

Fundamental aspects of copper electrodeposition in the hydrogen co-deposition range

This a review paper considering fundamental aspects of copper electrodeposition at high overpotentials where parallel to copper electrodeposition, hydrogen evolution reaction occurs. The two types of copper deposits are formed in the hydrogen co-deposition range: (a) the open and porous structures denoted as the honeycomb-like ones, and (b) powdered deposits. Phenomenology of the formation of the honeycomb-like structure, as well as factors affecting the formation of this type of structure are described in detail. The increase of the specific surface area of the honeycomb-like structure by the application of the periodically changing regimes of electrolysis, such as pulsating overpotential (PO) regime is considered. Correlation between the shape of copper powder particles and the quantity of evolved hydrogen by which they are formed was also presented.

1. BASIC FACTS

Irregular copper deposits are formed by electrodeposition at high current densities and overpotentials where parallel to copper electrodeposition process, hydrogen evolution reaction occurs. Two types of copper deposits are formed in hydrogen co-deposition range: a) open and porous structures with extremely high surface area, known as 3-D foam or honeycomb-like ones, and b) powdered deposits.

The most often employed electrolytes for the electrodeposition of copper are those based on aqueous solutions of sulfuric acid (H_2SO_4) and cupric sulfate (CuSO_4) [1]. There is an ionic equilibrium of a lot of species, such as bisulfate ions (HSO_4^-), cupric ions (Cu^{2+}), aqueous cupric sulfate ($\text{CuSO}_{4(\text{aq})}$), hydrogen ions (H^+), and sulfate ions (SO_4^{2-}), in the $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ system [2 – 4]. Pitzer's model [5] was used to calculate the ionic equilibrium of these species over a wide range of concentrations and temperatures [4]. Using this model, the dependence of the relative concentration of hydrogen ions (H^+) on H_2SO_4 concentration for different copper concentration is done and it was shown that increasing the copper concentration produces a sharp decrease in the hydrogen ion concentration, while increasing the concentration of sulfuric acid produces an increase in the hydrogen ion concentration (see Fig. 9 in Ref. [4]). Due to parallel evaluating of both copper electrodeposition and hydrogen evolution at high current densities and overpotentials, electrodeposition processes in the hydrogen co-deposition range are very suitable for experimental verification of this ionic equilibrium [6, 7].

In potentiostatic regimes of electrolysis, hydrogen evolution, as the second reaction, starts at some overpo

tential belonging to the plateau of the limiting diffusion current density. Increasing overpotential intensifies hydrogen evolution reaction, and at some overpotential outside the plateau of the limiting diffusion current density, hydrogen evolution becomes vigorous enough to change hydrodynamic conditions in the near-electrode layer [8]. For example, for copper solution containing 0.15 M CuSO_4 in 0.50 M H_2SO_4 , the plateau of the limiting diffusion current density corresponds to overpotentials between 350 and 750 mV. Cauliflower-like agglomerates of copper grains were formed at an overpotential of 550 mV, where there was no hydrogen evolution. Very branchy copper dendrites were formed at an overpotential of 700 mV where hydrogen evolution was very small, and corresponded to the average current efficiency of hydrogen evolution of about 2.0%. The open and porous structures, denoted as honeycomb-like ones, were formed at overpotentials of 800 and 1000 mV which were about 50 and 250 mV outside the plateau of the limiting diffusion current density. The average current efficiencies of hydrogen evolution by which these honeycomb-like structures are formed were: 10.8% at an overpotential of 800 mV, and 30.0% at an overpotential of 1000 mV [8]. The main characteristics of this structure type are: holes or pores formed by attached hydrogen bubbles and agglomerates of copper grains formed around them. The concept "effective overpotential" was proposed to explain the formation of this type of structure. According to this concept, when hydrogen evolution is vigorous enough to change hydrodynamic conditions in the near-electrode layer, then, electrodeposition process occurs at some overpotential which is effectively lower than the specified one. This overpotential is denoted by "effective overpotential" of electrodeposition process. Irregular copper deposits formed in the hydrogen co-deposition range are of very developed surface area, and the new method for the estimation of their specific surface area was proposed [9].

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2. OPEN AND POROUS STRUCTURES (3D-FOAM OR HONEYCOMB-LIKE ONES)

Investigation of formation of open and porous structures by electrodeposition processes was initiated by Shin *et al.* in 2003 [10 – 12]. As already mentioned, the main characteristics of this structure type are holes or pores formed by attached hydrogen bubbles which can be surrounded not only by agglomerates of copper grains but also by dendritic particles. Due to very high surface area of these structures, they are very suitable to be used as electrodes in many electrochemical devices, such as fuel cells, batteries and chemical sensors [10 – 12], as well as in catalysis [13].

