Cross-section analysis of the morphology of electrodeposited copper obtained in the hydrogen co-deposition range

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Abstract: Cross-section analysis of copper deposits electrodeposited in the hydrogen co-deposition range at a constant overpotential and in a pulsating overpotential (PO) regime was performed. It was shown that a complete structural analysis of these technologically very important electrodes is impossible without an analysis of their internal structure. An insight into the compactness (or porosity) of the deposits, as well as into the depth of the holes, can only be obtained by this type of analysis.

Keywords: electrodeposition; cross-section analysis; hydrogen; copper.

INTRODUCTION

Electrodeposition is a very suitable way to obtain open porous structures of copper and copper–tin alloys with an extremely high surface area. These structures are of high technological significance because they are ideally suited for electrodes in many electrochemical devices, such as fuel cells, batteries and chemical sensors.[1–3] They can be electrodeposited in both galvanostatic[1–3] and potentiostatic[4–12] regimes of electrolysis. The basic characteristics of these electrodes, denoted as both 3-D foam[1–3] and honeycomb-like ones,[4–12] are holes or pores formed due to attached hydrogen bubbles with agglomerates of copper grains among them. In constant regimes of electrolysis, the number, distribution and pore size can easily be controlled by the choice of appropriate electrolysis parameters.[7] In relation to constant regimes of electrolysis, a decrease in the diameter of the holes formed by attached hydrogen bubbles and an increase in their number can be achieved by the addition of specific substances to the plating bath,[2] or by application of periodically changing regimes of electrolysis.[13]

The use of the scanning electron microscopy (SEM) technique was the most often used way for the examination of the structure of copper electrodes with an extremely high surface area. However, the use of this technique gives only information concerning the "top view" of these electrodes. Considering the high technological significance of deposits with an extremely high surface area, a complete analysis of deposits obtained in hydrogen co-deposition range is required. The detailed analysis cannot be realized without an insight into the interior of these structures. The most suitable way for a detailed analysis of deposits is cross-section analysis, because this type of analysis can give information related to the mechanism of formation and growth of deposits. For this reason, the aim of this study was the cross-section analysis of copper deposits obtained in the hydrogen co-deposition range at a constant overpotential and in a pulsating overpotential (PO) regime.

EXPERIMENTAL

Copper was electrodeposited from 0.15 M $CuSO_4$ in 0.50 M H_2SO_4 in an open cell at a temperature of 20±0.5 °C. Potentiostatic and square-wave pulsating overpotential techniques were used for the electrodeposition of copper. In the constant overpotential electrolysis, the employed deposition overpotential was 1000 mV. In the pulsating overpotential deposition, an overpotential amplitude of 1000 mV and a pulse duration of 10 ms were applied in all experiments. The pause duration was selected to be: 5, 20, 50 and 100 ms. Electrodeposition of copper was performed at cylindrical copper electrodes. In all experiments, the geometric surface area of the copper electrodes was 0.50 cm^2. The counter electrode was a copper foil of 0.80 dm^2 surface area placed close to the walls of the cell, while the reference electrode was a copper wire, the tip of which was positioned at a distance of 0.2 cm from the surface of the working electrode. Copper was electrodeposited with electricity quantities of 10 mA h cm^{-2}.

Doubly distilled water and analytical grade chemicals were used for the preparation of the solution for the electrodeposition of copper.

Cross-section analysis of the copper electrodes was performed using a Zeiss Axiovert 25 optical microscope equipped with a Panasonic WV-CD50 digital camera. In order to observe the cross-section of an obtained deposit, the electrode together with the deposit was mounted and fixed by an epoxy resin. In this way, the cross-section represented the plain parallel to the line of deposit growth. The samples were polished several times and the cross-section structure was observed in a non-etched state.

