

Electrodeposition of copper on cold rolled copper substrate

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Abstract: *The microscopic and macroscopic views of copper electrodeposits obtained on plastically deformed copper substrates of different deformation degrees have been investigated. Experiments have been performed under galvanostatic conditions. There appear, depending upon the degree of reduction realized during substrate rolling, three types of deposit: epitaxial, homogenous and texture. Epitaxial growth is observed on unreformed substrate and on the substrates with lesser deformation degree (up to 60 %). With the increase of the substrate reduction degree, heterogeneous type of the deposit appeared and the phenomenon of twinning was stated. On very much deformed substrates, as well as in presence of organic additives, field oriented texture type of the deposit is obtained. On very deformed substrates macroscopic uneven deposits appeared, with the linear structure which follows the direction of substrate rolling. Possible explanations of this phenomenon are given.*

KEYWORDS: ELECTROLYSIS, MODELING, DEFORMED COPPER SUBSTRATE, COPPER ELECTRODEPOSITS, DEFORMATION DEGREE, UNDEFORMED AND DEFORMED SUBSTRATE, MICROSTRUCTURE, COLD ROLLING

1. Introduction

The form and structure of metal deposits, which were obtained during electrodeposition, depends, first of all, on overpotential of deposition and desorption of ions and molecules from the solution [1]. According to Fischer [2], there are following types of polycrystalline electrodeposits:

- field orientated isolated crystals type, basis-oriented reproduction type, twinning intermediate type, field oriented texture type, unorientated dispersion type;

This points to a fact that structure of the substrate on which electrodeposition takes place, can also influence the structure of the deposit. In practice, the cases show the tendency that crystallization in the first layer of metal deposit on electrode of the same metal, takes place in the same way in which crystal surfaces of the substrate are oriented (epitaxial growth). This phenomenon also appears during deposition on the substrates made of other metals if crystal lattice parameters don't differ more than 15%. With the increase of deposit thickness there happens discontinuance of the epitaxial growth. Twinned crystals, and, in some cases, texture appears. Pangarov [1] explains these phenomena by the introduction of the principle of minimal energy.

Examining layers of electrolytic alloys obtained on single-crystal substrates, Lagiewka [3] identified three zones, in which the crystallites counting upwards from the substrate, take epitaxial, twin and random orientations. He developed X-ray method for direct determination of the ratio of the epitaxial zone in electrolytic Cu-Cd alloys layers. Epitaxial zone thickness decreases with the increase of the negative potential. Setty and Wilman [4], as well as Bebczuk de Cuzminsky [5, 6] have examined electrodeposition of copper on single-crystal copper substrate under galvanostatic conditions. They have come to a fact that for the stated current density, they get thicker epitaxial layers on the (111) substrates, compared with these on a (110) substrate. The preferred orientation during the thin-film growth appear to be due to low interfacial energies. This has been explained by the influence of the surface density of atoms on those surfaces and the corresponding value of free energy.

Shirokoff and Erb [7] studied the epitaxial silver on silicon single-crystals and concluded that obtained preferred orientations are believed to be due to low interfacial energies. Also, the researches on single crystals [8, 9] have been taken into consideration, as well as the investigation by Maizelis et al. [10].

Cisyewski and Allan [11] have done a considerable review of literature dealing with the examination of epitaxial growth of metals on metal substrates by research using field electron emission microscopy. It is especially striking that many cases of metal/metal epitaxy, the dominant factor determining the epitaxial relationship is the alignment of close-packed atomic rows in low-index crystallographic planes of each metal.

In regard to the fact that energetic condition of metal surface is changed during plastic deformation and that crystal lattice deforms also, there has been put an assignment to discover the

influence of the deformation degree of polycrystalline copper substrate on the structure of copper electrodeposit at different current densities both in and without the presence of the neutral organic compounds. Experience about deformed copper base and electrodeposition of copper on copper substrate was basis for our goal here, which was to achieve starting wire dies profile, using reverse drawing process modeling in electrolyte bath with gradual rounding of profiles [12, 13].

