
A preliminary voltammetric study of anodized aluminium containing copper deposited into the oxide pores

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Investigation of anodized Al was carried out in an Sn(II) containing solution by linear potential sweep voltammetry. Prior to voltammetric experiment, Al was anodized in oxalic acid solution, then subjected to chemical treatment in acid solution and deposition of some Cu quantity in the Al oxide pores. Based on the results obtained, it was assumed that anodized Al electrode after the foregoing treatment behaves electrochemically as a system of microelectrode arrays. Changes in the microelectrode behaviour are explained by the features of reacting ion diffusion in the pores and in the solution at the electrode surface.

Key words: anodized Al electrode, Al oxide pores, Cu deposition, voltammetric investigation, microelectrode behaviour

INTRODUCTION

Investigation of the possibilities to deposit metals into the pores of Al anodic oxides by direct current has attracted wider attention in the recent years. The demand for such investigation was induced by a search for new nanostructured materials which are required in a variety of applications. Anodized Al is important in this respect because of a great number of pores orderly distributed on the surface. These pores can be filled with the metals with desired properties.

However, electrodeposition of metals into the pores of Al anodic oxide by direct current meets some serious problems. Of them, most significant is elimination of the barrier layer which forms at the pore bottom during the anodizing process and possesses the insulator properties. It has been proposed to reduce the thickness of the barrier layer by a gradual decrease in voltage to some minimum value at the end of anodizing [1]. Chemical means, namely, reaction with phosphoric acid have been also proposed for widening the pores with simultaneous elimination of barrier layer [2].

On the other hand, no easy and plausible means are available for evaluation of the effectiveness of barrier layer elimination. This problem is important for the development of nanostructured materials on the basis of anodized Al. We assume that electrochemical methods may be useful in approaching this

problem. Furthermore, the electrochemical properties of such systems still remain an open question.

This work seeks to present some data on the electrochemical behaviour of anodized and chemically treated Al containing in the oxide pores some quantities of Cu deposited by direct current.

EXPERIMENTAL

Plates of Al trade mark AD0M were used for experiments. The surface of Al was pretreated in a solution containing 0.5 mol/l NaOH for 2 min at 60 °C, rinsed in distilled water, treated in HNO₃ (1 : 1) for 0.5 min at 20 °C and rinsed in distilled water again. Anodizing was carried out for 80 min at 100 V and 20 °C in a solution containing 0.4% oxalic acid with a stepwise decrease in voltage at the end of anodizing. The voltage was decreased by 10 V at the intervals of 5 min. A B5-10 power source was used for anodizing.

The test electrode after anodizing was rinsed in distilled water, treated for 35 min in immersion solution containing (mol/l): Zn(BF₄)₂ – 0.17, Ni(BF₄)₂ – 0.87 and NH₄BF₄ – 0.38 at pH 4 and 15 °C [3] and rinsed in distilled water again. Then different quantities of Cu were deposited into the pores of Al oxide. Cu deposition was carried out at –0.2 V (*vs.* Ag /AgCl electrode) and 0.04 to 0.1 mA (electrode area 1 cm²) in a solution containing (mol/l): Cu₂P₂O₇ – 0.083, K₄P₂O₇ – 0.92, (NH₄)₂C₂O₄ – 0.15 and

Na_2CO_3 – 0.19 at pH 8.8 and 15 °C. The Cu quantity deposited in the Al oxide pores was evaluated from the current quantity consumed assuming the 100 percent efficiency of Cu deposition. A B5-43 power source was used for Cu deposition.

Solutions for Al surface treatment, anodizing and Cu deposition were prepared from reagent grade salts.

Thereafter the test electrode was rinsed for 10 min in distilled water to remove the remains of Cu plating solution from the pores and immersed in the test solution containing 0.01 mol/l SnSO_4 (reagent grade) and 0.1 mol/l H_2SO_4 (chemically pure) for 5 min to equalize the Sn(II) concentration in the pores. The experiment was carried out at 15 °C by linear potential sweep voltammetry, using a PI-50-1 potentiostat. Partial control of the experiment was performed by computer. Data recording was carried out on a PDA1 recorder and computer.

