Morphology, structure and hardness of electrolytically produced copper coatings

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Abstract: Influence of various parameters of electrodeposition, such as type of cathode, composition of the electrolyte and thickness of the coating, on morphology, structure and hardness of copper coatings has been investigated. The Cu coatings thickness from 20 and 40 μm produced by the galvanostatic regime of electrolysis on Si(111) and brass cathodes from electrolytes without and with an addition of leveling/brightening additives were characterized by SEM and AFM techniques. The Vickers microindentation was used for a hardness analysis of the produced coatings, using the Chicot–Lesage (C–L) composite hardness model for estimation of their hardness. The mat microcrystalline fine-grained Cu coatings with the strong (220) preferred orientation were obtained from additive free electrolyte, and the smooth mirror bright nanocrystalline Cu coatings with the strong (200) preferred orientation were obtained from the electrolyte containing additives. Hardness analysis showed that the mat coatings were harder than the mirror bright coatings, that can be explained phenomena on grain boundary.

Parameters of the electrodeposition: a) type of cathode: brass and Si(111), b) thickness of the coatings: 20 and 40 μm, and c) composition of the electrolytes: **electrolyte (I)** – 240 g L^{-1} $CuSO_4 \cdot 5H_2O$ in 60 g L^{-1} H_2SO_4 (the basic sulfate electrolyte) and **electrolyte (II)** – 240 g L^{-1} $CuSO_4 \cdot 5H_2O$, 60 g L^{-1} H_2SO_4, 0.124 g L^{-1} NaCl, 1 g L^{-1} PEG 6000 (polyethylene glycol), 0.0015 g L^{-1} MPSA (3–Mercapto–1–propanesulfonic acid), (the electrolyte with levelling/brightening additives) – j = 50 mA cm^{-2}.

Analysis of the copper coatings electrodeposited on the brass cathode; 20 μm

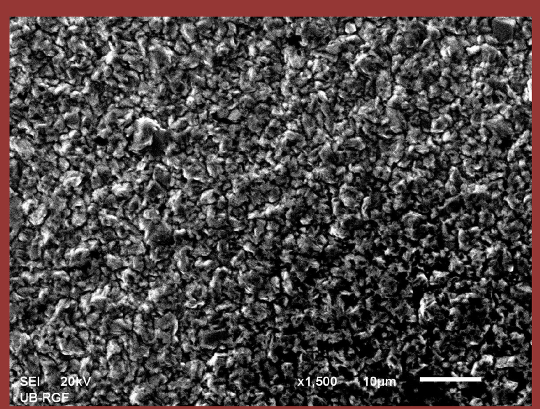
Analysis of the copper coatings electrodeposited on the Si(111) cathode; 20 μm

Analysis of the copper coatings electrodeposited on the Si(111) cathode; 40 μm

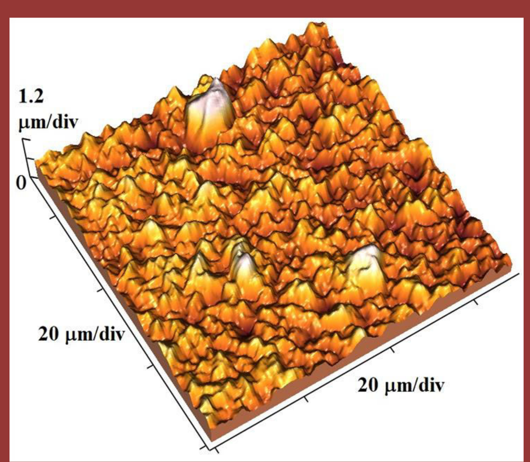
Structural analysis

Brass cathode; 20 μm

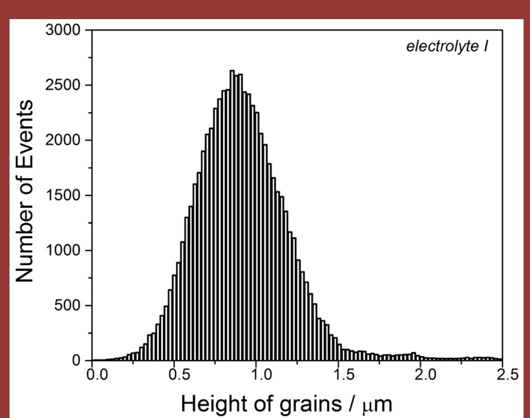
electrolyte (I)

