
Some features of the effect of immersion solution on aluminium anodized in oxalic and phosphoric acid solutions

**Algimantas Timinskas and
Vilhelmas Skominas**

*Institute of Chemistry,
A. Goštauto 9,
LT-2600 Vilnius, Lithuania*

To eliminate the barrier layer in the pores of Al anodic oxide formed in oxalic acid and phosphoric acid solutions, the fluoborate immersion solution was used. Treatment in the immersion solution made it possible to deposit Cu in the pores of Al oxide at the potential commonly used for Cu deposition on metal electrodes.

Key words: anodizing, Al oxide film, pores, barrier layer, immersion solution

INTRODUCTION

Anodic oxide films on Al surface are characterized by relatively ordered arrays of rather uniform pores of nanometric dimensions. Therefore a considerable interest was expressed in using anodized Al to prepare ordered nanostructures able to display some important properties, for example, anisotropic magnetization. This may be realized by electrodeposition of certain metals and alloys into the pores of Al oxide. Here it is necessary to point out that the possibilities of such a process are severely limited by a barrier layer formed at the bottom of pores in the course of anodizing. Metal deposition may be successful in the presence of this layer using, as a rule, alternating current electrolysis. However, deposition of some metals and especially alloys may be realized in a required way only by direct current electrolysis. Therefore, elimination of the barrier layer in Al oxide pores becomes a problem of great importance.

One of the methods that has been proposed along this line was a decrease in the barrier layer thickness by a stepwise decrease in voltage at the end of anodizing [1]. However, complete elimination of the barrier layer is not possible in this case. Efforts have been also made to act upon the Al anodic oxide chemically in the phosphoric acid solution with the aim to widen the pores and to dissolve the barrier layer [2].

In this work, an attempt was made to eliminate the barrier layer by the two following procedures: initially by a stepwise decrease in voltage at the end of anodizing and subsequently by a chemical dissolution in the immersion solution, which is commonly used for the treatment of Al prior to electroplating.

EXPERIMENTAL

Plates of Al, trade mark AD0M (99.5%), and those of a high-purity Al (99.99%) were used in the experiments. Prior to experiments they were etched for 2 min in 1.0 mol/l NaOH solution at 40 °C, rinsed in distilled water, treated in diluted (1:1) HNO₃ at 20 °C and rinsed in distilled water again. Then Al was anodized in 0.5 mol/l oxalic acid or 0.5 mol/l phosphoric acid solutions.

The anodized Al specimens were treated in the immersion solution containing (mol/l): Ni(BF₄)₂ – 0.87, Zn(BF₄)₂ – 0.17 and NH₄BF₄ – 0.38. pH = 4.0, *t* = 20 °C [3]. Change in potential during treatment of the anodized Al in the immersion solution was recorded using an S8-13 oscillograph. The potential in the Figures is presented vs. a standard hydrogen electrode.

Cu electrodeposition in the pores of Al anodic oxide was carried out at a constant potential (–0.2 and –0.5 V) in the solution containing (mol/l): Cu₂P₂O₇ – 0.08, K₄P₂O₇ – 0.92, (NH₄)₂C₂O₄ – 0.15 and Na₂CO₃ – 0.19; pH = 8.8 and *t* = 60 °C.

The surface and sections of the specimens after treatment were subjected to investigation and analysis by SEM technique using JXA-50A microscope and electron probe microanalyzer.

RESULTS AND DISCUSSION

The oxalic and phosphoric acid solutions were chosen for Al anodizing because of the possibility to form an Al anodic oxide film with relatively large pores (pore diameter from 30 to 80 nm) [4]. In addition, it has been argued that the phosphoric acid solution permits anodizing at high voltages without

excessive heat evolution [1]. Unfortunately, this statement was not confirmed in our experiments, since the anodizing process of Al (AD0M) was possible to conduct at 100 V only in solution cooled to 15 °C.

Initial voltage for Al anodizing in the oxalic acid solution was 50 V. In all cases Al was anodized at initial voltage for 80 min. Subsequently, the voltage was stepped down from the initial value to 0.1 V in steps of 10 V. The anodizing process lasted for 5 min at each voltage step.