The way of preparing of porous electrodes by electrochemical deposition processes is denoted as gas bubble dynamic template method, where the hydrogen bubbles function as a dynamic template for the formation of this type of electrodes. The advantage of producing of porous materials by this hydrogen bubble dynamic template method compared with hard template methods, such as porous polycarbonate membranes [14, 15], anodic alumina membrane [16 – 18], colloidal crystals [19, 20], echinoid skeletal structures [21] and polystyrene spheres [22, 23], is in low cost, ease of preparation, facile control of structure, and facile one-step synthesis process, including preparation of the template, metal deposition, and elimination of the template [24].

2.1. Phenomenology of formation of the honeycomb-like structures

Formation of the honeycomb-like electrodes can be briefly considered as follows: in the initial stage of the electrodeposition process, both nuclei of deposited metal and “nuclei” of hydrogen bubbles are formed at the active sites of the electrode surface [25]. The hydrogen bubbles isolate the substrate and then the current lines are concentrated around them making rings consisted of agglomerates of grains of deposited metal. The current lines are also concentrated at the metal nuclei formed in the initial stage between the hydrogen bubbles forming copper grains agglomerates of them. In the growth process, due to current density distribution effect, both hydrogen evolution and copper nucleation primarily occur at top of these agglomerates. Some of new, freshly formed hydrogen bubbles will coalesce with hydrogen bubbles formed in the initial stage of electrodeposition process, leading to their growth with electrolysis time. When the critical size of these hydrogen bubbles to detach from electrode surface is reached, they will detach from electrode surface forming holes of regular shapes at electrode surface. Simultaneously, holes of irregular shape are formed at electrode surface of agglomerates copper grains formed between hydrogen bubbles [25]. These holes are situated between regular holes. For longer electrodeposition time, coalescence of closely formed hydrogen bubbles occurs, leading to the

formation of large, so-called coalesced holes [25]. This process makes the wall of the hole by very porous. Meanwhile, some of new freshly formed hydrogen bubbles will not coalesce with previously formed hydrogen bubbles because they are situated between freshly formed copper nucleus, and these hydrogen bubbles have not enough place to develop in large hydrogen bubbles. These hydrogen bubbles will detach very fast from electrode surface forming channel structure through the interior of the deposit [26].

2.2. Factors affecting number, size and distribution of holes in the honeycomb-like structures

Electrodeposition technique is suitable way to get open and porous structure because it is very easy to control number, size and distribution of holes by the choice of appropriate electrodeposition conditions [26].

Factors affecting number, size and distribution of holes are:

- a) preparation of working electrode,
- b) concentration of Cu(II) ions,
- c) concentration of sulfuric acid,
- d) temperature of electrolysis, and
- e) time of electrolysis.

2.2.1. Preparation of working electrode

The number, size and distribution of holes in the honeycomb-like electrodes strongly depended on type of working electrode used for copper electrodeposition [25, 27]. The strong difference in the initial stage of their formation, as well as in the formed honeycomb-like structures was observed in the dependence of the type of used working electrode. The number of hydrogen bubbles formed at the electrode with large number of active centers, where irregularities at electrode surface represent active centers for formation of both hydrogen bubbles and agglomerates of copper grains, was several times higher than the number of holes formed at the electrode with “killed” active centers, where active centers were removed by the formation of uniform thin copper film by electrodeposition at some lower overpotential [25].

2.2.2. Concentration of Cu(II) ions

For the examination of the effect of Cu(II) ions concentration on copper electrodeposition in the hydrogen co-deposition range, copper solutions containing 0.075 M, 0.30 M and 0.60 M CuSO₄ in 0.50 M H₂SO₄ were analyzed [26, 28]. The sharp decrease in the average current efficiencies of hydrogen evolution with the increase of Cu(II) ion concentration was observed at an overpotential of 1000 mV, which was about 250 mV outside the plateau of the limiting diffusion current density for all analyzed solutions [26]. The tendency of the decrease of the average current efficiencies of hydrogen evolution with the increasing Cu(II) ions concentration was in good agreement with the prediction

of the ionic equilibrium of the species in the $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ system [4]. The honeycomb-like copper deposit, constructed from holes or pores formed by attached hydrogen bubbles and agglomerates of copper grains formed around them, was formed by the electrodeposition from 0.075 M CuSO_4 in 0.50 M H_2SO_4 . The two types of holes were formed during electrodeposition from 0.30 M CuSO_4 in 0.50 M H_2SO_4 . The one type of holes was the one forming honeycomb-like structure. The second type of holes is denoted as dish-like hole. This type of hole was described for the first time in this investigation. Finally, dish-like holes were only formed during copper electrodeposition from 0.60 M CuSO_4 in 0.50 M H_2SO_4 [26]. The bottom of the dish-like holes was compact, while the walls of these holes were porous. It is necessary to note that branchy dendrites were formed between dish-like holes, as well as at shoulders of holes with longer electrodeposition times. Anyway, the appearance of dendrites between holes, as well as at shoulders of holes clearly points out the decreased effectiveness of solution stirring by evolved hydrogen when the concentration of Cu(II) ions is increased.

