СОЈУЗ НА ХЕМИЧАРИТЕ И ТЕХНОЛОЗИТЕ НА МАКЕДОНИЈА
THE SOCIETY OF CHEMISTS AND TECHNOLOGISTS OF MACEDONIA

XX КОНГРЕС НА ХЕМИЧАРИТЕ И ТЕХНОЛОЗИТЕ НА МАКЕДОНИЈА

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SOME QUESTIONS ABOUT MORPHOLOGY AND STRUCTURE OF ELECTRODEPOSITED METAL COATINGS

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Introduction

The relationship between the light-reflecting property generally referred to as the brightness, and structure of electrodeposits has been the subject of many investigations. These studies have led to two theories. One theory [1,2] states that electrodeposits are bright if their microstructure consist of crystallites smaller than the wavelength of visible light, i.e., smaller than 0.4 μm. At the same time, for the surface to be bright, a roughness of less than 0.15 μm and 0.025 μm is required, according to Refs. [3,4], respectively.

The second theory [5,6] states that the more oriented the grain structure, the brighter the deposit, the brightnes being dependent on the degree to which the morphological components of the surface of electrodeposits are in plane [7]. On the other hand, it has been found that a major fraction of mirror-bright (Ni) metal electrodeposits exhibit no preferred orientation [4]. Hence, both theories do not hold.

The conditions which must be fulfilled in order for the metal surfaces to exhibit mirror brightness have not been classified and systematized yet. Progress in the investigation of the structure of bright metal surfaces has accelerated recently, thank to the development of the Scanning Tunnelling Microscopy (STM) and Atomic Force Microscopy (AFM) techniques [8,9].

It has been shown by these techniques that the reason of the mirror brightness of electropolished copper surfaces might be that large parts of the surface consists of small, flat and mutually parallel metal crystals, which exhibit smootthness on the atomic level. For this reason, it was considered necesarry to examine whether this conclusion about the structural features of electropolished mirror bright metal surfaces is also valid and for bright metal coatings obtained by electrodeposition.

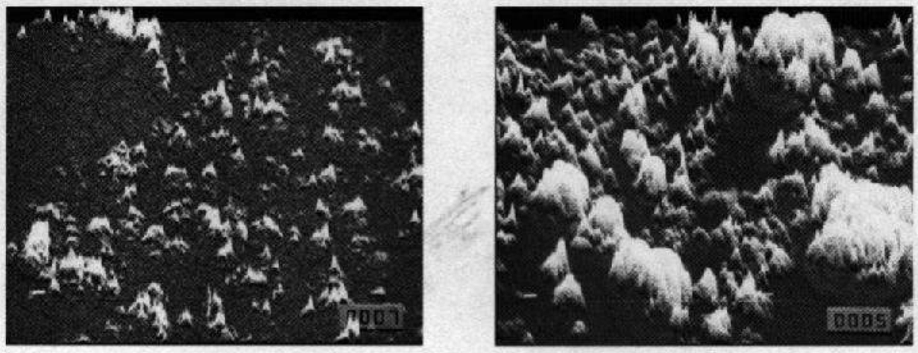
Experimental

Samples of rolled copper (5x5x0.05) cm were treated mechanicaly, then electrochemicaly polished in representative electrolyte for electrochemical polishing (740 gdm^{-3} H_3PO_4 + 60 gdm^{-3} CrO_3; j = 40 Adm^{-2}, t = 30^{0}C, τ = 3 min). On this already prepared surface substrate, copper was electrodeposited galvanostatically from acid sulfate electrolyte with or withoute presence of brightening addition agents (240 g/dm^3 $CuSO_4 .5 H_2O$ + 60 g/dm^3 H_2SO_4, j = 1 Adm^{-2}, t = 25^{0}C).

The morphology and the topography of the surfaces were detrmined by a SEM (JEOL T20), STM (NanoScope III in air) and AFM (Multi Mode Scaning Probe Microscope-"Digital Instruments").

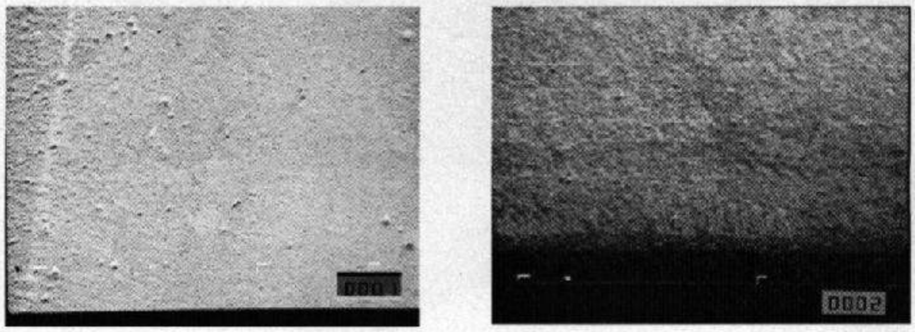
Results and Discussion

In Fig. 1 (a and b) are presented the SEM's micrographs (topography) of copper deposits which is obtained by backscattered electrones from acid sulfate electrolyte without the brightening agents (additives), the thicknesses 15 μm and 50 μm, respectively, and in Fig. 2 (a and b) of the SEM's micrographs the surfaces of copper coatings of the same thicknesses which were obtained from electrolyte with the brightening additives were shown.