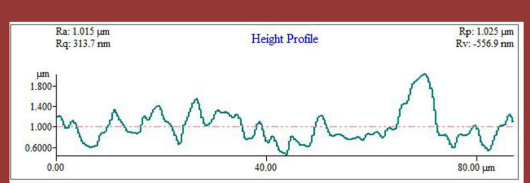


○ fine-grained with mat appearance

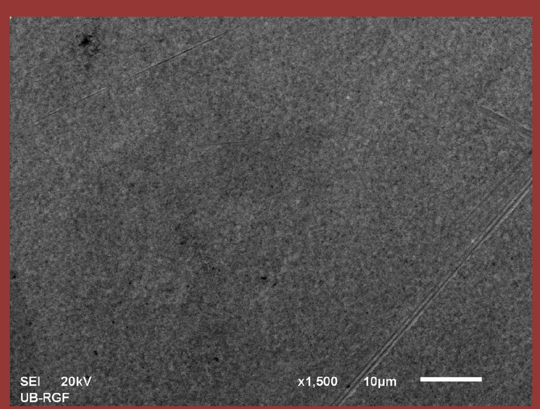


R_a = 231.60 ± 10.6 nm

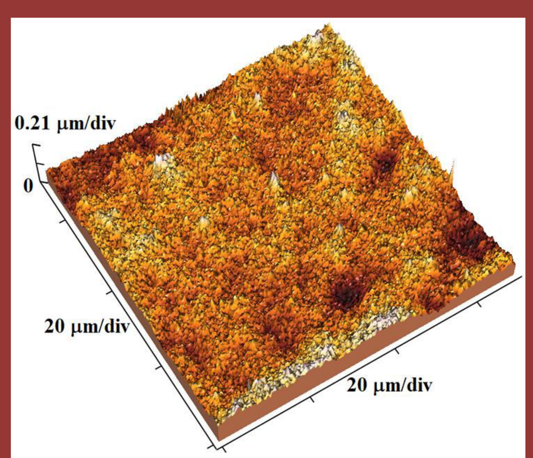




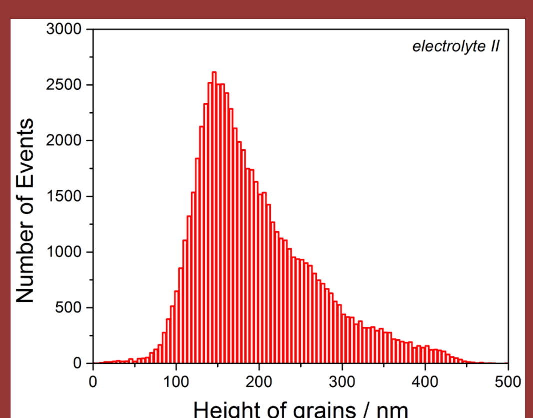
electrolyte (II)

