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The effects of the pause to pulse ratio in the regime of pulsating overpotential on the formation of honeycomb-like structures

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ABSTRACT

The formation of honeycomb-like structures in the pulsating overpotential (PO) regime was examined by scanning electron microscopy (SEM). The honeycomb-like structures obtained with a square-wave PO of different pause to pulse ratios were compared to the one obtained in the constant potentiostatic regime. Increasing the pause to pulse ratio led to a decrease of the diameter of the holes formed by attached hydrogen bubbles, as well as to an increase in the number of holes formed at the surface area of copper electrodes. The size of the agglomerates of copper grains, of which the walls of the holes were constructed, was reduced with increasing duration of the pause. Also, the uniformity of the honeycomb-like structures was increased by application of the PO regime. It was shown that the effects attained by application of this regime were comparable with those obtained by electrodeposition in a constant potential regime with the addition of specific additives.

1. Introduction

Electrodeposition is a very valuable way of obtaining open porous structures of copper and copper–tin alloys with an extremely high surface area, because such structures are ideally suited for electrodes in many electrochemical devices, such as fuel cells, batteries and chemical sensors [1–3]. Such copper structures, denoted as both 3D foam [1–3] and honeycomb-like ones [4–10], are obtained at high current densities and overpotentials, where parallel to copper electrodeposition, the hydrogen evolution reaction occurs. The basic characteristics of these electrodes are: holes or pores formed due to attached hydrogen bubbles with agglomerates of copper grains among them. The walls of the holes are also very porous and they are composed of disperse agglomerates of copper grains [7] or of dendritic particles [2].

The number, distribution and pore size can be easily controlled by the choice of appropriate electrolysis parameters [7]. Increasing overpotential, decreasing concentration of Cu(II) ions and increasing concentration of H_2SO_4 as the supporting electrolyte intensifies the hydrogen evolution reaction and, consequently, the number of holes formed per mm^2 surface area of electrode is increased [5,7,10]. The average diameter of the holes increases with electrolysis time due to the growth of the hydrogen bubbles with time, as well as due to a coalescence of neighboring hydrogen bubbles. Increasing the quantity of evolved hydrogen is useful for increasing the specific surface area of these deposits, but the adhesion and compactness of the formed copper particles decrease simultaneously [2].

In order to increase the specific surface area and hence enhance the effectiveness/activity of the porous electrodes, it is necessary to reduce the size of the pores, as well as the branches in the foam or agglomerates of copper grains in the honeycomb-like structures. The microstructural characteristics of the foam structure, such as pore size and wall density, can be improved by the addition of specific substances, known as additives, to the plating solution [2]. It was shown [2] that the addition of acetic acid to the copper sulfate solution reduces the pore size in the foam structure, while the addition of chloride ions dramatically reduces the size of the copper branches. The mechanical strength of the foam structure can be improved by the addition of $(NH_4)^+$, Cl^-, polyethylene glycol and 3-mercapto-1-propane sulfonic acid to the deposition bath [11].

Thus, the microstructure of the foam structures was improved by the addition of different additives. Meanwhile, electroplating practice shows a consumption of additives during metal electrodeposition; therefore, the concentration must be corrected during the process. The consumption of additives occurs by removal with the plated objects, by their incorporation into the deposit (co-deposition) and by reaction on the plated object [12,13]. It has been known for a long time [14–16] that the use of periodically changing regimes of electrolysis, such as pulsating overpotential, pulsating and reversing current, as well as the superimposition of an