RESULTS AND DISCUSSION

It was shown by the scanning electron microscopy (SEM) technique that honeycomb-like deposits are formed by copper electrodepositions from 0.15 M $CuSO_4$ in 0.50 M H_2SO_4 at a constant overpotential of 1000 mV.[4–6,9] Honeycomb-like deposits can also be formed in the pulsating overpotential (PO) regime.[13] If the following parameters of a square wave PO were applied: an amplitude overpotential of 1000 mV, a deposition pulse of 10 ms and pause durations of 1, 5, 10, 20 and 50 ms, increasing the pause duration led to a decrease of the average diameter of the holes formed by attached hydrogen bubbles, as well as to an increase

in the number of holes formed at surface of copper electrodes compared to the size and number of holes obtained in the constant electrolysis regime.[13,14] Holes formed due to attached hydrogen bubbles were also formed in the PO regime with a pause duration of 100 ms, but their shape, size and number were completely different from those formed with shorter pause durations.[14]

The dependences of the average current on the electrodeposition time obtained at a constant overpotential of 1000 mV and in the PO regime with pause durations of 5, 20, 50 and 100 ms are shown in Fig. 1. From Fig. 1, it can be seen that increasing the pause duration led to a decrease of the average electrodeposition current. Also, these values were smaller than the current obtained in the constant regime of electrodeposition.
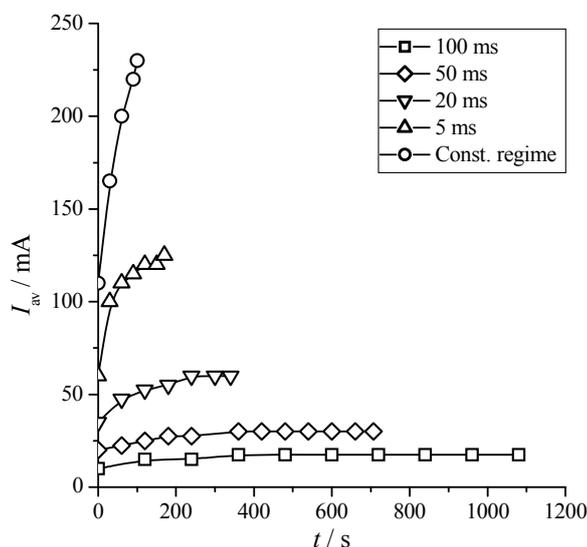
Fig. 1. The dependences of the average current on electrodeposition time, obtained at a constant overpotential of 1000 mV, and in the pulsating overpotential (PO) regime with pause durations of 5, 20, 50 and 100 ms.

Figure 2a shows the cross-section of a honeycomb-like structure electrodeposited from 0.15 M $CuSO_4$ in 0.50 H_2SO_4 at an overpotential of 1000 mV with a quantity of electricity of 10 mA h cm^{-2}. From this Figure, all elements of which honeycomb-like structures are constructed can be seen: "regular holes" formed by both attached hydrogen bubbles (part in circle denoted with A in Fig. 2a) and coalescence of neighboring hydrogen bubbles (part in circle denoted with B in Fig. 2a) and "irregular holes" formed due to the effect of current distribution at the growing surface (parts denoted by arrows labeled C in Fig. 2a).[6] The presence of channel structures formed through the interior of the deposit can be easily observed by cross-section analysis of this deposit at a higher magnification (Fig. 2b).

The mechanism of the formation of honeycomb-like structures was widely studied,[4–7] and it can be briefly presented as follows: in the initial stage of the electrodeposition process, both nuclei of copper and "nuclei" of hydrogen bub-

bles are formed at the active sites of the electrode surface.[6] The hydrogen bubbles isolate the substrate and then the current lines are concentrated around them making rings consisting of agglomerates of copper grains. The current lines are also concentrated at the nuclei of the copper formed in the initial stage between the hydrogen bubbles.

