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Phenomenology of a formation of a honeycomb-like structure during copper electrodeposition

N. D. Nikolić · K. I. Popov · Lj. J. Pavlović ·
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Abstract In this paper, the phenomenology of a formation of a honeycomb-like structure was considered. Copper deposits obtained at overpotential of 1000 mV were examined by scanning electron microscopy (SEM) technique. It was shown that two groups of craters or holes were formed by the electrodeposition at this overpotential. The origin of one group is associated with hydrogen evolution and the attachment of hydrogen bubbles at the surface area of an electrode. For the origin of the other group, a current distribution at the growing surface was very important. The effect of preparing a working electrode onto the formation of a honeycomb-like structure is also considered.

Keywords Electroplating · Scanning electron microscopy (SEM) · Copper · Hydrogen evolution · Crater or hole

Introduction

It was shown recently [1] that electrodeposition at high overpotentials, at which the process of copper electrodeposition was competitive with the process of hydrogen evolution (in the examined system it was at overpotentials of 800 mV and larger ones), led to a formation of copper deposits with an extremely high surface area. The main characteristics of these copper deposits were craters or holes formed primarily due to the attachment of hydrogen bubbles and to agglomerates of copper grains between them. These copper deposits were denoted as a honeycomb-like structure. In addition, an analysis of the shape, size and distribution of these craters or holes obtained by a potentiostatic electrodeposition at overpotential of 1000 mV at cylindrical copper electrodes, which were firstly covered with a thin copper film through electrodeposition at overpotential of 300 mV for 2 min, was done [2].

Then, it was discussed that morphologies of copper deposits with the stated characteristics could probably be used as electrodes in many electronic devices, such as fuel cells, batteries and sensors [3]. Furthermore, copper electrodes with extremely high surface area are probably relevant for evaluating some electrochemical reactions. For example, it was known that copper shows a high activity for nitrate ion reduction [4] as well as for a reaction in which nitrate reduces to ammonia in high yield in aqueous acidic perchlorate and sulphate media [5].

Having in view the possibility of a practical application of copper deposits with a high developed surface area as electrodes for solid oxide fuel cells and for evaluating electrochemical reactions, it is necessary to better understand the formation of this copper structure. For that reason, the subject of this paper will be an analysis of the formation of a honeycomb-like structure.

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Experimental

Copper was potentiostatically deposited from 0.15 M $CuSO_4$ in 0.50 M H_2SO_4, in an open cell, and at a room temperature of (18.0 ± 1.0) °C. A doubly distilled water and analytical grade chemicals were used for the preparation of

the solution for electrodeposition of copper. Reference and counter electrodes were of a pure copper.

The electrodepositions of copper were performed onto cylindrical copper electrodes at overpotential of 1000 mV. The diameter and the surface area of copper electrodes were 0.15 cm and 0.50 cm^2, respectively. The following times of electrodepositions were applied: 10, 30, 60, 120 and 150 s.

In addition, copper was electrodeposited at the over-potential of 1000 mV onto a cylindrical copper electrode, which was firstly covered with a thin copper film through electrodeposition at overpotential of 300 mV from the same copper plating solution for 2 min. The time of electrode-position was 10 s. The specification of experimental procedure for a formation of this working electrode was given in [2, 6, 7].

Copper deposits were examined by the scanning electron microscopy (SEM) JOEL T20 model.

Results and discussion

Figure 1 shows the dependence of the current density of electrodeposition, i, on electrodeposition time, t, for over-potential of electrodeposition of 1000 mV. At this over-potential, the process of copper electrodeposition is competitive with the process of hydrogen evolution. The average current efficiency of hydrogen evolution is 30.0% [1]. Morphologies of copper deposits corresponding to electrodeposition times of 10, 30, 60, 120 and 150 s were analysed by the SEM technique. Figures 2, 3, 4, 5, 6 and 7 show SEM microphotographs of copper deposits obtained with the stated electrodeposition times.

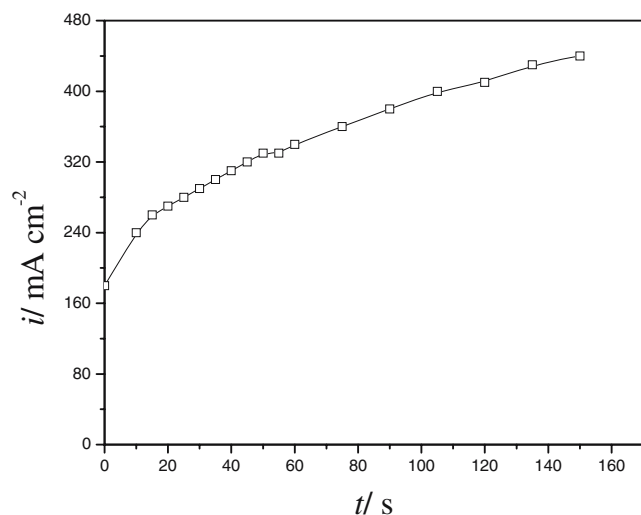The initial stage of the electrodeposition at the over-potential of 1000 mV corresponding to the electrodeposi-tion time of 10 s is given in Fig. 2a–d. The parallelism between the process of the copper electrodeposition and the hydrogen evolution can be easily seen in Fig. 2a. From this figure, both the sites of the formation of hydrogen bubbles (i.e. sites at which the hydrogen evolution starts) and the agglomerates of copper grains between them can be noticed.