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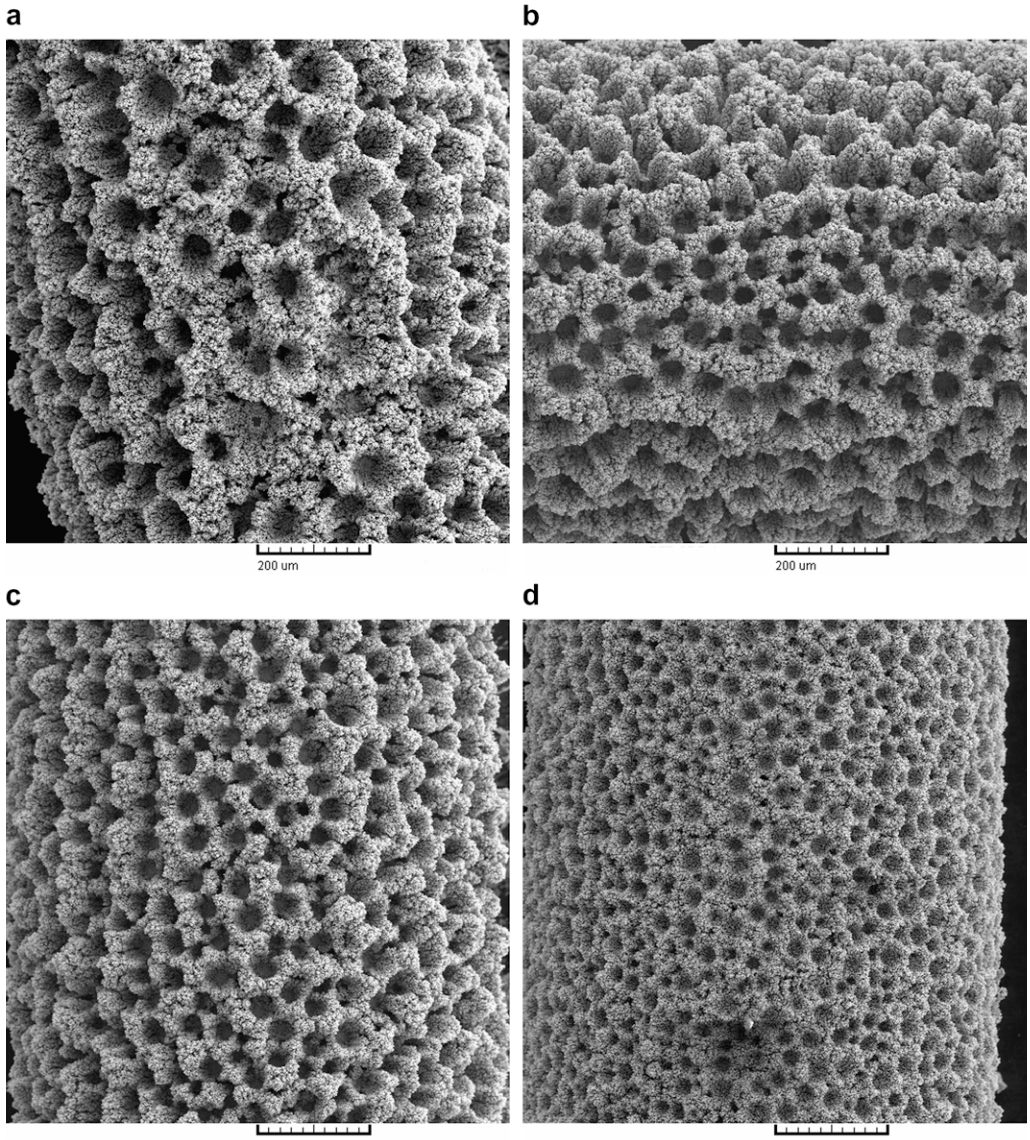

Fig. 1. Copper deposits electrodeposited from 0.15 M $CuSO_4$ in 0.50 M H_2SO_4: (a) at a constant overpotential of 1000 mV and PO regime with a pause duration of: (b) 1 ms, (c) 10 ms and (d) 50 ms.

alternating current on a direct current, can produce a similar effect on a quality of deposits to the use of additives. The aim of this paper was to examine the effect of pulsating overpotential on the formation of highly porous honeycomb-like structures.

2. 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. The 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, the overpotential amplitude was also 1000 mV. The pause to pulse ratio was varied from 0.1 to 5 with a pulse duration of 10 ms, while the pause durations were 1, 10, 20 or 50 ms. In all experiments, the geometric surface area of the copper electrode, S_o, 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 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 a quantity of electricity 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.

The obtained copper deposits were examined using a scanning electron microscope – TESCAN Digital Microscopy.

3. Results and discussion

Fig. 1 shows the SEM microphotographs of the copper deposits obtained at a constant overpotential of 1000 mV (Fig. 1a) and those obtained in the pulsating overpotential (PO) regime (Fig. 1b–d). As can be seen from Fig. 1, the honeycomb-like structures were formed in all cases. A detailed analysis of these copper deposits revealed a strong effect of the pause duration on the microstructural characteristics of the formed honeycomb-like structures. At the first sight, a decrease in the size of the holes and an increase in their number can be noticed. The dependences of the average diameter of the holes and of the number of holes formed per

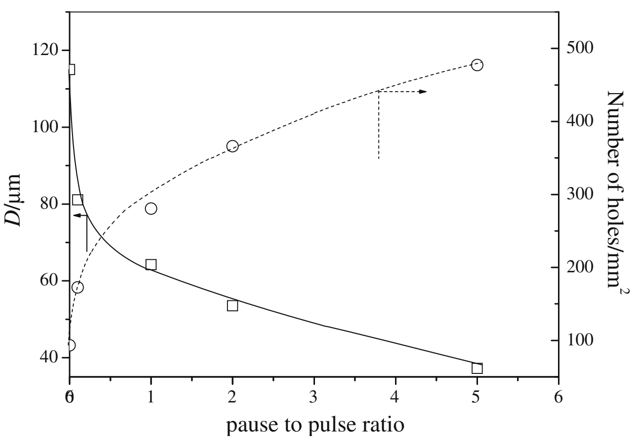

Fig. 2. The dependences of the average diameter, *D*, of the surface holes (□) and the number of holes per mm^2 surface area of the copper electrode (○) on the pause to pulse ratio.

mm^2 surface area of the copper electrodes on the pause to pulse ratio are shown in Fig. 2.