The diagrammatic plot of voltage and current density vs. time during the stepwise decrease in voltage at the end of Al (AD0M) anodizing in the phosphoric acid solution is shown in Fig. 1. Each step of voltage decrease causes the initial drop in current density. Thereafter, the current density undergoes a rise to a new value, which is determined by a new lower thickness of the barrier layer formed at lower voltage. Finally, at the end of voltage decreasing process, the barrier layer becomes very thin. Current density also falls very much, and even a weak cathodic current instead of anodic was observed at 0.1 V. Similar results were also obtained in the other cases of anodizing studied.

We attempted to eliminate the thinned barrier layer remaining after the above anodizing process, using an acid immersion solution which is commonly destined for treatment of Al prior to electroplating. When Al is immersed in a solution of this type, dissolution of the oxide film formed most often by air oxidation on Al takes place at the first stages and deposition of metals due to reduction of metal ions from the immersion solution by dissolving Al begins thereafter. It was believed that the same processes could be possible also in the pores of Al anodic oxide. Coincidentally with these processes, reaction of the immersion solution with walls

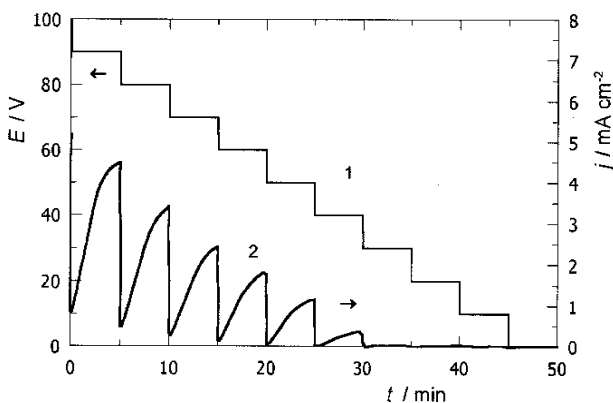


Fig. 1. Current changes with time (2) at a stepwise potential decrease (1) following Al (AD0M) anodizing for 80 min in 0.5 mol/l phosphoric acid solution. Each potential step is equal to 10 V at time intervals of 5 min

of the pores and, as a consequence, the widening of pores were also expected.

An acid fluoborate immersion solution was chosen for treatment of anodized Al. This solution [3] was known to display a good dissolving action on the Al oxide formed by air-oxidation. Deposition of Zn–Ni alloy rich in Zn took place at the Al surface after dissolution of the oxide film.

The process of attack of the immersion solution on anodized Al was studied in the same way as the Al preparation prior to electroplating, *i. e.* by means of examination of the potential variations with time.

When air-oxidized Al was treated in the immersion solution prior to electroplating, a rapid shift of potential to negative values was observed at the initial time of immersion, what was associated with dissolution of the oxide film. After completion of this process, Zn–Ni alloy deposition started. The latter process was characterized by a constant potential value equal approximately to -0.8 V. The time of transition from the oxide dissolution to alloy deposition depended on the properties of Al (purity, state of surface oxidation and the like).

As an example, dependence of the potential change at air-oxidized Al in the immersion solution on the purity of Al is shown in Fig. 2. The data obtained show that the oxide film formed in the process of air oxidation is dissolved rather rapidly in the immersion solution. Moreover, the oxide film formed at high-purity Al (99.99%) is much more resistant to the immersion solution than that formed at Al, trade mark AD0M (99.5%).

To investigate the action of the fluoborate immersion solution on anodised Al, the specimens of