It can be seen from Fig. 2b that the hydrogen evolution is initiated at irregularities at an electrode surface. The irregularities at an electrode surface represent the most convenient sites for the beginning of hydrogen evolution, i.e. for the formation of hydrogen bubbles. The true position of the formation of a hydrogen bubble can be seen from Fig. 2c showing a bare part of the copper electrode (part in cycle in Fig. 2c).

The mechanism of formation of bubbles at an electrode has been described for a long time [8–11]. The gas formed at the electrode dissolves in the electrolyte, which becomes supersaturated. At the nucleation sites on the electrode, small bubbles are formed, grow to a certain size and are then detached. The higher the current density, the more the solution becomes saturated; more and more nucleation sites become active, and also the rate of growth of the bubbles increases [8]. Jenssen and Hoogland [8] also pointed out that at lower current densities, only the irregularities at the edges (formed by the cutting of the foil) are active, and the amount of bubbles formed at the lower edge is sufficient to take up all the hydrogen formed. This is no longer the case at higher current density, and then bubbles are also formed at the less deformed surface.

Figure 2d shows typical agglomerates consisted of relatively small copper grains (parts in ellipses in this figure). The different size and periodicity of agglomerates of copper grains can be explained as follows: It was assumed [12] that the active centres have different activity or different critical overpotential with respect to the formation of nuclei. The nuclei can be formed on those centres whose critical overpotential is lower or equal to the overpotential externally applied to the cell. The higher the applied overpotential, the greater the number of active sites takes part in nucleation process. The active sites are mainly placed on the irregularities at an electrode surface [13], as can be seen in Fig. 2b. On the other hand, nucleation does not occur simultaneously over the entire cathode surface, but it is a process extended in time so that crystals generated earlier may be considerably larger in size than the ones generated later. Besides, in the case of fast electrodeposition processes, the nucleation exclusion zones around already existing nuclei are formed [14, 15], and in the case of the slower ones, there is an effect on the nucleation rate distribution around growing grains [16, 17]. This causes the periodicity in the surface structure of polycrystalline electrolytic deposits [18–20].

Fig. 1 The dependence of the current density of electrodeposition on the time of electropositon, for the electrodepositon at 1000 mV

Fig. 2 Copper deposit obtained at overpotential of 1000 mV. Time of electrolysis, 10 s. Magnification: **a** ×2,000, **b** ×750, **c** ×5,000, **d** ×5,000
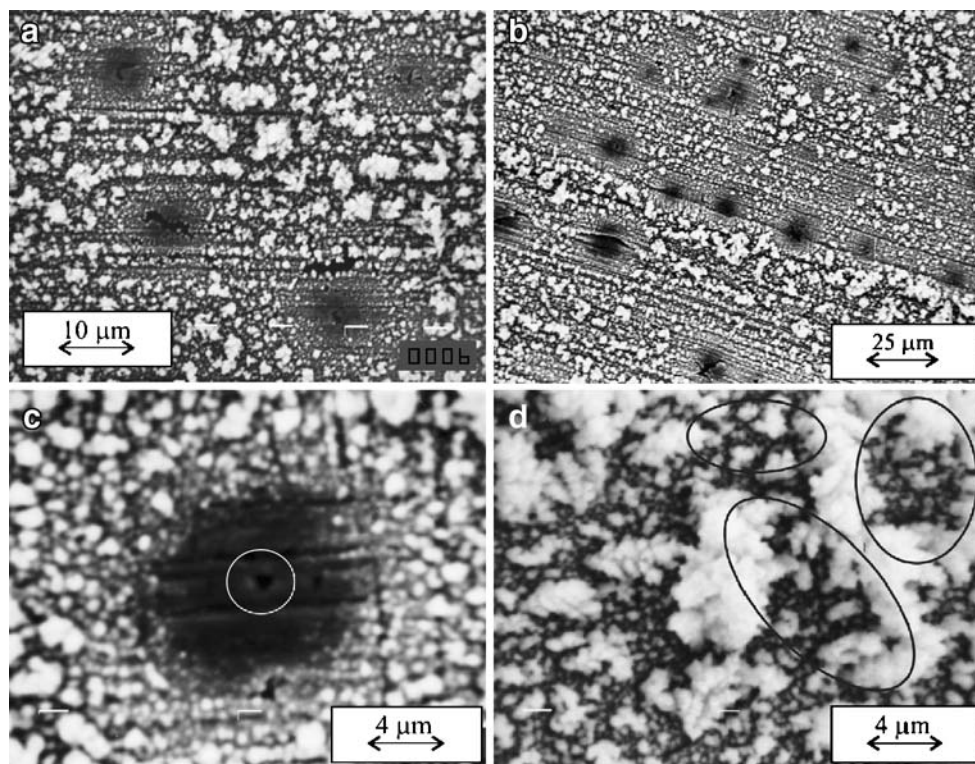
The copper deposit obtained with the electrodeposition time of 30 s is given in Fig. 3, from which can be seen two characteristic groups of holes or craters. The origin of one group of holes is of the attachment of hydrogen bubbles at surface area of an electrode. These holes have regular circular shapes and, in Fig. 3, they are given in cycles. The second group of holes have irregular shapes, and these holes are given in ellipses in Fig. 3. The formation of these irregular craters is not associated with the process of hydrogen evolution, and it can be assumed that the origin
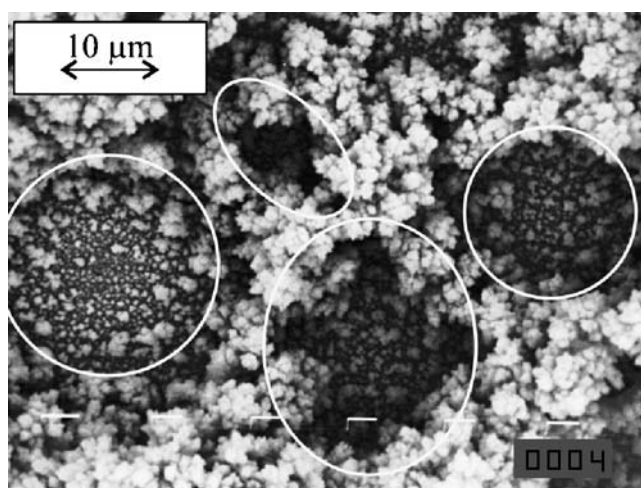