(a)

(b)

(c)
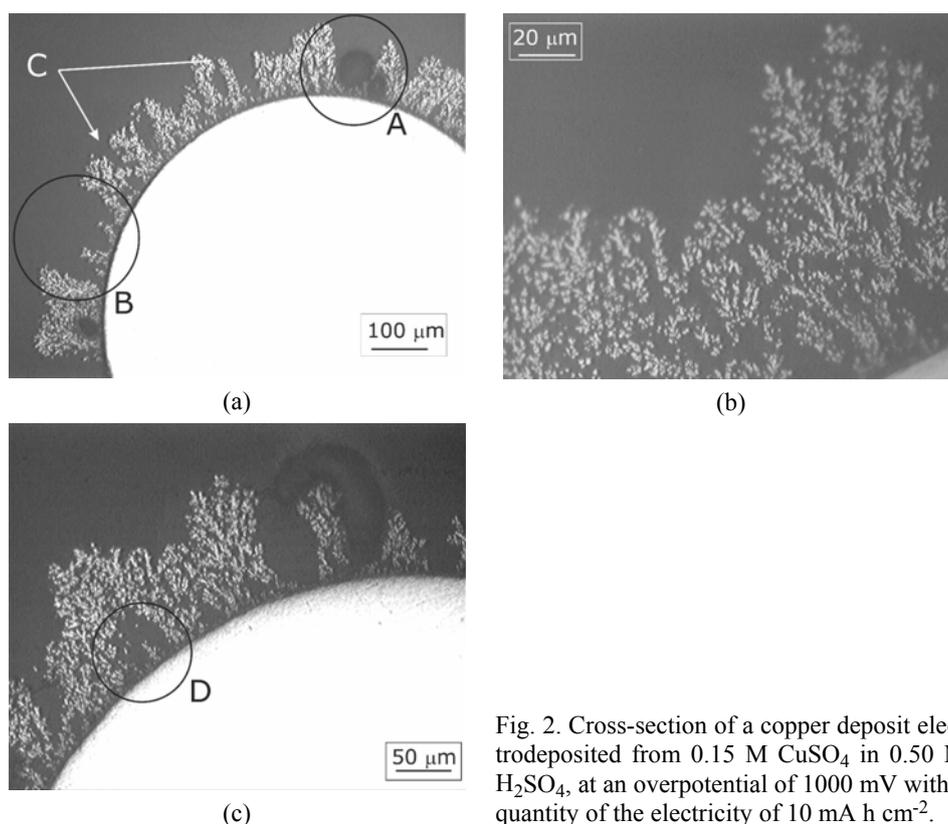
Fig. 2. Cross-section of a copper deposit electrodeposited from 0.15 M CuSO$_4$ in 0.50 M H$_2$SO$_4$, at an overpotential of 1000 mV with a quantity of the electricity of 10 mA h cm^{-2}.

As a result of the current distribution at the growing copper surface, new copper nucleation and hydrogen evolution occurs primarily at the top of these agglomerates. Some of the new, small, freshly-formed hydrogen bubbles which are formed at agglomerates around previously formed large hydrogen bubbles coalesce with them, leading to their growth with electrolysis time as already shown.[6] After detachment of these hydrogen bubbles from the electrode surface, "regular holes" are formed. In the growth process, the coalescence of closely-formed large hydrogen bubbles can also be observed.

Simultaneously, holes of irregular shapes are formed from nuclei of copper formed in the initial stage of the electrodeposition. The current distribution at the growing copper surface is responsible for the formation of this type of hole.[6]

Meanwhile, some of the freshly-formed hydrogen bubbles will not find a way to coalesce with the large hydrogen bubbles because they are situated among copper nuclei which initiate a barrier for their development into large hydrogen bubbles. This effect, together with the already discussed current density distribution leads to the formation of a porous channel structure through the interior of the copper deposit (Fig. 2b).

In the process of copper growth, due to the effect of the current distribution, some relatively large hydrogen bubbles can remain included in the interior of copper structure (part in the circle denoted with D in Fig. 2c), making the honeycomb-like structure obtained at a constant overpotential very porous. This enhanced porosity could not be seen by the SEM technique. Hence, complete analysis of the honeycomb-like structures was impossible without cross-section analysis.