2. Experimental technique

The substrate, on which the electrodeposits of copper has been deposited, was a wire made of OFHC (oxygen free high conductivity) copper obtained by dip-forming method which had the initial diameter 15.8 mm. This wire was then rolled on rolling mill as described before [14], stating the realized deformation by the total relative reduction ϵ being 98.7%. In the table 1 the plan of passes has been shown, which has corresponding relative reduction and obtained hardness of samples in the middle and on the edge. Measuring the hardness, the indenting force of 5 daN has been used. Out of these samples, three groups have been formed:

- on samples 0, 3, 7, 10 and 16 electrodeposition of copper has been carried out from synthetic electrolyte which contained 39 g/L Cu^{2+} as CuSO_4 and 168.5 g/L H_2SO_4 without the addition of organic additives,

- on samples 0, 2, 5, 8, 11 and 14 electrodeposition of copper has been carried out from the electrolyte which is used in cells for obtaining the starting cathode sheets in copper refinery. This electrolyte contains the same concentration of cupric ions and sulphuric acid as well as previous synthetic one, but there are thiourea and gelatin there also in ratio 1:1.

Table 1. Plan of passes with hardness measurements

No. passes	b (mm)	h (mm)	h/h ₀ %	Hardnes (HV)	
				middle	edge
0	Ø15.8	Ø15.8	0	/	/
1	16.9	11.68	26.7	99.7	105
2	16.96	9.82	37.85	110	112
3	17.15	8.7	44.9	110	106
4	17.08	8.03	49.2	103	112
5	17.3	7.23	54.2	122	122
6	17.1	6.5	58.8	123	121
7	17.46	5.8	63.3	114	120
8	17.62	5.03	68.2	115	122
9	17.95	4.25	73.1	126	120
10	18.3	3.5	77.85	122	123
11	18.62	2.8	82.3	127	124
12	19.07	2.1	86.7	135	129
13	19.9	1.35	91.45	134	136
14	20.5	0.72	95.4	127	128
15	21.12	0.33	97.9	126	130
16	21.77	0.2	98.7	132	129

- in the third series of experiments, the substrate was made of parts obtained by cutting a sample wire number 16 (with the

deformation degree being 98.7%). Electrodeposition has been carried out the same like the first series, using the synthetic electrolyte without the addition of the organic compounds, at various current densities.

Before the process of electrodeposition, the samples have been prepared in the following manner:

- on each sample, the constant surface of 2 cm² in the middle part has been defined, so that the influence of the effect of the uneven deformation on the sample width has been reduced, and the remnant has been protected by lacquer resistant to carbon-tetrachloride, diluted nitric acid 1:1 and distilled water.
- just before the experiment, the sample has been washed out by carbon-tetrachloride, diluted nitric acid 1:1 and distilled water,
- anodic polishing of the samples has been done by the 50mA current going on for 10 min,
- after anodic polishing, the electrodes were thoroughly washed out by distilled water and sunk in electrolyte, from which electrodeposition of copper has been done and the voltage has been switched on,
- anode is also made of OFHC copper.

After the completed process of electrolytic deposition, the samples were brought out under the voltage from the electrolyte, they were washed out by the distilled water and alcohol and dried in the air. Then, microscopic examination of the texture and metallographic examination of the deposit structure, were done.

Metallographic examination were done transversally to the direction of rolling. The samples were first dipped into polyacrilate mass and then ground on grinding paper, the fineness of which was 3 to 4/0 and polished by alumina. After polishing the structure was "developed" by ferric-chloride.

3. Experimental results

The first group of experiments has been carried out with the constant current density being 50 A/m². As a substrate for electrodeposition the samples marked as 0, 3, 7, 10 and 16 have been used, to which relative reduction of 0%, 44.9%, 63.3%, 77.85% and 98.7% correspond, respectively. In figures 1 to 5 microstructure of the obtained electrodeposits being magnified 500 times, is shown.

In Figure 1 it is given the microphotography of the substrate made of undeformed wire and grains of the deposit which succeed the substrate growth. The deposit is distinctly massive-grained, so partly it has been separated from the substrate during metallographic preparation. Also on the substrate which had 44.9% deformation degree, massive-grained, clearly defined layer of the deposit has been obtained (Figure 2), which has a distinct epitaxial growth as well as on the undeformed substrate.