Fig. 3 Copper deposit obtained at overpotential of 1000 mV. Time of electrolysis, 30 s. Magnification, ×2,000

of these holes is of the agglomerates of relatively small copper grains shown in Fig. 2d. However, in Fig. 3, it can be seen that the copper electrodeposition process with the electrodeposition time of 30 s led to the formation of a honeycomb-like structure.

The formation of both groups of craters or holes, which make the honeycomb-like copper structure, will be discussed. The formation of craters or holes as a consequence of the hydrogen evolution can be explained by the analysis of Figs. 2a,c and 3 in the following way: In the initial stage of the electrodeposition, hydrogen bubbles are formed at active sites at an electrode surface (Fig. 2a,b), and copper growth is blocked at these sites. These hydrogen bubbles grow with a time of electrodeposition, and in one moment, they get detached from an electrode surface realising a fresh electrode surface for a new copper nucleation. This can be seen from Figs. 2c and 3, showing a bare copper electrode at a position where the formation of a hydrogen bubble begins (Fig. 2c) and a position of already formed hole covered with a thin copper film (parts in cycles in Fig. 3). Craters or holes formed in this way show regular circular shapes. However, the processes of the formation of hydrogen bubbles at active sites, their detachment from an electrode surface when critical size is reached as well as their repeated formation at growing electrode represent successive steps that led to the formation of this type of holes. The typical crater or hole formed due to the attachment of hydrogen bubbles (regular hole), which is
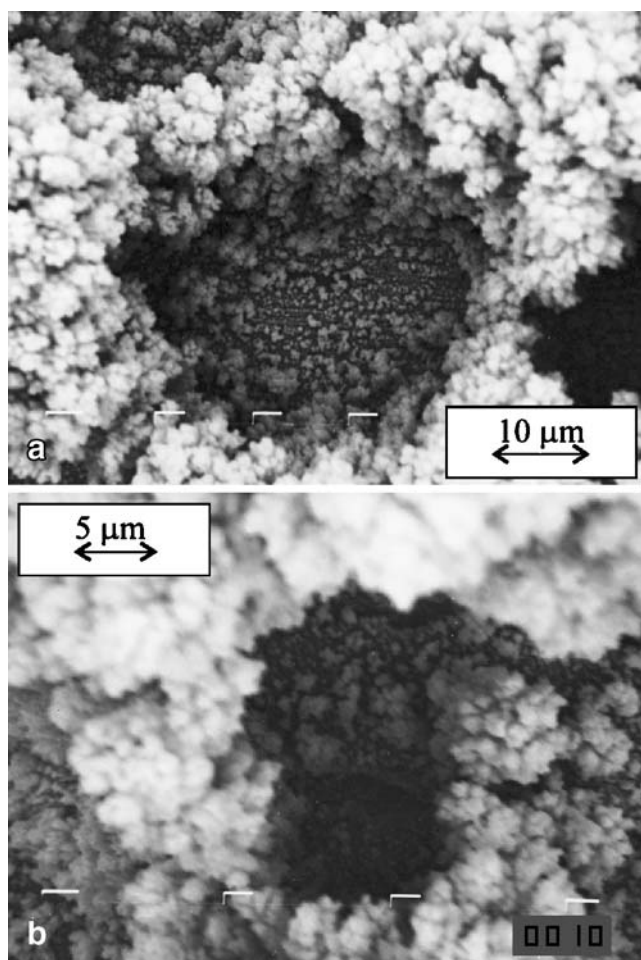
Fig. 4 Copper deposit obtained at overpotential of 1000 mV. Time of electrolysis, 60 s. Magnification: **a** ×2,000, **b** ×3,500