a) b)

Fig.1. SEM micrographs (topography) of electrodeposited mat copper coatings: a) 15μm, b) 50μm.X750.



a) b)

Fig.2. SEM micrographs (topography) of electrodeposited bright copper coatings: a) 15μm, b) 50μm.X750.

As expected, with the increase of deposition time, that is, with the increase of thicknesses of mat coatings, the roughness increases also [10,11]. From SEM images it is obvious that mat coatings have bigger roughness (Fig. 1a and 1b) compared to ones with bright coatings (Fig, 2a and 2b), which means that brightening additive acts as leveling agent. In order for one substance to become applicable as a leveling agent, it has to build in crystal lattice of a metal which is deposited or to electrochemically react on the cathode. Both of these processes have to be under full diffusion control and the same effect of leveling can be explained as an amplification of surface irregularities under conditions of the full diffusion control of metal deposition.

In Fig. 3, 3D AFM image (4x4)μm (a and b) is given and 2D AFM image (4x4)μm (c and d) – view from above, copper coatings deposited in the absence of the brightening additives, thicknesses: a, c) 15μm and b, d) 50μm, and in Fig. 4: 3D AFM image was shown (4x4)μm (a and b) and 2D AFM image (4x4)μm (c and d)-view from above, in the presence of the brightening agents, thicknesses: a, c) 15μm and b, d) 50μm.

Analyzing Figs. 3 and 4, trend of increase in surface roughness with increasing deposition time is obvious, when the coating is deposited in the absence of the brightening additives (leveling). Consequently, increase of coating's thickness leads to increase in amplification of surface irregularities, which is in accordance with the literature quotes [10-12]. Besides, with brightening additives (leveling additives) complete decrease in the roughness amplitude is obtained (from couple of hundreds of nm to couple nm), which leads to mirror brightness.

Investigation of tested surfaces on submicron level led to a conclusion that amplitude of roughness (about 2nm) are quite small from the lowest wavelenght of visible light, i.e., smaller than 0.4μm. However, the cause of high mirror brightness doesn't lay just in the height of roughness amplitude.

Looking at the topography of the surface coatings confirmed that the cause of high mirror brightness lays in large portion of smaller plains and paralel pieces of surfaces that are smooth at atomic level. Increase in degree arrangements of galvanic coating's structure leads to increase in degree and mirror reflection.