The grains of the substrate with the 63.3% deformation degree are elongated (Figure 3). The limits of deposits grains are determined by the elongated grains of the substrate, while the grain growth of the deposit is defined by the direction of the electric field.

In Figure 4 the deformed substrate, $\epsilon=77.85\%$, has very elongated grains and transitive type of deposit. Some substrate grains keep on epitaxial growth, while the growth of other grains is under the influence of the electric field direction. It is here that clear twinning of some crystals appears.



Fig. 1. Optical micrograph of copper deposit obtained from pure sulphate electrolyte on undeformed copper substrate, $j=5 \text{ mA/cm}^2$

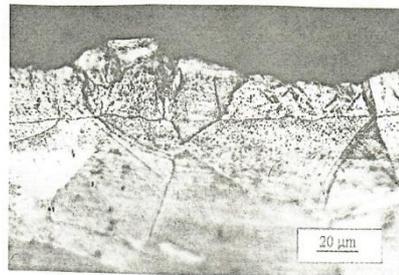


Fig. 2. Optical micrograph of copper deposit obtained from pure sulphate electrolyte on cold rolled copper substrate, $\epsilon=44.9\%$, $j=5 \text{ mA/cm}^2$

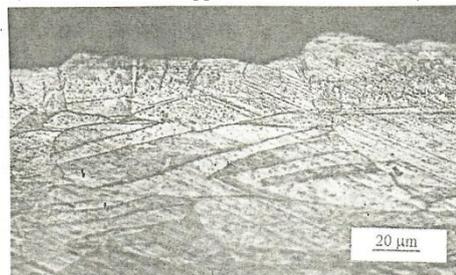


Fig. 3. Optical micrograph of copper deposit obtained from pure sulphate electrolyte on cold rolled copper substrate, $\epsilon=63.3\%$, $j=5 \text{ mA/cm}^2$

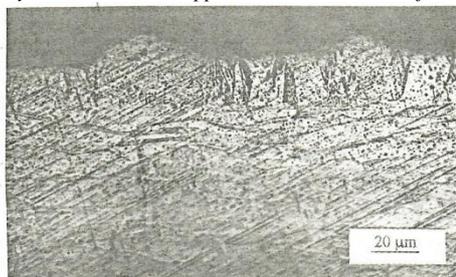


Fig. 4. Optical micrograph of copper deposit obtained from pure sulphate electrolyte on cold rolled copper substrate, $\epsilon=77.85\%$, $j=5 \text{ mA/cm}^2$

Figure 5 shows microstructure of copper electrodeposit obtained on the sample of wire number 16 with relative reduction of 98.7%. The grains of the substrate are so deformed that can be seen only as fibers. The deposit is clearly defined with periodical exchange of somewhat larger grains and grouped dendrites. The growth is totally defined by the direction of electric field. Macrostructure of this deposit in form of longitudinal rows with fine structure (Fig. 6), clearly marks the direction of sample rolling.

This series of experiments which were carried out by the use of synthetic electrolyte without the addition of the organic additives, has shown that epitaxial growth of electrodeposits is getting weaker with growth of the substrate deformation degree. With the considerable degrees of deformation, conditions are fulfilled for the appearance of crystal twinning, and microstructure is no longer homogenous, but linear with rows which follow the direction of rolling.

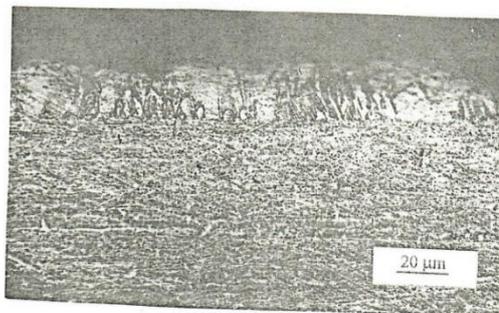


Fig. 5. Optical micrograph of copper deposit obtained from pure sulphate electrolyte on cold rolled copper substrate, $\epsilon=98.7\%$, $j=5 \text{ mA/cm}^2$

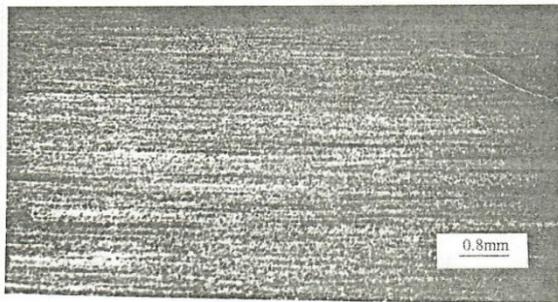


Fig. 6. Macrolook of the electrodeposit shown on Fig. 5.