processes at lateral sides of the agglomerates and enhancing the nucleation processes at the top of the agglomerates. In addition, these agglomerates initiate walls, which will limit the growth of hydrogen bubbles. Hence, as a result of all these parallel processes, holes of "irregular" shapes are formed. These holes are situated among those formed due to the attachment of hydrogen bubbles, and these craters are deeper that those obtained due to the attachment of hydrogen bubbles. The typical "irregular hole" is given in Fig. 4b, presenting a hole obtained with the electrodeposition time of 60 s.

Mechanisms describing the formation of holes of this type are based on the amplification of electrode surface coarseness [21, 22] in diffusion-controlled electrodeposition and to the tip [23] and edge [24] effects of current density distribution at electrode surface. More about these mechanisms can be found in [25].

However, the origin of these holes is the agglomerates of copper grains formed in the initial stage of electrodeposition process. Meanwhile, the final shape of these holes is
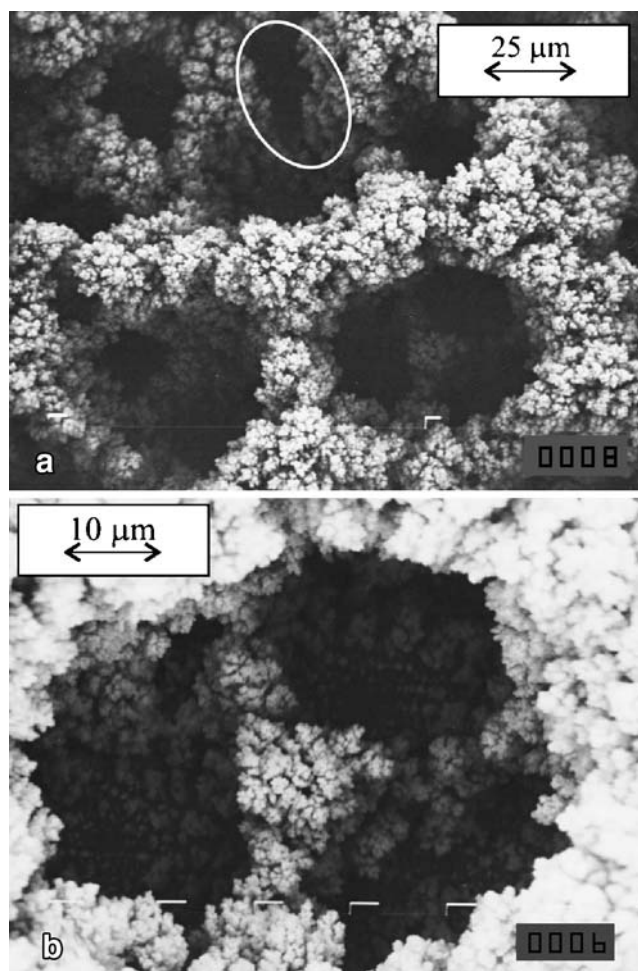
obtained with the electrodeposition time of 60 s, is shown in Fig. 4a.

The explanation for the formation of the second group of craters can be given as follows: As already pointed out, at the overpotential of 1000 mV, the process of hydrogen evolution is competitive with the process of copper electrodeposition. As a consequence of a parallel evaluation of these processes, both the sites of a formation of hydrogen bubbles and the agglomerates of copper grains between them were obtained (Fig. 2). The agglomerates of these copper grains exactly represent nucleation centres for the formation of craters or holes belonging to the other group (parts in ellipses in Fig. 2d). The further electrolysis process leads to copper nucleation and growth primarily at these agglomerates owing to the concentration of current lines at them, which will lead to a joining closely formed agglomerates and a formation of hole in one moment. This effect of current distribution at growing surface will be enhanced by the additional physical blocking of copper growth by the hydrogen bubbles preventing nucleation