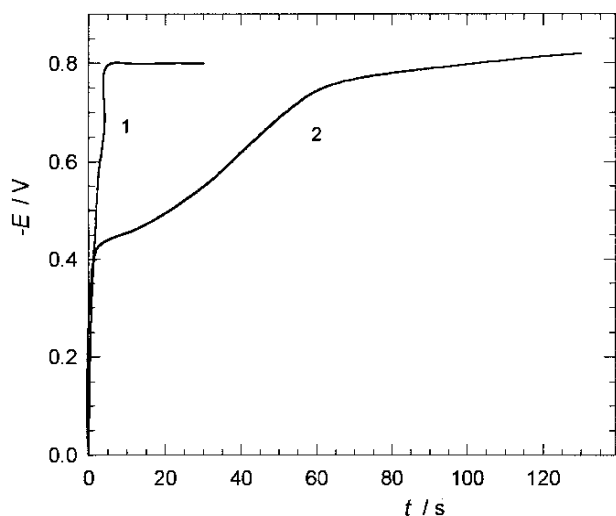


Fig. 2. Potential change with time at air-oxidized Al in the immersion solution containing (mol/l): $\text{Ni}(\text{BF}_4)_2 - 0.87$, $\text{Zn}(\text{BF}_4)_2 - 0.17$ and $\text{NH}_4\text{BF}_4 - 0.38$. (1) – Al (99.5%) and (2) – Al (99.99%)

anodised Al obtained after each stage of voltage decrease at the end of anodising were kept in the immersion solution and the E-t curves were recorded. The common feature of these curves is a very slow change in potential to some constant negative value, as compared with similar curves obtained in the case of air-oxidized Al. Constant potential values were set in the time up to 900 s from the beginning of immersion. This is much more than in the case of air-oxidized Al.

Figure 3 shows potential changes in the immersion solution depending on the voltage which is set at the end of Al (ADOM) anodising in the oxalic acid solution. It may be noticed from these data that there is no clear relation between the voltage at the end of anodising and the time needed to attain the steady state potential value in the immersion solution. One can see even the opposite view here: some increase in time may be observed, when the specimens obtained after the initial stages of voltage decrease in the anodizing process are exposed to the immersion solution.

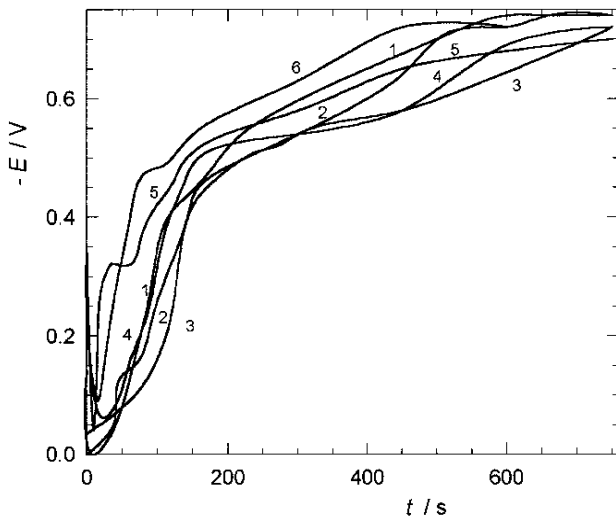


Fig. 3. Potential change with time in the immersion solution, as in Fig. 2, at Al anodized in 0.5 mol/l oxalic acid solution without potential decrease at the end of anodizing (1) and following the potential steps to: 40 (2), 30 (3), 20 (4), 10 (5) and 0.1 (6) V

The potential attained an essentially constant value in the immersion solution most rapidly (in the range of 450 s), when voltage was stepped down at the end of anodizing to 0.1 V. The constant potential value was obtained to be -0.72 V. This value is more positive than the potential of air-oxidized Al established in the same immersion solution, which, as seen from Fig. 2, is equal to -0.8 V.

The rate of potential changes at Al (ADOM) anodized in a phosphoric acid solution with the exposure time to the immersion solution was increased

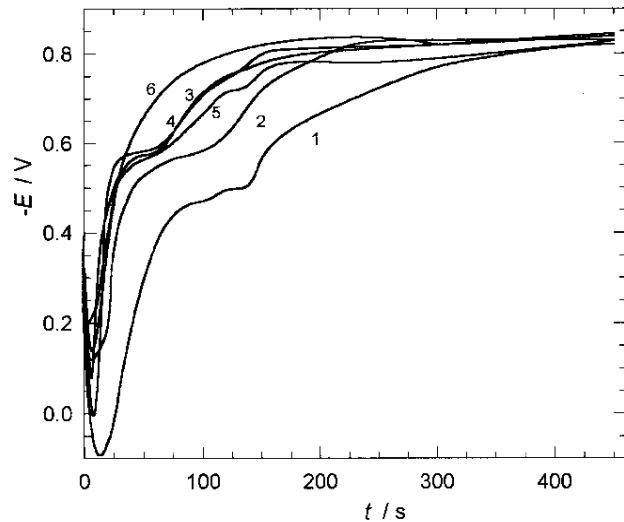


Fig. 4. The same as in Fig. 3, at Al anodized in 0.5 mol/l phosphoric acid solution without potential decrease at the end of anodizing (1) and following the potential steps to: 80 (2), 60 (3), 40 (4), 20 (5) and 0.1 (6) V