Analysis of the honeycomb-like structures also showed a decrease of the portion of holes formed by coalesced hydrogen bubbles to the overall number of formed holes with increasing pause to pulse ratio. Coalesced holes can be observed in the copper structures obtained at the constant overpotential and those obtained with pause to pulse ratios up to two. Larger pause to pulse ratios led to an inhibition of bubble coalescence. The typical holes obtained at a constant overpotential of 1000 mV and in PO regime with a pause duration of 50 ms are shown in Fig. 3a and b, respectively. Analysis of the interior of these holes showed that the size of the agglomerates of copper grains from which the hole walls were constructed was reduced with prolonged pause duration. In this way, the pores in the hole walls were increased, thus facilitating the transport of electroactive species through the interior of the structures, which is very desirable for the evaluation of electrochemical reactions. The uniformity of the honeycomb-like structures, determined by the hole size distribution and by the compactness of the agglomerates of copper grains formed among

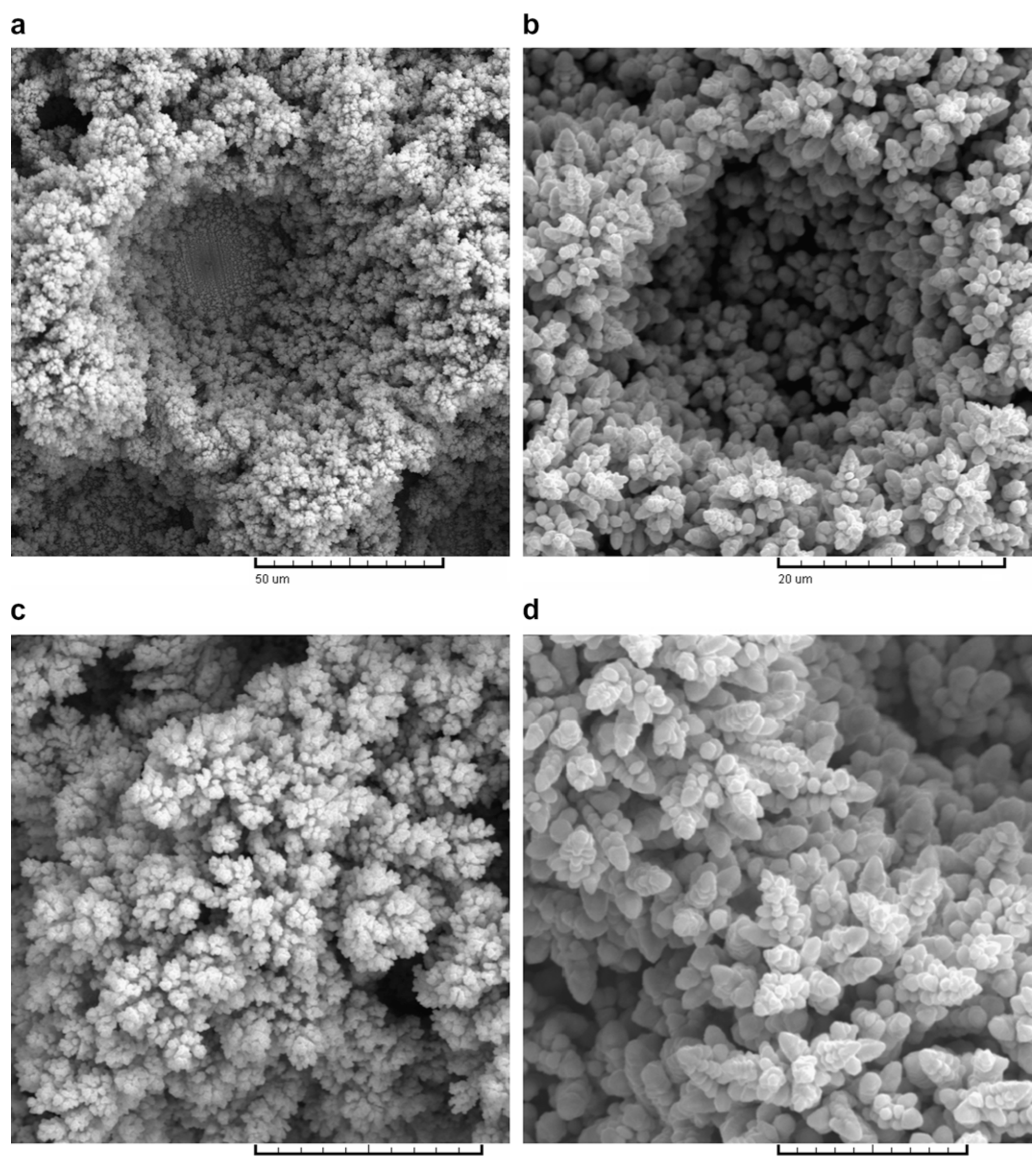

Fig. 3. Copper deposits electrodeposited from 0.15 M $CuSO_4$ in 0.50 M H_2SO_4: (a) and (c) at a constant overpotential of 1000 mV, (b) and (d) PO regime with a pause duration of 50 ms.

the holes were also increased by the application of the PO regime. By prolonging the duration of the pause, the holes approached each other, while the dispersity of the agglomerates formed among them was decreased (Fig. 3c and d, respectively).

The effect of increasing the pause to pulse ratio on the morphology of honeycomb-like copper structures can be explained as follows [16]: the formation of the initial bubbles does not occur simultaneously over the entire cathode surface, but is a process extended in time. The walls of the holes around the earlier formed hydrogen bubbles can be considerably higher than those around the latter formed ones. The higher the walls are the larger is the current density on them due to a concentration of the current lines (edge effect) [6]. Hence, the size of holes formed earlier increases faster than the size of the later formed ones and the lower holes can be consumed by the larger ones or their further growth can be prevented. The grain size of the copper electrodeposited between holes increases with increasing pause to pulse ratio due to the selective dissolution of grains during the pauses. It was shown [17] that the smaller grains would dissolve faster than the larger ones due to the Kelvin effect [18]. In addition, the structure of the grains becomes more regular with increasing pause duration due to the fact that the adatoms in non-stable positions dissolve faster than the atoms in a stable position in lattice [16]. Finally, the deposit at the shoulders of the holes dissolve faster due to the edge effect, which also leads to the formation of a more homogenous distributed deposit with increasing pause duration and to an increased number of less deep holes.