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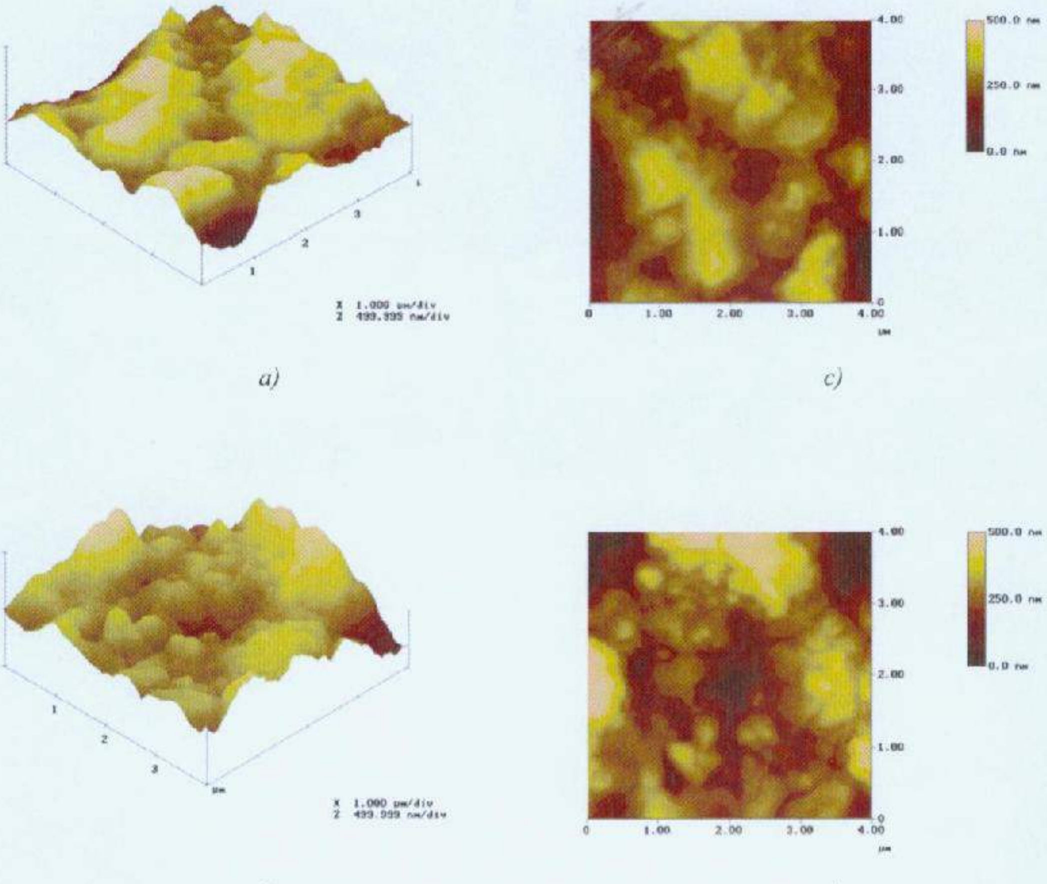
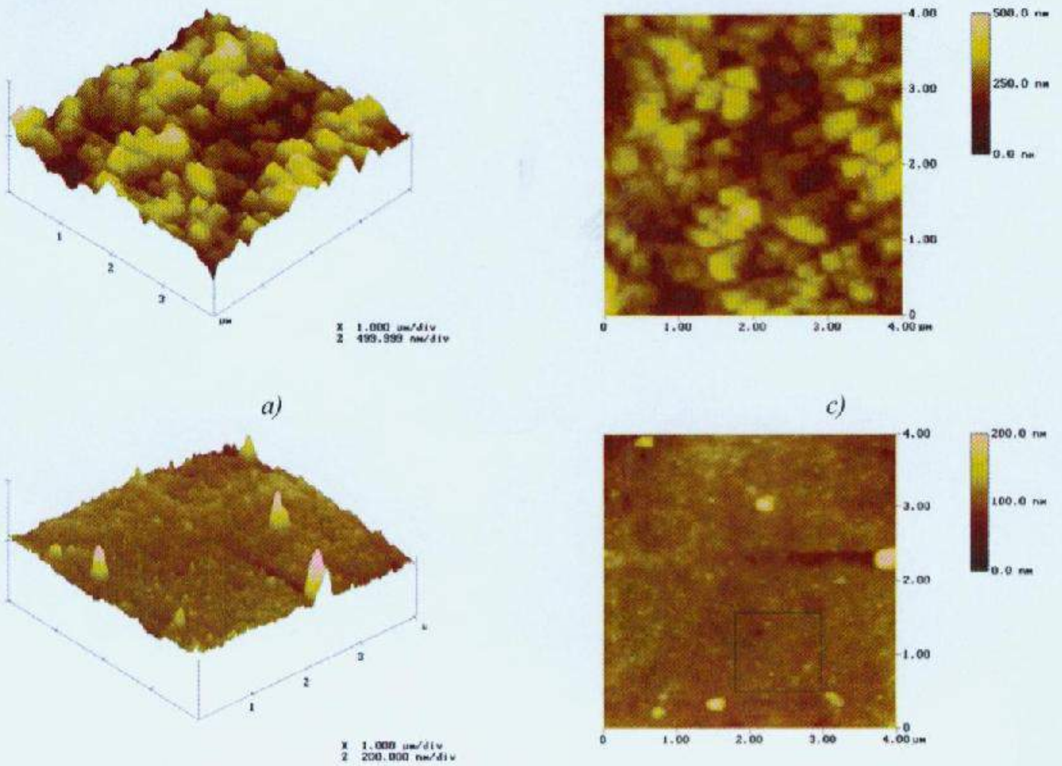


Fig. 3. 3D AFM images (4X4) µm (a,b) and 2D AFM images(4X4) µm (c i d)- view from above of electrodeposited mat copper coatings. The thicknesses of the observed copper coatings: a, c) 15 µm and b, d) 50 µm. Average roughness: a,c) Ra=75,31 nm, b,d) R_a= 103,84 nm.



b) *d)*

Fig. 4. 3D AFM images (4X4) μm (a,b) and 2D AFM images(4X4) μm (c i d)- view from above of electrodeposited bright copper coatings. The thicknesses of the observed copper coatings: a, c) 15 μm and b, d) 50 μm. Average roughness: a,c) Ra=62,63 nm, b,d) R_a= 12,18 nm; (box statistics R_a= 6,68nm).

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On the other hand, the structural details which determine the brightness of an electrochemically polished metal surfaces are different to those of bright metal coatings obtained by electrodeposition in the presence of brightening agents. In the first case, the brightness of the electropolished metal surface is determined by the large areas of flat and parallel to the base structures, which exhibited smoothness on the atomic level. In the second case, the brightness of metal coatings obtained by electrodeposition is determined by the fine-grained deposit, which are flat and mutually parallel with smoothness on the atomic level [9].

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