The cross-section of morphology of the electrodeposited copper obtained in the PO regime with pause durations of 5, 20, 50 and 100 ms are shown in Fig. 3.
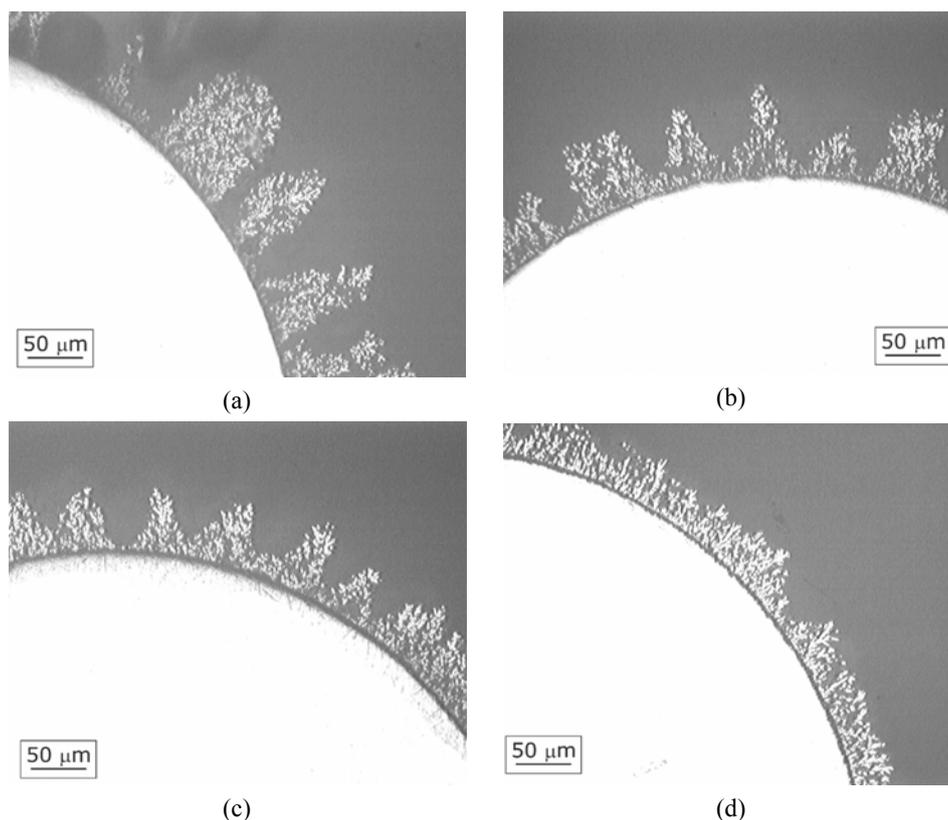
Fig. 3. Cross-section of copper deposits electrodeposited from 0.15 M CuSO$_4$ in 0.50 M H$_2$SO$_4$ in the pulsating overpotential (PO) regime with a pause duration of: a) 5, b) 20, c) 50 and d) 100 ms.