Voltammetric experiments were carried out in a standard three-electrode electrochemical cell, using a standard Ag/AgCl electrode as a reference electrode and Pt plate as an auxiliary electrode. The potential in the Figures is given vs. the steady-state potential in the test solution.

RESULTS AND DISCUSSION

To ease the metal deposition by direct current in the pores of Al anodic oxide, a treatment in the immersion solution was first used. The acid immersion solution which had been proposed for Al treatment prior to electroplating was used for this purpose. The action of this solution, as is well known, involves a removal of oxide layer from Al and a simultaneous deposition of thin metal coating on the oxide-free Al surface [3]. Based on such properties of immersion solution, there was reason to hope that this solution could be applicable for preparation of anodized Al to deposit metals into the oxide pores with the aid of direct current. Acid immersion solution could first of all be able to dissolve the barrier layer which was thin as compared with the total oxide layer thickness. The chemical dissolving ability of the immersion solution used should be no less than that of phosphoric acid used for this purpose [2]. However, one more function of immersion solution, namely, formation of a thin metal layer on Al surface which is more resistant to oxidation than Al should also be important. A Zn–Ni layer is deposited from the immersion solution used.

The preceding treatment of anodized Al made it possible to conduct the Cu deposition in the oxide pores at a potential similar to the Cu deposition

potential under usual conditions. This shows that Cu deposition takes place in the pores free of a barrier layer. However, the low deposition current also suggests Cu deposition to take place at a small electrode area.

After some experiments searching for an electrochemical process most suitable for voltammetric investigation at anodized Al, Sn(II) cathodic reduction was chosen. The process of Sn deposition has several advantages. Firstly, the process takes place at a sufficiently positive potential and low overpotential, *i. e.* under conditions near to reversible, what, in addition to a high hydrogen overpotential at Sn, allows to avoid hydrogen discharge in the potential range of Sn(II) reduction. Secondly, the kinetic parameters of the process are well known since they have been thoroughly investigated. The main shortage of the process is the employment for Sn deposition of strongly acid solutions. Therefore, the properties of Al oxide layer can be changed due to a chemical action during a longer exposure of the electrode to the solution. In this connection, the acidity of the test solution was lowered to an acceptable minimum.

Since anodized Al electrodes exhibit the properties of porous electrodes, they contain solutions in the pores, which may be removed and replaced with other solutions only over a much longer time as compared with metal electrodes. It was noticed, for example, that Cu deposition wave appeared in the voltammograms obtained in Sn(II) containing solution, when the electrode was not carefully rinsed after Cu deposition. Therefore, the electrode after Cu deposition was kept in distilled water until Cu(II) ions were removed from the pores. The electrode was also kept longer in the test solution prior to voltammetric experiment to equalize the Sn(II) ion concentration in the pores.

On the other hand, a long exposure to water or solution of an anodized Al electrode is connected with some danger of changing its electrochemical properties. The main change may develop due to hydration of Al oxide in water and some solutions tending to decrease the pore diameter. Although this process is known to proceed slowly at room temperature, its results can appear after a long time of exposure. This is one of the problem which needs to be studied in more detail.

When kept in a test solution containing Sn(II), the anodized Al electrode containing some Cu quantity in the oxide pores acquires the potential – 0.35 to –0.4 V (vs. Ag/AgCl) which is close to the Sn/Sn(II) system potential. The nature of the processes giving such a result is for the present unclear. This favors Sn deposition to take place at a low overpotential. The potential range of Sn deposition

is close to that observed in Sn deposition at metal electrodes in a similar solution.

Voltammetric investigation showed that the Sn deposition voltammograms were independent of the potential sweep rate ν in the range 0.05 to 0.5 V/s of ν studied at a lower Cu quantity deposited in the pores. Moreover, the voltammograms obtained had no peak current and resembled the steady state polarization curves.