with a decrease in voltage at the end of anodizing (Fig. 4). The constant potential value was settled in the shortest time, when the voltage at the end of anodizing was dropped to 0.1 V. The data also showed that the potential of Al anodized in the phosphoric acid solution was settled constant more rapidly than of Al anodized in the oxalic acid solution. Furthermore, the constant potential value was from -0.80 to -0.82 V, what, as indicated above, is close to the potential obtained for air-oxidized Al in the immersion solution.

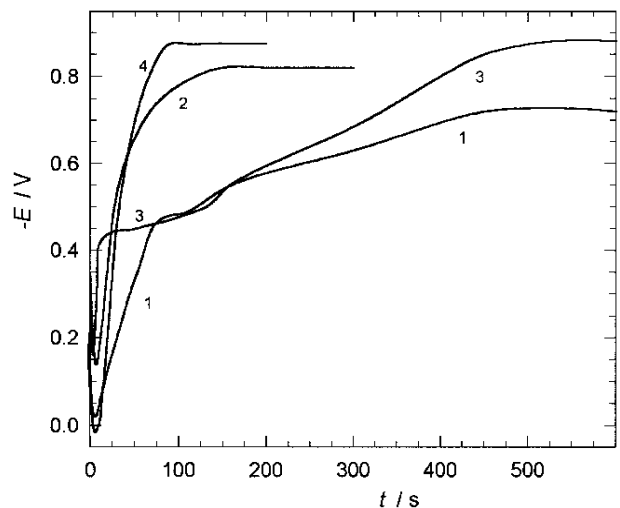


Fig. 5. Potential change with time in the immersion solution as in Fig. 2, at Al (99.5%) (1 and 2) and Al (99.99%) (3 and 4) anodized in the 0.5 mol/l oxalic acid (1 and 3) and 0.5 mol/l phosphoric acid (2 and 4) solutions following a potential decrease at the end of anodizing to 0.1 V

Oxide films obtained in the oxalic acid solution at high-purity Al behaved somewhat differently in the immersion solution. Potential changes with time suggest the immersion solution to cause a more effective elimination of the barrier layer in this case (Fig. 5). The constant potential value from -0.80 to -0.85 V was obtained.

Potential changes in the immersion solution for Al anodized in the phosphoric acid solution were found to be only slightly dependent on the type of Al, since the $E-t$ curves for high-purity Al were close to the curves for Al (AD0M). These results suggest that the Al oxide film formed in phosphoric acid solution may be more readily prepared for metal deposition at a low potential than that formed in oxalic acid solution.

It should be considered that changes in the potential of anodized Al during treatment in the immersion solution reflect changes in surface state. For anodized Al, these changes imply dissolution of the barrier layer in the oxide pores only, but not a complete elimination of anodic oxide. Therefore, when the potential of anodized Al becomes close to that of air-oxidized Al in the immersion solution, *i. e.* close to -0.8 V, it may be considered as an evidence of complete dissolution of the barrier layer in the oxide pores and formation of the immersion metal (presumably Zn–Ni alloy) layer instead. Conversely, the more positive potential values attained in the immersion solution suggest incomplete elimination of the barrier layer and, as a consequence, difficulties in the formation of the immersion layer at the pore bottoms. And finally, metal deposition in the oxide pores at a low potential is also expected to be possible, when the potential of the anodized Al in the immersion solution attains the value no less than -0.8 V.

Attempts were made to verify the above considerations by analytical methods. In fact, X-ray spectral analysis showed that only traces of Zn and Ni were found in the Al (AD0M) oxide film obtained by anodizing in the oxalic acid solution and subjected to treatment in the immersion solution, where the potential of only -0.72 V was attained. Attempts to deposit Cu at the potential commonly used for Cu deposition at metal electrodes were also unsuccessful.