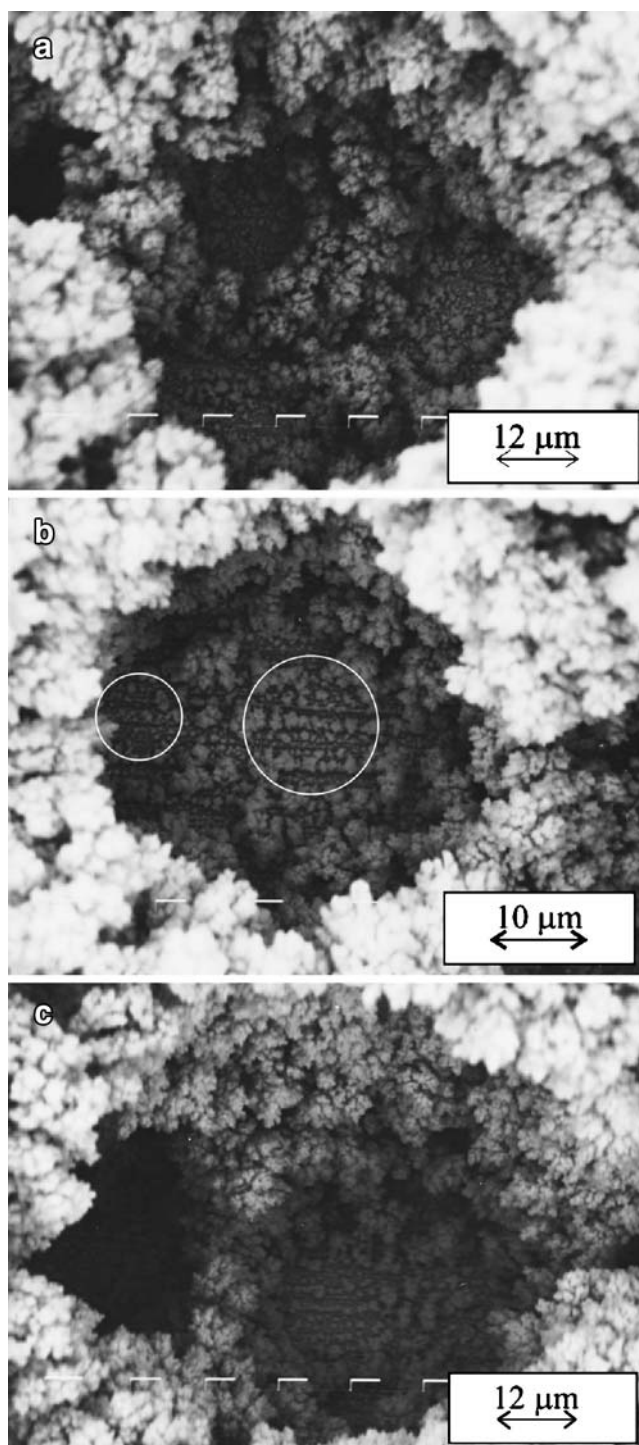Fig. 5 Copper deposit obtained at overpotential of 1000 mV. Time of electrolysis, 120 s. Magnification: **a** ×750, **b** ×2,000

Fig. 6 Copper deposit obtained at overpotential of 1000 mV. Time of electrolysis, 150 s. Magnification: **a** ×1,500, **b** ×2,000, **c** ×1,500

this way are larger than those formed by individual hydrogen bubbles. The number of craters formed of coalesced hydrogen bubbles increases with electrolysis time. The typical crater formed in this way is given in Fig. 5, presenting the morphology of the copper deposit obtained at 1000 mV with a time of electrolysis of 120 s. In Fig. 5a, it can be seen that a structure of craters or holes formed of coalesced hydrogen bubbles consisted of smaller holes which were mutually separated by a "bridge" of copper agglomerates as can be seen in Fig. 5b, showing the hole from Fig. 5a at higher magnification. It can be seen from this figure that the agglomerates of copper grains that separate smaller holes inside a large hole are at a lower level than the agglomerates of copper grains around a large hole. However, the formation of this hole is a consequence of a coalescence of closely formed hydrogen bubbles. In the growth process, closely formed hydrogen bubbles do not have enough place to develop, and then these hydrogen bubbles mutually coalesce constituting a large hole. On the other hand, the presence of holes formed from initially formed copper agglomerates can also be noticed (part in ellipse in Fig. 5a).

The morphologies of the copper deposits obtained at the overpotential of 1000 mV with electrolysis time of 150 s are shown in Fig. 6. Electrodeposition process with this electrolysis time led to the formation of three characteristic classes of craters or holes, which are given in Fig. 6a–c.

The first class represents a crater or a hole shown in Fig. 6a. The origin of this class of craters is from the attachment of hydrogen bubbles. It can be noticed in Fig. 6a that some of the bottoms of the small holes inside the large hole are not at the same level. This points out the continuity of the processes of formation, mutually coalescence and detachment of hydrogen bubbles.

On the other hand, the formation of two, very close to each other, hydrogen bubbles (parts in cycles in Fig. 6b) leads to their coalescence in the initial stage, and as a result of this process, large and very deep craters are formed (Fig. 6b). Craters or holes formed on this way belong to the second class of the formed craters.

The third class of craters are craters obtained by a coalescence of the holes formed due to the attachment of hydrogen bubbles and those of the initially formed copper agglomerates. Hence, this class of craters represents a combination of both groups of craters, i.e. those formed due to the attachment of hydrogen bubbles and of an initially formed copper agglomerates. This class of holes is shown in Fig. 6c. However, for the formation of this class of holes, except the effect of hydrogen evolution, current distribution at growing surface is very important.

The electrodeposition process of 150 s did not lead to a significant change of diameters of the formed craters with respect to the ones obtained with the electrolysis time of

determined by the effect of current distribution at growing surface, which is enhanced by physical blocking of copper surface by the growing hydrogen bubbles.