2.2.3. Concentration of sulfuric acid

The effect of H_2SO_4 on copper electrodeposition processes was examined keeping the concentration of Cu(II) ions constant (0.15 M CuSO_4), while concentration of H_2SO_4 were varied, and they were: 0.125 M, 0.25 M and 1.0 M H_2SO_4 [29]. As expected, the increasing H_2SO_4 concentration led to the increase of the average current efficiencies of hydrogen evolution. The main characteristics of electrodeposition processes from the solutions with different H_2SO_4 concentrations at an overpotential of 1000 mV were holes or pores surrounded by agglomerates of copper grains. The number of holes increased with the increasing H_2SO_4 concentration, while the hole size decreased with the increasing H_2SO_4 concentration. Also, orientation of holes was changed from random oriented holes to holes which were lined up in parallel row [29].

2.2.4. Temperature of electrolysis

The increase of temperature of electrolysis leads to an intensification of hydrogen evolution reaction [30]. Meanwhile, despite intensification of hydrogen evolution with the increasing temperature, the decrease of number of holes formed per mm^2 surface area of electrodes and the increase of their average diameter was observed during copper electrodeposition at an overpotential of 800 mV. In order to explain this unexpected trend in the development of morphology of electrodeposited copper, the effect of temperature on some properties of electroplating solution, such as viscosity and surface tension was considered [30]. The increase of temperature causes the decrease of both the viscosity [31] and the surface tension of this solution [32]. The decrease of the surface tension of the solution lowers the break-off diameter of

hydrogen bubble from the electrode surface [32], while the decreased viscosity of the solution probably facilitates a transport of the detached hydrogen bubbles through the interior of the deposit forming the channel structure through it. Anyway, increasing temperature led to redistribution of evolved hydrogen from those creating honeycomb-like structure to structure with dominant presence of agglomerates of copper grains surrounded by irregular channels of evolved hydrogen (that is a channel structure).

2.2.5. Time of electrolysis

The size of 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. In the growth process, due to current density distribution effect, some hydrogen bubbles can remain captive in the interior of deposit making the honeycomb-like structure by very porous [33].

2.3. The increase of the specific surface of open and porous copper electrodes

Hence, the increasing overpotential, the decreasing concentration of Cu(II) ions and the increasing H_2SO_4 concentration intensify hydrogen evolution reaction. Intensification of hydrogen evolution leads to an increase of the number of formed holes, as well as to a decrease of hole size. Meanwhile, the ratio of the coalesced holes to the overall number of formed holes increased with the intensification of hydrogen evolution. The coalescence process is very unsuitable in the process of formation of honeycomb-like deposits as possible electrodes in electrochemical devices, because coalescence of closely formed hydrogen bubbles decreases the overall number of the formed holes, and increases hole size. This leads to the decrease of the specific surface area of this deposit type.

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 two ways are proposed to suppress a coalescence of closely formed hydrogen bubbles and hence to increase the specific surface area of open and porous copper electrodes. The first way is the addition of specific substances, known as additives, to the electroplating solution [11]. So, the decrease of diameter of holes, as well as the increase of their number in 3D foam copper structures can be realized by the addition of acetic acid to the copper sulfate solution [11]. Also, the addition of chloride ions dramatically reduces the size of the copper branches in the walls of holes. The reduction in pore size is a result of lowering hydrophobic force of the generated hydrogen gas by adding bubble stabilizer (e.g., acetic acid) that suppresses the coalescence of bubbles, while the decrease in branch size in the foam wall is a consequence of the catalytic effect of chloride

ions on the copper deposition reaction. Mechanical strength of the foam structure can be improved by the addition of $(\text{NH}_4)^+$, Cl^- , polyethylene glycol and 3-mercapto-1-propane sulfonic acid to the deposition bath [34]. The foam structure obtained by a combination of these additives was a highly porous with better mechanical strength than the one obtained without additives, owing to higher compactness of crystallites. The use of additives in electroplating practice leads to their consumption during electrodeposition processes and the requirement for their permanent control is necessary. The consumption of additives occurs due to removal with the plated objects, by their incorporation in the deposit (co-deposition) and by reaction on the plated object [35, 36].