Quite different analytical results were obtained when the potential in the immersion solution was changed to about -0.8 V. Zn was found analytically in the oxide films in this case after treatment in the immersion solution. However, only traces of Ni were determined. Cu electrodeposition was also successful, and Cu was determined analytically in the oxide. Zn and Cu were accumulated in the areas of

the oxide near the bottoms of the pores (Figs. 6 and 7).

The above results confirm that the potential of anodized Al settled in the immersion solution may serve as an indication of the barrier layer elimination and immersion metal layer formation instead. As in the case of Al treatment prior to metal deposition, immersion layer is dissolved in the process of Cu deposition, since Zn was not determined after Cu deposition (Fig. 6b).

Microscopic observation showed that the surface of Al oxide film was not essentially changed after treatment in the immersion solution and Cu deposition, since pores of fairly regular shapes were retained. Therefore, it may be supposed that potential

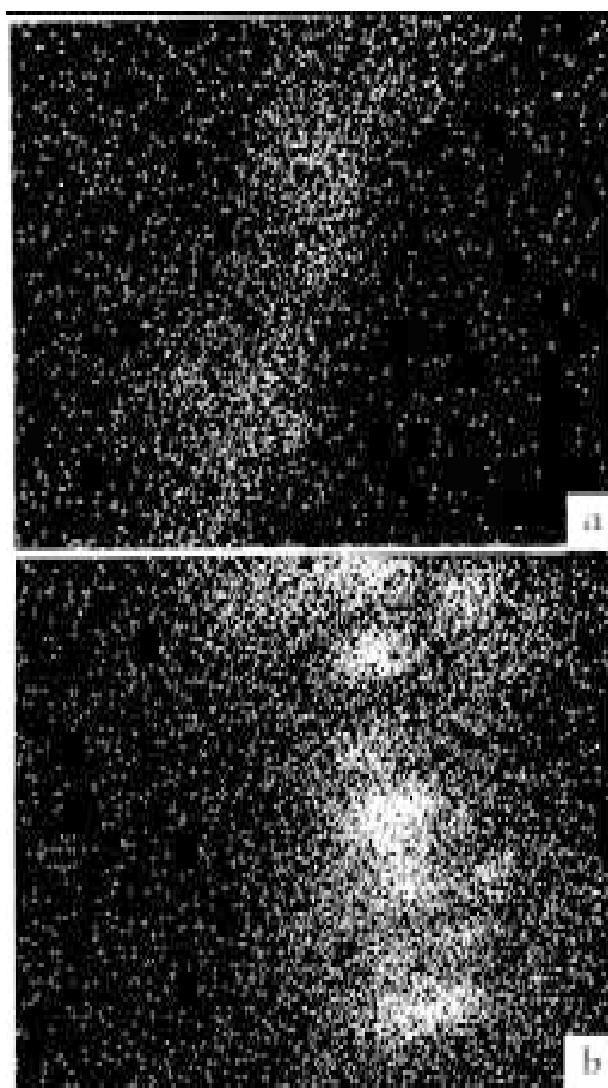


Fig. 6. Changes in quantity of Zn (a) and Cu (b) in the section of Al (99.5%) oxide film obtained in 0.5 mol/l phosphoric acid solution after treatment in the fluoborate immersion solution for 10 min (a) and after Cu deposition in the pyrophosphate plating solution at -0.5 V for 15 min (b). $\times 1700$ (a) and $\times 5000$ (b)