With the evaluating electrodeposition process, closely formed hydrogen bubbles mutually coalesce forming a new hydrogen bubble. The diameters of the craters formed in

Fig. 7 Copper deposits obtained at overpotential of 1000 mV. Magnification, ×150. Time of electrolysis: **a** 10 s, **b** 30 s, **c** 60 s, **d** 120 s, **e** 150 s
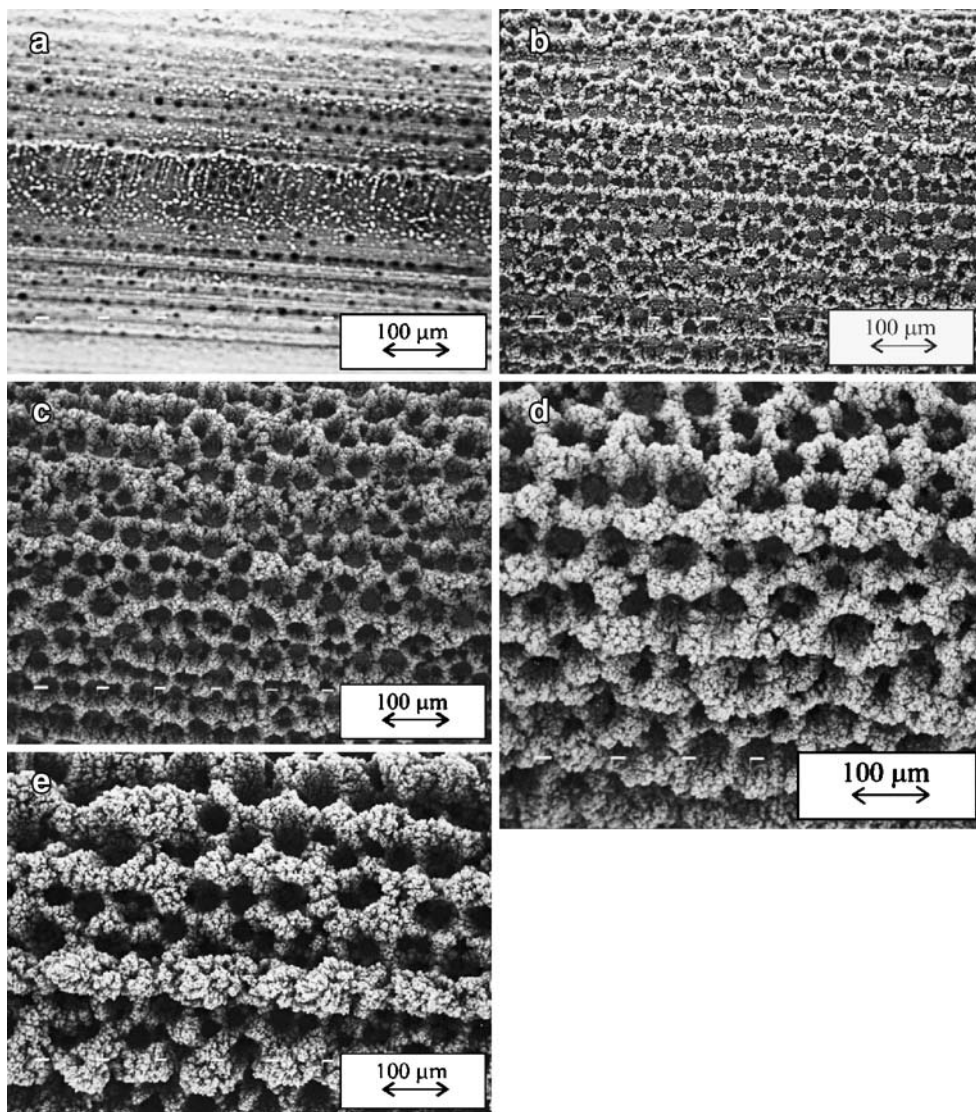
120 s. It was noticed that a considerable decrease in the number of craters formed from an initially formed copper agglomerates with respect to the number of these craters was obtained with lower times of electrolysis. This decrease is a consequence of a current distribution at the growing surface, which leads to the closing of the structure of this type of craters with electrolysis time, as well as the fact that these craters mainly become a part of some large holes (Fig. 6c).

The decrease in a number of craters per surface area of copper electrode can be easily observed in Fig. 7, showing morphologies of copper deposits obtained with times of electrolysis of 10, 30, 60, 120 and 150 s. As already mentioned, this decrease is a consequence of the increase in diameters of craters formed due to the attachment of hydrogen bubbles owing to the growth of hydrogen bubbles with a time of electrolysis, as well as of a coalescence of a closely formed hydrogen bubbles with longer times of electrolysis. On the other hand, the number of craters

formed of an initially formed copper agglomerates also decreases with electrolysis times, and it can be expected that these craters will completely disappear with a longer time of electrolysis. This is due to the current distribution at a copper growing surface; i.e. the fact that a new copper nucleation and growth primarily takes place at the edges of these holes, which will lead to totally closing and losing of craters or holes from this group with longer electrolysis times. In this way, only the craters or holes formed due to the hydrogen evolution will remain at a surface area of electrode.