With increase in Cu quantity in the Al oxide pores, Sn deposition voltammograms started to depend on ν (Fig. 1), and this dependence shows a rise when Cu quantity is further increased (Fig. 2). Coincidentally with increase in dependence on ν , the peak current appears increasingly more clearly and the voltammograms take a shape that is closer to the traditional potential sweep voltammograms.

Figure 3 shows a conventional $j_p - \nu^{1/2}$ dependence constructed from the voltammetric data. As is seen, this dependence can be approximated by straight lines in the ν range studied. A slope of the lines that indicate the magnitude of j_p dependence on ν increases with increase in Cu quantity in the pores. The Sn deposition rate is also essentially increased.

Let us try, if only to some extent, to discuss these at a glance somewhat unusual data, since some features of the data obtained are worth consider-

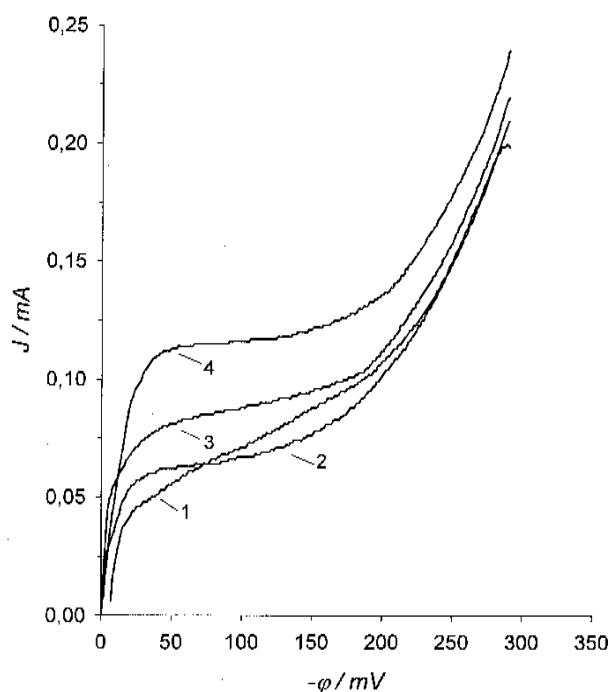


Fig. 1. Voltammograms obtained at anodized Al in solution containing 0.01 mol/l SnSO_4 and 0.1 mol/l H_2SO_4 at ν (V/s): 0.05 (1), 0.1 (2), 0.2 (3) and 0.5 (4). Cu quantity previously deposited in the oxide pores is equal to 35×10^{-6} g. Surface area of the electrode is 1 cm^2

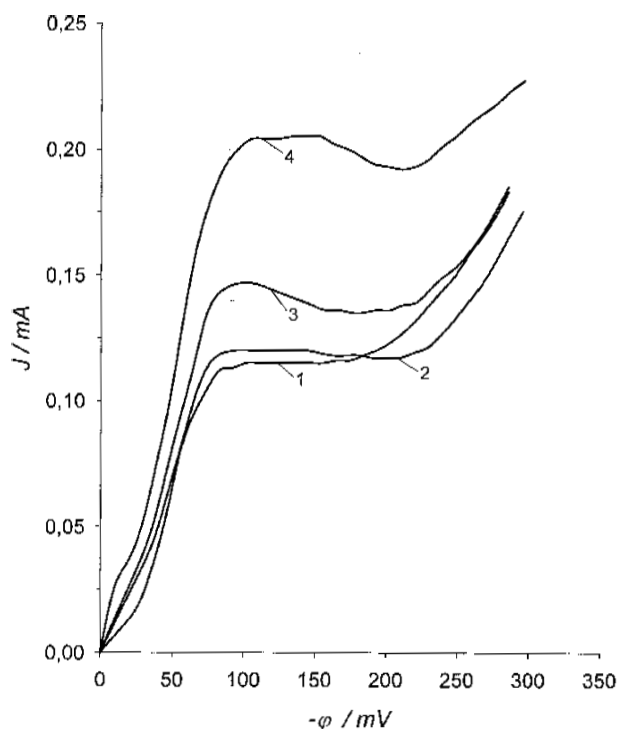


Fig. 2. The same as in Fig. 1 at Cu quantity in the oxide pores equal to 40×10^{-6} g

ation and, where possible, explanation of their nature.