On undeformed polycrystalline substrate, its influence on the orientation of the deposit is strongest and disappears last. The factors which can earlier end the substrate influence on the form of the deposit are the existence of more concentrated defects, adsorptions etc. With plastically deformed substrates there appears proportional growth of the number of defects, so that epitaxial growth is observed on the undeformed substrate and on the substrates with lesser deformation degree (up to about 60%) and when the number of defects per surface unit gets to a certain value, transitional (heterogeneous) type of crystal growth appears. On surfaces with the biggest deformation degree the quantity of defects is so big that epitaxial growth is completely omitted. However, macroscopic uneven deposit appears, with the linear structure which follows the direction of substrate rolling. Since it is known that plastic deformation always gets to the formation of relief (traces of gliding both on grain edges and inside the grains themselves), the possible explanation of this phenomenon is that defects (which represent the centers of nucleation) haven't been arranged evenly on the surface of the substrate, but they have been concentrated alongside certain lines parallel to the deformation direction.

The next possible cause is the fact that surfaces are different at certain grains on the surface of the sample. The grains are very much elongated by the plastic deformation, and the rate of the deposition growth is biggest on surfaces with the greatest Millers index values, so the deposit can look as in Fig. 6.

Also, the interesting phenomenon is the appearance of the twins in the deposits obtained on substrates with bigger relative reduction. The phenomenon of twinning in initial stadiums of electrocrystallization of copper on neutral substrates has been described in detail by Mamontov et al. [15, 16]. Sulphate electrolyte and current densities of 1 to 10 A/m² have been used. The deposit consisted of spheroids while their nucleus becomes first, and then in the next stage of growth the periphery of spheroids appears. The defects which result in twinning, appear together with the becoming of embryo.

The appearance of twins in electrodeposit is shown here, also happens at the very beginning of the process. Twin crystals become narrower with the growth (in the direction of electric field) and they end in the form of pyramids, so that they are present in the part of the deposit which is right next to the substrate, while, first of all, the conditions for total epitaxy must be eliminated. This was also noted in literature which treats electrodeposition on single-crystal substrates.

With spheroids, twins appeared on their periphery also. By this analogy, they could be expected in later layers of electrodeposit over epitaxial layer on less deformed substrates.

II group of experiments

In Figure 7 it is shown the microstructure of electrodeposit obtained on the substrate which had relative reduction of 54.2% by the use of electrolytes which contain the organic additives. This deposit looks typically like all electrodeposits obtained under the same condition on the substrates with relative reduction of 37.85 to 95.4%. Starting from the least deformed substrates already, what dominates is the growth of crystals in the direction of the electric field normally to the basic structure – the deposit shows the

characteristic texture, so that the typical example of field-oriented texture type of the deposit was obtained. Macrostructure of the deposit is smooth, which is, also, the result of the presence of gelatin and thiocarbamide in electrolyte. It was observed that the number of crystals are so much more tiny as the degree of substrate deformation is bigger.

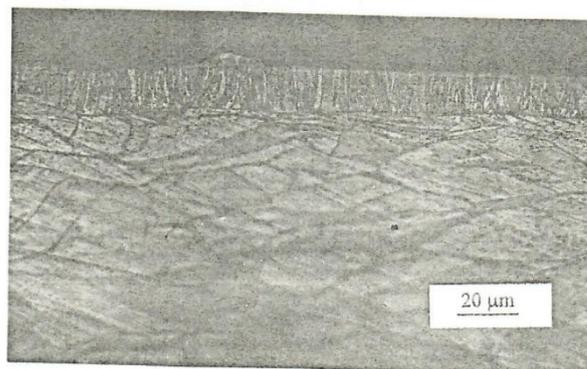


Fig. 7. Microstructure of copper deposit obtained from sulphate electrolyte containing thiourea and gelatin in ratio 1/1, on cold rolled copper substrate, $\epsilon=54.2\%$, $j=10 \text{ mA/cm}^2$

