in AOF was examined using a JXA-50A microscope-microanalyzer. Samples prior to examination were placed into epoxy resin and polished perpendicularly. The content of Cu in the films and in Hg was measured using atomic absorption spectroscopy. For this purpose Cu was dissolved in HNO₃ and the concentration of the solution was measured.

RESULTS AND DISCUSSION

When the AOF–Hg electrode is made a cathode in CuSO₄ solution, at the beginning of electrolysis the only visible process is the H₂ formation between AOF and Hg. This implies that H⁺ ions pass through the barrier layer and discharge on Hg surface. No H₂ evolution on the opposite side of the oxide film was observed. This shows that the barrier layer is impermeable for gaseous H₂. Usually during electrolysis the Hg level in the glass pipe was kept 2 cm above the top edge of AOF, but special experiments were

made with an electrode filled with a Hg pill of 10 cm. This produces pressure that exceeds 130 g/cm². Even under such conditions no H₂ evolution at the electrolyte AOF interface occurred.

From this experiment two important conclusions can be drawn. First, the barrier layer during electrolysis remains undestroyed. Second, that barrier layer is remarkably dense, if it can block the penetration of gas at a sufficiently high pressure, being itself only about 150 Å thick.

After electrolysis Hg was poured out of the pipe and tested for Cu presence. No traces of Cu were found. The volume of evolved gas was also measured and was found to correspond to the total amount of current passed. Therefore, processes that occur in the bottoms of the pores are as follows: H⁺ ion extraction from the electrolyte in the pores, their migration through the barrier layer, discharge on the Hg surface and finally escape of the formed gas from the reaction site. H⁺ ion extraction causes an increase in the pH value of the electrolyte contained in the pores, therefore Cu hydroxide precipitates. This is indicated by a slight green coloration of the film, which is almost invisible while precipitation takes place in the pores and becomes more distinct when later a dense film of Cu hydroxide forms on the top of the film.

Figure 3 shows a voltage–time relationship during electrolysis of AOF–Hg electrode in CuSO₄ solution at a constant current density. Curves in Fig. 3 are smoothened, but in fact they oscillate because of gas evolution between Hg and AOF, thereby permanently changing the contact area. A rapid voltage increase reflects hydroxide accumulation in the pores and later on the surface of the electrode. It implies a very low ion permeability of the deposits. This hydroxide characteristic will be shown to be

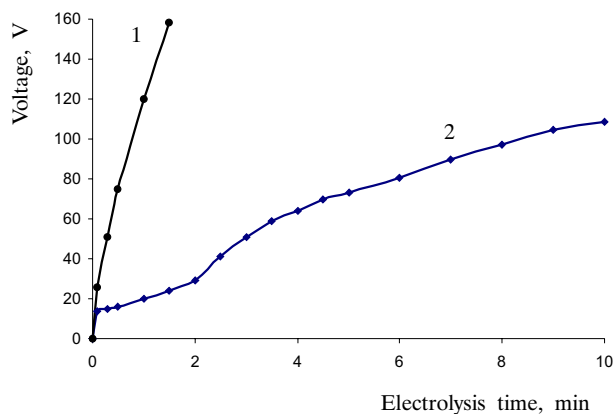


Fig. 3. Voltage–time relationship during electrolysis of AOF–Hg electrode in: 1 – 0.1 M, 2 – 0.5 M CuSO₄ at i_k : 1–4, 2–2.5 mA/cm²

the main factor that determines precipitate distribution in the pores.

The distribution of Cu hydroxide in the films after electrolysis in different conditions is shown in Fig. 4. As can be seen from Fig. 4 (curve 1), when electrolysis is carried out using the uninterrupted direct current, Cu hydroxide precipitates in a whole length of the pores, but with a significant increase of its concentration towards the AOF–electrolyte interface. Such behavior can be explained in the following way. H^+ ions are extracted from the pores. This causes precipitation of Cu^{2+} ions contained in the pores. Cu^{2+} ions that come from the electrolyte enter the pores where pH has already been increased, and therefore precipitate near the entrance. As was mentioned above, basing on Fig. 3 data, Cu hydroxide which forms in these conditions is very dense, therefore it prevents a new portion of Cu^{2+} ions from entering the pores. The result of such kind of electrolysis is Cu distribution as is shown in Fig. 4 (curve 1). Cu hydroxide is concentrated mostly at the pore entrance and blocks it; pores themselves contain only the amount of Cu that filled the pores before electrolysis and the amount that entered the pores until they were blocked.