As may be seen, a very low current was obtained in voltammetric measurements. Of course, some decrease in current had to be expected because of metal deposition in the pores which have the area well less than the electrode area. However, the current was still much lower than it should be according to the porosity of Al oxide obtained by anodizing in oxalic acid, which may reach 25 to 30% [4]. This may be associated with insufficient pore activation that leads to metal deposition not in each pore. It is hoped on this basis that measurements of the voltammetric current can become useful in investigating the treatment of anodized Al prior to metal deposition.

A further important result is an essentially reduced j_p dependence on ν , what is quite different from the results known for large metal electrodes, where this dependence is expressed by known equations [5]. A reduced j_p dependence on ν or complete absence of it is a characteristic feature of small electrodes only [6]. Therefore, the $j_p - \nu^{1/2}$ dependence of a similar type for anodized Al should be assigned to the microelectrode behaviour following from the small pore diameter of anodized Al.

The case when the current is independent of ν , known as steady state diffusion conditions, is observed at rather small electrodes. This result was also obtained in our experiments at a lower Cu quantity

preliminary deposited in the oxide pores. However, one essential difference may be seen in our case. The fact is that in the case of anodized Al the diffusion layer starts to form not at the electrode plane as it does in the conventional microelectrodes, but deep in the pores, where the microelectrode rules are not complied with. Here an ordinary linear diffusion of the reacting ions exists. Therefore, a normal j_p dependence on ν should be observed in such a situation. Since the current was obtained to be independent of ν , it follows that the diffusion layer reaches the top of pores soon after the start of voltammetric experiment and then a radial diffusion enters the total diffusion process creating a microelectrode effect.

Using the equation which gives an association between the diffusion current and electrolysis time at small electrodes [7] and the known association between the diffusion current and diffusion layer thickness for linear diffusion, the following expression for the limiting expansion of diffusion layer with time at sufficiently short times was obtained [8, 9]:

$$\delta_1 = (\pi D t)^{1/2}. \quad (1)$$

With a knowledge of pore depth, a time the diffusion layer takes to reach the top of pores may be found. So, it was assessed that with a use of $\nu = 100$ mV/s and at pore depth 5 to 10 μm what was the case in our experiments, diffusion may appear at the electrode surface after a change in potential from 1.2 to 4.8 mV, *i. e.* well before reaching the peak current. Therefore, it is a natural result when the diffusion is controlled by the bulk solution and a microelectrode effect is created at the small pores, even though metal deposition takes place in the depth of these pores.

An increase in peak current with increase in Cu quantity deposited previously in the pores (Fig. 3) most simply can be explained by an increase in the pore area which is active for metal deposition. However, this effect has been also observed at metal deposition in polycarbonate membranes [10], where an increase in the active area with increase in metal quantity deposited had no real grounds. Therefore, it may be assumed that the main reason for increase in current mentioned above is a decrease in pore depth and, as a consequence, an increase in diffusion from the layers of solution at the electrode surface.

As follows from [6], an increase in j_p dependence on ν observed with increase in Cu quantity in the pores implies an increase in microelectrode dimensions. Based on the results in [6], attempts were made to evaluate the microelectrode radii in Sn deposition process at the anodized Al electrodes con-