It can be seen that the compactness of the formed copper deposits increased with increasing pause duration. Also, the compactness of the deposits obtained in the PO regimes was larger than the one obtained in the constant regime of electrolysis (Fig. 2a). Prolonging the pause duration leads to a suppression of the coalescence of neighboring hydrogen bubbles. Coalesced hydrogen bubbles can be observed in the honeycomb-like structures obtained with a pause duration up to 20 ms. It can be seen from Figs. 2a and 3 that the application of a PO regime also leads to a loss of "irregular holes" formed due to the effect of the current distribution at growing copper surfaces. With prolonged pause duration, the pores or channels formed through the interior of the deposits were mutually coalesced, forming larger pores. In this way, the transport of electro-active species through the interior of the structures was facilitated, which is very desirable for an evaluation of electrochemical reactions.[1] Also, a decrease of the depth of the holes with the application of a PO regime can be observed. Prolonging the pause duration also leads to the appearance of dendrites in these copper structures. Dendritic particles were especially visible in the copper deposit obtained with a pause duration of 100 ms (Fig. 4). From Figs. 2 and 3, it is clear that the increase in the number of holes by the application of a PO regime cannot be only ascribed to suppressed coalescence of neighboring hydrogen bubbles, but to an improved current distribution at the growing copper surface by which the inclusion of hydrogen bubbles in the deposit was prevented. The effects observed by application of a PO regime are ascribed to the current density during the "off" periods (*i.e.*, during the duration of pause). Although this current density can be neglected in comparison with the current density during the "on" periods (*i.e.*, during the duration of the deposition pulses), it is clear that its effect on the formation of these deposits is very important.[13,14]
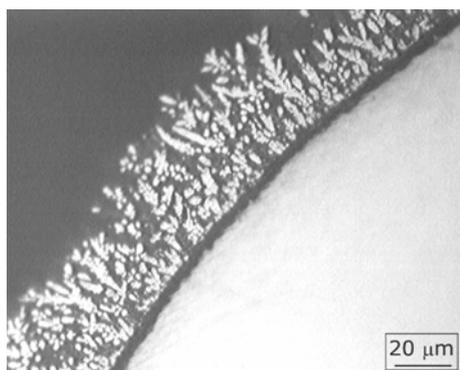
Fig. 4. Cross-section of a copper deposit electrodeposited from 0.15 M $CuSO_4$ in 0.50 M H_2SO_4 in the pulsating overpotential (PO) regime with a pause duration of 100 ms.

The formation of honeycomb-like structures is accompanied by vigorous hydrogen evolution, leading to a change in the hydrodynamic conditions in the near-electrode layer. The vigorous hydrogen evolution is only one of the possible

ways of changing the hydrodynamic conditions in the near-electrode layer. For example, a change of the hydrodynamic conditions can also be realized under imposed magnetic fields (magnetohydrodynamic effects),[15,16] in an ultrasonic field[17] or by rotating the electrode.[18] Certainly, the appearance of dendritic forms clearly indicates to a decreased effectiveness of the stirring of the copper solution by evolved hydrogen with increasing pause duration.

On the basis of the previous consideration, it is very clear that an estimation of porosity (or compactness) of deposits, the depth of holes and the size of the pores inside a structure is impossible without cross-section analysis of the deposit. This makes that cross-section analysis a necessity for a complete analysis of porous deposits.

On the other hand, the increased surface roughness at low levels of coarseness can be of interest for the polarization behavior of such electrodes. Obviously, an increased roughness at a low level of coarseness can lead to an increase of the apparent exchange current density, producing the same effect as a decrease of the reacting ion concentration, as stated in previous papers.[19,20] This will be the subject of our further investigations.

CONCLUSIONS

It has been shown that a complete analysis of honeycomb-like deposits, as potential electrodes for electrochemical devices, is impossible without the recognition of their internal structure. The pore size in the interior of a structure, the depth of both "regular" and "irregular" holes, as well as the overall compactness of a structure can only be estimated by cross-section analysis of these deposits.

И З В О Д

МОРФОЛОГИЈА ПОПРЕЧНОГ ПРЕСЕКА ПРЕВЛАКА БАКРА ДОБИЈЕНИХ ЕЛЕКТРОХЕМИЈСКИМ ТАЛОЖЕЊЕМ У ОБЛАСТИ КО-ДЕПОЗИЦИЈЕ ВОДОНИКА

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Урађена је анализа попречних пресека талога бакра добијених у области ко-депозиције водоника на константној пренапетости и режимом пулсирајуће пренапетости. Показано је да комплетна структурна анализа ових технолошки веома важних електрода није могућа без анализе њихове унутрашње структуре. Увид у компактност (или порозност) талога, као и у дубину рупа може да се добије само овим типом анализе.

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