III group of experiments

The third group of experiments has been carried out on the substrate which had reduction degree of 98.7%. The same electrolyte has been used as in the first group (so, there were no organic additives). The current density varied from 5 to 25 mA/cm². The experiment with 5 mA/cm² belongs to the first series also, and is shown in Fig. 5. In all experiments of the third series, field oriented texture type of the deposit was obtained. The deposit is uneven. In Fig. 8 microstructure is shown, and in Fig. 8a macrolook of the deposit obtained by the current density of 10 mA/cm². In Figs. 9 and 9a, micro and macrostructure of the deposit obtained by the current density of 15 mA/cm² is shown. The deposit has more tiny, the orientation of the grain growth in the direction of electric field is clearer. Somewhat bigger grains of rectangular form alternate with pillar-like crystals. Macrostructure has two layers visually. The layer next to very deformed substrate is defined longitudinally while that layer extends to the layer of considerably rougher grains in the form of notches, little stars and irregular circles. Deposits are grouped in the form of bands – thicker in the middle of the band than on the edge. Twins appear.

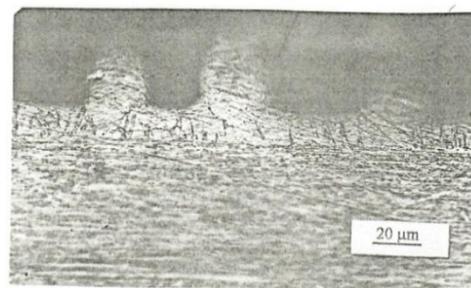


Fig. 8. Optical micrograph of copper deposit obtained from pure sulphate electrolyte on cold rolled copper substrate, $\epsilon=98.7\%$, $j=10 \text{ mA/cm}^2$



Fig. 8a. Macrolook of the electrodeposit shown on Fig. 8.

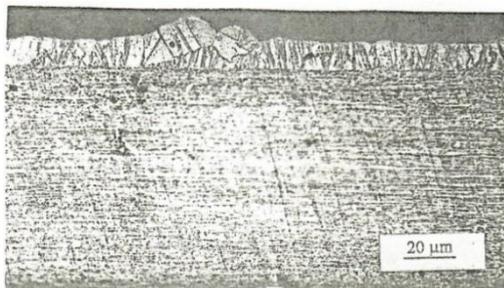


Fig. 9. Optical micrograph of copper deposit obtained from pure sulphate electrolyte on cold rolled copper substrate, $\epsilon=98.7\%$, $j=15 \text{ mA/cm}^2$

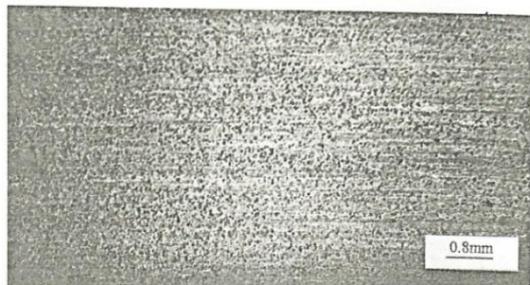


Fig. 9a. Macrolook of the electrodeposit shown on Fig. 9.

The structure of the deposit obtained with 20 and 25 mA/cm^2 is similar and has the form of pseudo-double layer. The growth of grains is determined by electric field.

4. Conclusion

During electrodeposition of copper from electrolytes which do not contain neutral organic additives on cold deformed copper substrate there appear, depending upon the degree of reduction realized during substrate rolling, three types of deposit: epitaxial, homogenous and texture.

Epitaxial growth is mostly noticeable on least deformed substrates. With the increase of the substrate reduction degree, there becomes heterogeneous type of the deposit, when it was stated a phenomenon of twinning, which become narrower with the growth of the deposit. On very much deformed substrates texture type of the deposit appear.

Macrostructure of the deposit which is obtained on very deformed substrates ($\epsilon=98.7\%$) is considerably linear and follows the direction of substrate rolling.

In the presence of organic additives, fields oriented texture type is obtained and tiny-grain structure of the electrodeposit, not depending on the degree of substrate deformation.

5. Literature

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