Figure 8 shows the dependence of average diameters of craters or holes, D, formed due to the attachment of hydrogen bubbles on electrolysis time, from which the increase in average diameters of holes with the electrolysis time can be clearly seen. The dependences of the number of craters or holes formed due to the attachment of hydrogen bubbles per mm^2 surface area (regular holes) and those formed due to the effect of current distribution (irregular
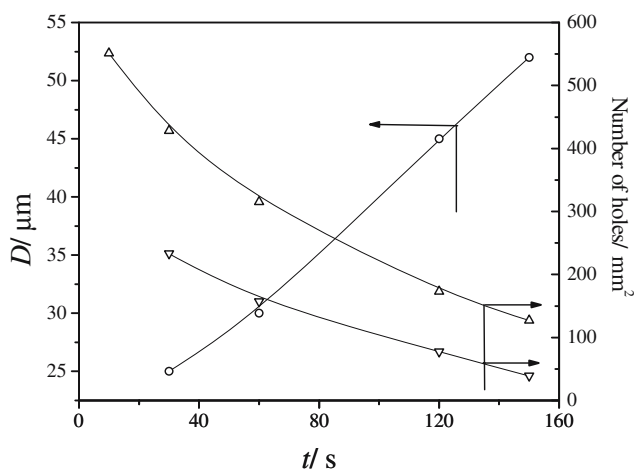
Fig. 8 The dependence of average diameters of the surface holes, D (*open circles*), number of "regular holes" per mm^2 surface area of copper electrodes (*open triangles*) and number of "irregular holes" per mm^2 surface area of copper electrodes (*inverted open triangles*) on electrolysis times

holes) on the electrolysis time are also shown in Fig. 8. The decrease in the number of both groups of craters or holes can be observed in this figure.

The logarithm of the number of "regular holes" per mm^2 surface area of copper electrode as a function of electrolysis time gives the straight line, which points out that the decrease in number of holes with electrolysis time follows the first order reaction low. This can be very useful in the determination of the mechanism of the formation and growth of holes during metal electrodeposition in the presence of hydrogen evolution, as well as in the investigation of the different parameters that affects the honeycomb-like copper structure formation.

Analysing the data in Fig. 8 and comparing with the same dependences given in our recent investigation [2], we can notice that average diameters of craters formed at cylindrical copper electrodes were about two times smaller than those obtained by electrodeposition onto copper electrodes previously covered with a thin copper film. On the other hand, the number of the formed craters per mm^2 surface area (regular holes) was approximately five to ten times larger than the number of craters per mm^2 surface area obtained by electrodeposition onto copper electrodes with uniform thin copper films.

The obtained differences clearly point out the significance of preparing a working electrode for electrodeposition processes at high overpotentials, at which there is a parallelism between the process of the copper electrodeposition and the hydrogen evolution. The observed differences in average diameters of the formed holes or craters as well as in the number of the formed craters or holes can be explained as follows: In this case, electrodepositions were performed onto copper electrodes without a previous

formation of uniform thin copper films. The surface area of these electrodes consisted of a large number of irregularities, which presented active sites, i.e. the most convenient sites for the formation of hydrogen bubbles. In the initial stage of electrodeposition process, relatively a large number of hydrogen bubbles is formed at these active centres, and during the electrodeposition process, craters or holes (i.e. honeycomb-like structure) are developed from these active centres. Because there is a large number of active centres situated closely to each other, which represent the "nuclei" for the formation of craters or holes, the formed craters will not have enough place to develop, and as a consequence, a honeycomb-like structure with a large number of craters or holes and of a relatively small diameter is formed.

On the other hand, the majority of the active centres was "killed" by the electrodeposition of uniform thin copper films at the overpotential of 300 mV [2]. Then, a higher energy is needed for the formation of hydrogen bubbles and, consequently, a smaller number of hydrogen bubbles is formed in the initial stage of electrodeposition. The formed hydrogen bubbles will not be excessively close to each other, and they will have enough space to develop at an electrode surface. The initial stage of the electrodeposition onto the copper electrode previously covered with uniform thin copper films is shown in Fig. 9. It can be seen in Fig. 9 that a smaller number of random oriented hydrogen bubbles is formed when electrodeposition was performed onto copper electrodes with "killed" active centres than onto copper electrodes without previous electrodeposition of thin copper films (Fig. 2). As a result of this process, a smaller number of craters or holes with larger diameters are formed than in the case of electrodeposition onto electrodes with active centres.
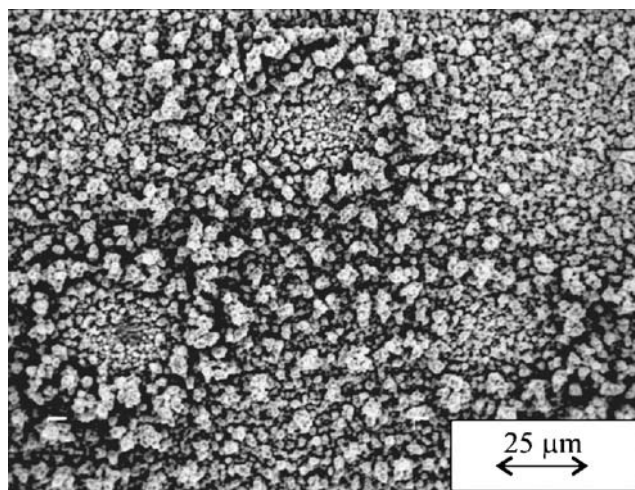