The quantity of evolved hydrogen which led to the formation of honeycomb-like structures at an overpotential of 1000 mV corresponded to an average current efficiency of hydrogen evolution of 30.0% [4]. The evolved hydrogen was sufficient to cause an effective stirring of the solution, thus decreasing the thickness of the cathode diffusion layer and increasing the limiting diffusion current density, and, consequently, leading to a change of hydrodynamic conditions in the near-electrode layer. The additional stirring of a solution by some external source, such as a magnetic field, ultrasound, rotating disc electrode, would probably revoke the positive effect of evolved hydrogen on the formation of this structure type.

Hence, it is very clear that the specific surface area of copper electrodes (determined by the sizes of the holes and agglomerates of copper grains in the walls of holes) increased with increasing pause to pulse ratio. The compactness of the agglomerates of copper grains formed among the holes was also increased. The effects of the application of the PO regime on the microstructural characteristics of the honeycomb-like structures were comparable with those obtained by electrodeposition in the constant potential regime in the presence of additives. In this way, electrodeposition in the presence of additives can be successfully replaced by electrodeposition from a basic solution by the use of periodically changing regimes of electrolysis, such as pulsating overpotential. This substitution is very important, as difficulties may arise from the use of additives in electroplating processes (permanent control of electroplating solution because of consumption of the additives, the possibility of contamination of the solution,...).

4. Conclusions

The effects of a regime of pulsating overpotential (PO) on the formation of the honeycomb-like structure were examined using scanning electron microscopy. The following parameters of a square-wave PO were employed: an amplitude overpotential of 1000 mV, a deposition pulse of 10 ms and pause durations of 1, 10, 20 and 50 ms (pause to pulse ratio were 0.1, 1, 2 and 5, respectively). The obtained honeycomb-like structures were compared with the one obtained at a constant overpotential of 1000 mV.

It was shown that the coalescence of neighboring hydrogen bubbles can be prevented by application of the PO regime. The number of holes formed due to the attached hydrogen bubbles increased, while their average diameter decreased with prolonged durations of the pause. A prolonged duration of the pause reduced the size of the copper agglomerates from which the hole walls were constructed. The uniformity of the honeycomb-like structures was also increased by application of the PO regime.

On the basis of the observed effects of the PO regime, it can be concluded that electrodeposition in the presence of additives can be successfully replaced by the choice of an appropriate square-wave PO.

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