The second way for suppression of coalescence of closely formed hydrogen bubbles is the application of periodically changing regimes of electrolysis, such as pulsating overpotential. This way is completely developed in Belgrade's research group. The noticeable increase of the number of holes, as well as the noticeable decrease of hole size due to suppression of coalescence of closely formed hydrogen bubbles can be attained if the appropriate parameters of square-waves pulsating overpotential (PO) were applied [37]. Also, the bottom of holes can be changed by the application of the PO regime from compact in the holes obtained in constant regimes of electrolysis to bottom consisted of small cauliflower-like agglomerates of copper grains in the holes obtained by the PO regimes [38].

The compactness of the honeycomb-like copper structures obtained by square-wave PO was larger than the one formed in the constant regimes of electrolysis [33]. Also, the compactness as well as suppression of coalescence of closely formed hydrogen bubbles increased with the increasing pause duration (keeping deposition pulse to be constant).

Analysis of the honeycomb-like structures obtained by the PO regimes with constant pause duration and different deposition pulses showed that the shortening of deposition pulse led to a decrease of the average current efficiency of hydrogen evolution needed for their formation [39]. Simultaneously, change of morphology of electrodeposited copper from cauliflower-like agglomerates of copper grains to very branchy dendrites was observed with the shortening deposition pulse. Due to suppression of coalescence of closely formed hydrogen bubbles, constant number of holes was formed in the interval of deposition pulses between 3 and 10 ms. Also, hole size and depth of holes did not depend on deposition pulse duration. Analysis of the specific energy consumption showed that the shortening of deposition pulse of 10 to 3 ms leads to the decrease of the specific energy consumption for about 15 %. Considering unchanged number of holes with the approximate same hole size and depth of holes, it is clear that the use of shorter deposition pulses enabled energy savings in

formation of this structure type, what is very important for possible application of these structures as electrodes.

3. POWDERED DEPOSITS

Formation of powdered deposits by electrolytic processes has been the subject of many investigations for a very long time [40 – 44]. Meanwhile, the only study which considered the correlation between the shape of powder particles and the quantity of hydrogen generated during electrolytic process was presented recently [45]. It was shown [45] that two types of copper powder particles are formed in the dependence of quantity of evolved hydrogen. The first type are dendrites constructed of corn-cob – like forms as the basic element, and this type is formed with the quantity of evolved hydrogen which was insufficient to disturb diffusion layer of the macroelectrode and hence to change the hydrodynamic conditions in the near-electrode layer. The second type of particles was of cauliflower – like shape. Hydrogen evolution which led to the formation of this type of particles was enough vigorous to cause such stirring of the copper solution which leads to the decrease of the cathode diffusion layer thickness and to the increase of the limiting diffusion current density and hence to the change of the hydrodynamic conditions in the near-electrode layer.

4. SUMMARY

In this paper, fundamental aspects of copper electrodeposition in the hydrogen co-deposition range are considered. The two types of copper structures of very high technological significance are formed in this range: (a) open and porous structures, denoted as 3D foam or honeycomb-like ones, which are ideally suited for electrodes in many electrochemical devices, such as batteries, electrodes and sensors [10 – 12], and (b) powdered deposits which are widely used in the electrical and the electronics industries because of excellent electrical and thermal conductivities. More about the application of copper powder can be found in the Ref. [46].

Aside from the investigations of copper electrodeposition processes in the hydrogen co-deposition range, the special attention was also given to fundamental aspects of the other technological very important problems of this metal and its alloys, such as corrosion and corrosion inhibitors [47 – 58]. Also, copper electrodeposition in the presence of leveling and brightening additives, as well as the processes of electrochemical polishing of copper are widely studied [59 – 61].

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REZIME

Ovo je pregledni rad koji razmatra fundamentalne aspekte elektrohemijskog taloženja bakra na visokim prenapetostima gde paralelno procesu elektrohemijskog taloženja bakra se odigrava reakcija izdvajanja vodonika. Dva tipa taloga bakra su formirana u oblasti ko-depozicije vodonika: (a) otvorene i porozne strukture označene kao strukture pčelinjeg saća, i (b) praškasti talozi. Fenomenologija formiranja strukture pčelinjeg saća, kao i faktori koji utiču na formiranje ovog tipa strukture su detaljno opisani. Povećanje specifične površine strukture pčelinjeg saća primenom periodično promenljivih režima elektrolize, kao što je režim pulsirajuće prenapetosti (PP), je razmatran. Uzajamna veza između oblika čestica praha i količine vodonika izdvojene tokom njihovog formiranja je takođe predstavljena.