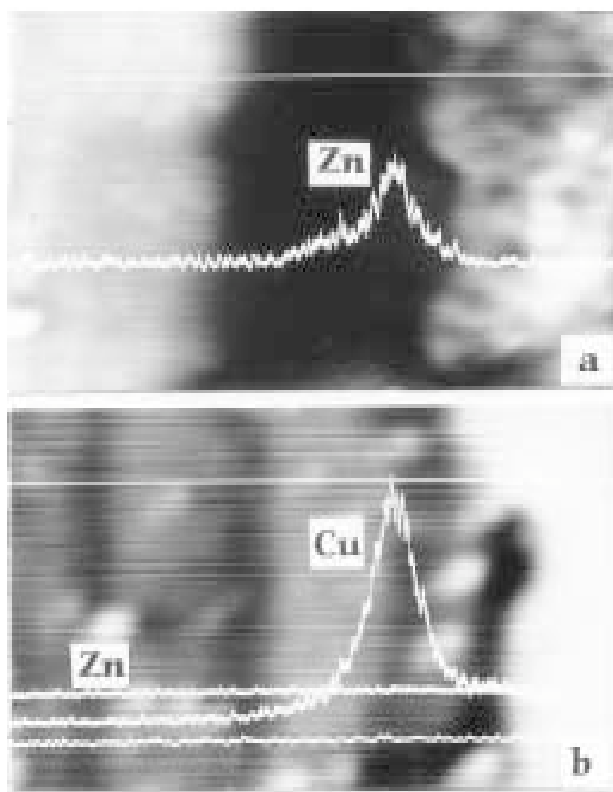


Fig. 7. Distribution of Zn (a) and Cu (b) in the section of Al (99.5%) oxide obtained in 0.5 mol/l phosphoric acid solution. The oxide treatment was the same as in Fig. 6. $\times 1700$ (a) and $\times 5000$ (b)

changes of anodized Al in the fluoborate immersion solution are associated mainly with changes in the barrier layer, dissolution of this layer and formation of immersion metal layer instead. These processes provide favourable conditions for metal deposition in the pores of Al oxide at the potential inherent in metal deposition at metal electrodes.

CONCLUSIONS

An immersion solution based on fluoborates dissolves the barrier layer in the pores of Al oxide obtained by anodizing in oxalic and phosphoric acid solutions and forms an immersion metal layer instead. This process may be tracked by the potential changes of anodized Al measured in the immersion solution. The effectiveness of elimination of the barrier layer formed in the oxalic acid solution depends on the purity of Al used for anodizing. Better elimination of the barrier layer was found for high-purity Al. The barrier layer of oxide films formed in the phosphoric acid solution was readily dissol-

ved in the immersion solution independent of the purity of Al used. Treatment in the fluoborate immersion solution is considered to provide a possibility to deposit metals into the Al oxide pores at the potential commonly used for metal deposition at metal electrodes.

ACKNOWLEDGEMENT

The authors thank Dr. E. Matulionis for X-ray spectral analysis of the Al oxide films.

Received
20 March 2000

References

1. R. C. Furneaux, W. R. Rigby, A. P. Davidson, *Nature*, **337**, 147 (1989).
2. D. AlMawlawi, N. Coombs, M. Moskovits, *J. Appl. Phys.*, **70**, 4421 (1991).
3. A. Timinskas, Z. Kaušpedas, *Chemija*, No **3**, 44 (1993).
4. C. A. Foss, G. L. Hornyak, J. A. Stockert, C. R. Martin, *J. Phys. Chem.* **98**, 2963 (1994).

A. Timinskas, V. Skominas

KAI KURIE IMERSINIO TIRPALO POVEIKIO ANODUOTAM OKSALO IR FOSFORO RŪGŠČIŲ TIRPALUOSE ALIUMINIUI BRUOŽAI

S a n t r a u k a

Barjeriniam sluoksniui pašalinti Al anodinio oksido, suformuoto oksalo ir fosforo rūgščių tirpaluose, porose panaudotas fluoroboratinis imersinis tirpalas. Apdorojimas imersiniame tirpale įgalino nusodinti Al oksido porose varį, esant potencialui, paprastai naudojamam Cu nusodinti ant metalinių elektrodų.

A. Тиминскас, В. Скоминас

НЕКОТОРЫЕ ОСОБЕННОСТИ ДЕЙСТВИЯ ИММЕРСИОННОГО РАСТВОРА НА АНОДИРОВАННЫЙ В РАСТВОРАХ ЩАВЕЛЕВОЙ И ФОСФОРНОЙ КИСЛОТ АЛЮМИНИЙ

Р е з ю м е

Для удаления барьерного слоя в порах анодного оксида Al, сформированного в растворах щавелевой и фосфорной кислот, использован фтороборатный иммерсионный раствор. Обработка в иммерсионном растворе позволила осадить Cu в порах оксида Al при потенциале, обычно используемом для осаждения Cu на металлических электродах.