Fig. 9 Copper deposit obtained at overpotential of 1000 mV at the working electrode previously covered by copper thin film. Time of electrolysis, 10 s. Magnification, ×750

It is necessary to note that the grains of which copper agglomerates are made were smaller for copper deposits obtained by the electrodeposition onto electrodes with larger number of active centres than for ones obtained onto electrodes with smaller number of active centres. Of course, this difference is associated with a different distribution of the formed hydrogen bubbles onto electrodes with different number of active centres. The increase in the number of hydrogen bubbles at an electrode surface will lead to a change of current distribution at the growing copper surface and, consequently, up to a decrease in the size of copper grains.

However, it can be seen from a previous discussion how the preparation of working electrode affects the size and distribution of the formed craters or holes. In this way, it is possible to get electrodes with larger or smaller diameters of holes, or with larger or smaller number of holes per surface area unit.

In this work, during electrolysis process, the direction of depositing copper (II) ions was oriented vertically to the direction of the gravitational force. The same honeycomb-like structure, but with bad distribution of craters or holes, is obtained when the direction of depositing copper (II) ions is oriented parallel to the direction of the gravitational force. The formation of a honeycomb-like structure on flat copper electrodes leads to the slight increase in the diameter of the formed craters or holes with respect to those formed onto cylindrical copper electrodes.

The formation of the honeycomb-like structure was recently explained by the concept of "effective over-potential" [1]. According to this concept, evolved hydrogen changes hydrodynamic conditions in the near-electrode layer, and then the electrodeposition process takes place at an overpotential which is effectively lower than the specified one. For that reason, this overpotential is denoted by "effective overpotential" of electrodeposition process. This effect is due to the increase in the limiting diffusion current density, and hence a decrease in degree of diffusion control due to a change of hydrodynamic conditions caused by evolved hydrogen. Then, the obtained metal morphologies are, at macro level, similar to the ones obtained at some lower overpotentials where the hydrogen evolution do not exist.

It seems that the phenomenology of copper electrodeposits formation in the presence of hydrogen codeposition is well done in this paper. Besides, the previous papers [1, 2] and this one represent the first sight in elucidation of the effect of hydrogen codeposition on the morphology of electrodeposited metals. During electrodeposition of some metals (nickel and cobalt, for example), the hydrogen is evaluated with relatively large current efficiencies, especially if they are deposited in the disperse form. It is necessary to note that the morphology of nickel and cobalt powder particles [26] is very similar to that of copper as presented in this paper. This means that regardless of the specific properties of each metal, there is an effect of hydrogen evolution, which makes the morphologies of different metals similar to each other. This is a very important conclusion which permits that the results of further investigations performed on copper electrodeposition can be generalized for all metals electrodeposited in similar conditions.

The electrodeposition of copper is the most suitable process for the elucidation of the mechanisms of the effect of hydrogen evolution on the morphology of deposits. This is because of the existence of the limiting diffusion current density overpotential region in which there is no hydrogen evolution and a region of overpotential in which hydrogen codeposition takes place with remarkable current efficiencies. These two regions of overpotentials are separated by critical value of overpotential for initiation of hydrogen evolution. This value varies with electrodeposition bath composition. This probably permits the comparison of the morphologies of copper electrodeposits obtained from different solutions at the same value of overpotential in the absence and in the presence of hydrogen codeposition.

Conclusions

Morphologies of copper deposits obtained at the overpotential of 1000 mV at which copper electrodeposition process was competitive with hydrogen evolution process were examined by the SEM technique.

Copper deposits with a very high surface area were obtained by the electrodeposition at this overpotential. The obtained copper structures were denoted as honeycomb-like structures. The main characteristics of a honeycomb-like structure are the presence of craters or holes, and it established a double origin of the formation of these craters or holes.

One group of craters or holes were craters formed due to the attachment of hydrogen bubbles as a result of the intensive hydrogen evolution at this overpotential. These craters had regular circular shapes. The diameter of these craters increased with a time of electrolysis due to the growth of hydrogen bubbles with electrolysis time, as well as of a coalescence of a closely formed hydrogen bubbles.

The origin of the other group of craters or holes is of the agglomerates of copper grains formed in the initial stage of electrodeposition. These craters had irregular shapes. Current distribution at growing surface of copper electrode was very important for the formation of craters or holes in this group.

The three classes of craters were formed by the combination of these groups of craters or holes for longer electrolysis times.

Furthermore, it was considered how the preparation of a working electrode affects the shape, size and distribution of craters or holes formed onto the growing surface of electrode.

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