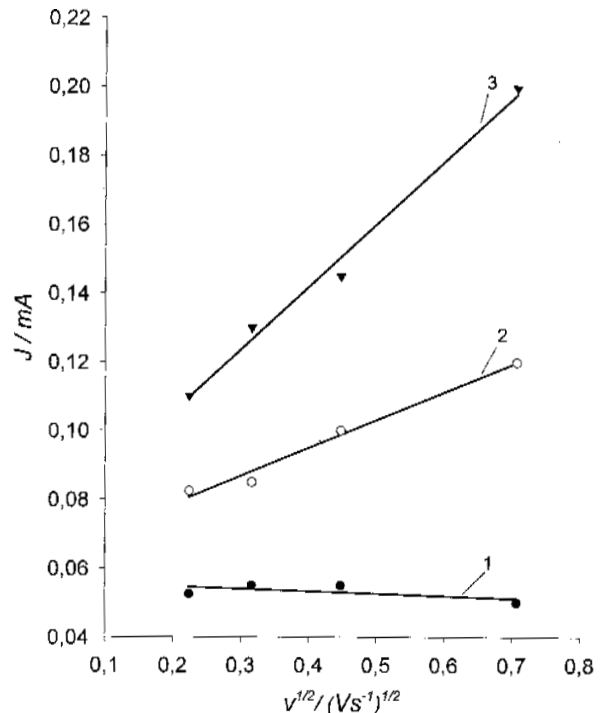


Fig. 3. Dependence of peak current j_p on ν at anodized Al electrode containing Cu in Al oxide pores ($\mu\text{g}/\text{cm}^2$): 25 (1), 35 (2) and 40 (3)

taining Cu quantities indicated in Fig. 3. The following results respective to an increasing Cu quantity were obtained: < 1 , ~ 10 and ~ 15 μm . With the structure of anodized Al surface in mind, it should be acknowledged that such a great increase in microelectrode dimensions is obviously only apparent, since it is not associated with a real increase in the active area of individual pores. The reason for an increase in microelectrode dimensions in this case may be explained again by a more rapid incorporation of the bulk solution into the total diffusion process. At a close distance between the pores, this to the overlapping of diffusion layers at the adjacent pores. A certain number of neighbouring pores begins to operate under these conditions as one larger microelectrode.

CONCLUSIONS

The anodized Al electrode after chemical treatment and Cu deposition in the oxide pores behaves as a system of microelectrode arrays in the linear potential sweep voltammetry. It is supposed that, depending on the Cu quantity deposited in the pores, the microelectrode properties can be exhibited by individual pores or their groups. Changes in the microelectrode behaviour are explained by the features of the reacting ion diffusion in the pores and in solution at the electrode surface.

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ANODUOTO ALIUMINIO SU NUSODINTU OKSIDO AKUTĖSE VARIU PRADINIS VOLTAMPEROMETRINIS TYRIMAS

S a n t r a u k a

Anoduoto Al tyrimas atliktas Sn(II) tirpale tiesinio potencialo skleidimo voltamperometrijos metodu. Prieš voltamperimetrinį eksperimentą Al buvo anoduojamas ok-

salo rūgštis tirpale, po to chemiškai apdorojamas rūgščiame tirpale ir Al oksido akutėse nusodinamas tam tikras Cu kiekis. Remiantis gautais rezultatais, daroma išvada, kad anoduoto Al elektrodas po anksčiau minėto apdorojimo elektrochemiškai elgiasi kaip mikroelektrodų aišbės sistema. Mikroelektrodų elgsenos pokyčiai aiškinami reaguojančių jonų difuzijos oksido akutėse ir tirpale prie elektrodo paviršiaus ypatumais.

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ПРЕДВАРИТЕЛЬНОЕ ВОЛЬТАМПЕРОМЕТРИЧЕСКОЕ ИЗУЧЕНИЕ АНОДИРОВАННОГО АЛЮМИНИЯ, СОДЕРЖАЩЕГО В ПОРАХ ОКСИДА ОСАЖДЕННУЮ МЕДЬ

Р е з ю м е

Изучение анодированного Al проведено в растворе, содержащем Sn(II), методом вольтамперометрии линейной развертки потенциала. Перед вольтамперометрическим измерением Al был анодирован в растворе щавелевой кислоты, затем подвергался химической обработке в кислом растворе и в поры оксида Al осаждалось определенное количество меди. На основании полученных данных считается, что электрод из анодированного Al после вышеуказанной обработки электрохимически ведет себя как система совокупности микроэлектродов. Изменения в поведении микроэлектродов объясняется особенностями диффузии реагирующих ионов в порах оксида и в растворе у поверхности электрода.