In order to increase the amount of deposits in the pores it is necessary to prevent their blockage. This can be done by extraction of H^+ ions in small

portions just sufficient to precipitate Cu^{2+} ions already contained in the film. Then the current must be interrupted to allow a new portion of electrolyte enter the pores. After the brake, a new portion of Cu is precipitated and the process is repeated as many times as necessary.

Examples of Cu distribution in the film after electrolysis, using the interrupted direct current are shown in Fig. 4, curves 3 and 4. One can see that the shorter the impulses, the nearer to the barrier layer Cu collects. These experiments also throw some light on the diffusion rate in the pores. The maximum in curve 4 is approximately in the center of the film, which is about $24\ \mu m$ thick. The position of the maximum can be interpreted as the distance from the barrier layer which is affected by H^+ ion decrease during a single impulse. Apart from the current type, the precipitate distribution is influenced also by electrolyte concentration. As can be seen from comparison of curves 1 and 2 in Fig. 4, with increasing electrolyte concentration the distribution tends to be more even and the amount of Cu increases. Besides, it can be mentioned that no metallic Cu is deposited on the bottoms of the pores from these solutions. This conclusion follows from the absence of any increase in Cu concentration near the barrier layer.

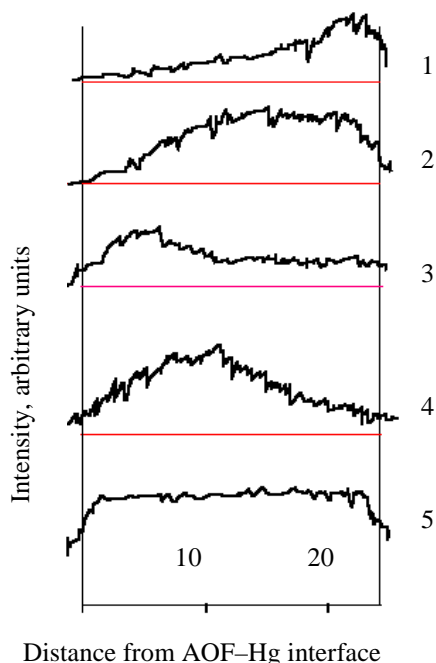


Fig. 4. Cu distribution along the pores in anodic film after electrolysis in: 1 – 0.1 M, 2, 3, 4 – 0.5 M $CuSO_4$ solution, at i_k : 1–4; 2, 3, 4 – 2.5 mA/cm². 1, 2 – constant current, 3 – impulses of 0.1 s followed by interruption of 0.4 s; 4 – impulses of 1 s, followed by interruption of 2 s; 5 – aluminium

CONCLUSIONS

Cu hydroxide can be deposited in the aluminium anodic oxide pores by extraction of H^+ ions through the barrier layer using an electrode in which aluminium is substituted with Hg. The barrier layer is permeable for H^+ ions and impermeable for Cu ions and gaseous H_2 . By altering the current form and the electrolyte concentration we can modify the distribution of the deposits in the anodic oxide pores. The shorter current impulses evoke the deposition nearer the barrier layer.

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CU HIDROKSIDO NUSODINIMAS ANODINIO
ALIUMINIO OKSIDO GARDELĖJE SELEKTYVIOS
JONŲ EKSTRAKCIJOS BŪDU

S a n t r a u k a

Pateiktas naujas nanostruktūrų formavimo anodinio aliuminio oksido gardelėje metodas. Vario hidroksido pavyzdžiu parodyta, kad metalų hidroksidai gali būti nusodinami anodinės plėvelės akutėse naudojant specialų elektrodą, kuriame aliuminis pakeistas gyvsidabriu. Šio būdo esmė yra tai, kad vandenilio jonai selektyviai ištraukiami iš akučių per barjerinį sluoksnį. Nustatyta, kad barjerinis sluoksnis laidus vandenilio jonams, bet nelaidus vario jonams ir dujiniam vandeniliui. Nusodinamo vario pasiskirstymą akutėse galima keisti keičiant srovės formą ir elektrolito koncentraciją.