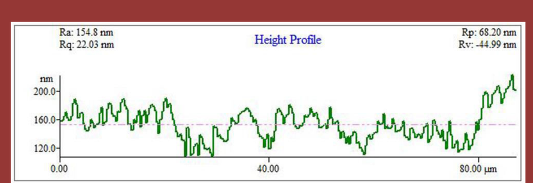


○ smooth with mirror bright appearance



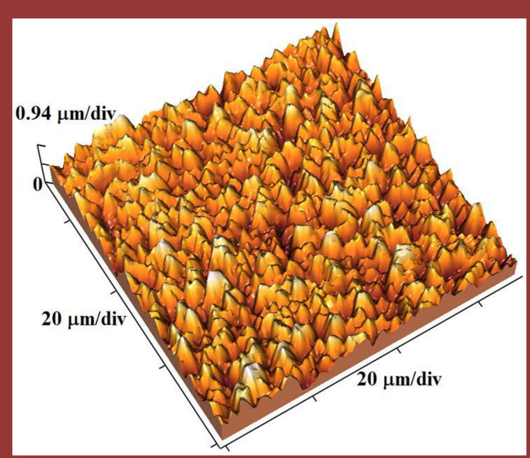
R_a = 28.25 ± 2.1nm



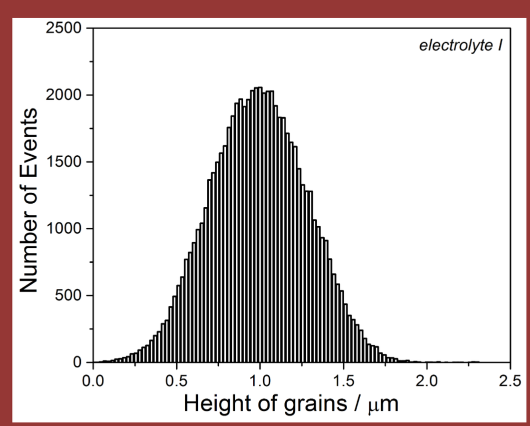


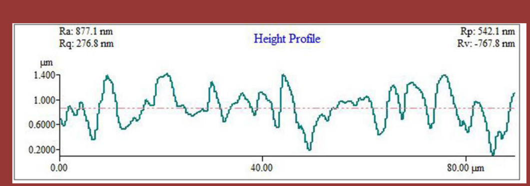
Si(111) cathode; 20 μm

electrolyte (I)

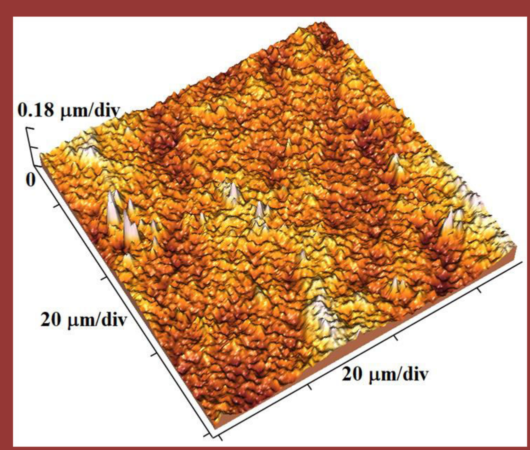


R_a = 216.81 ± 8.5 nm

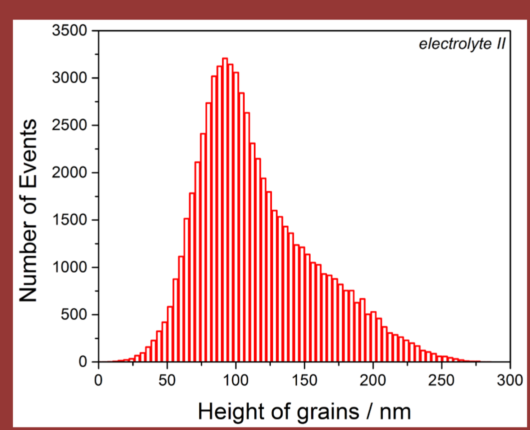


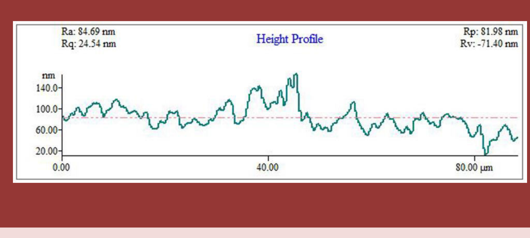


electrolyte (II)



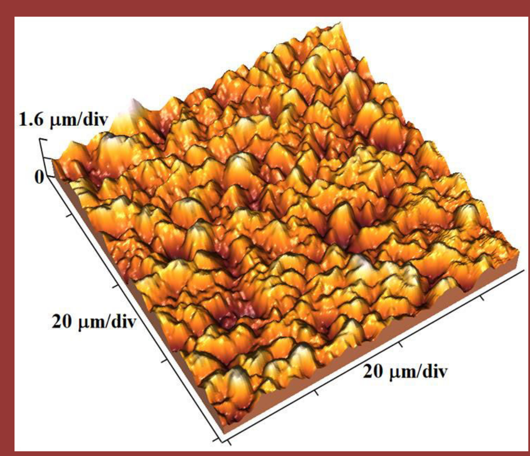
R_a = 20.96 ± 1.9 nm



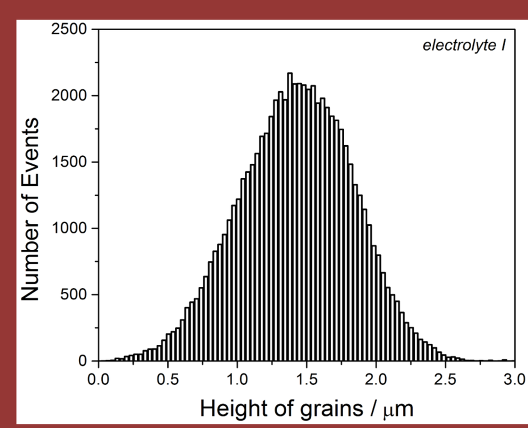


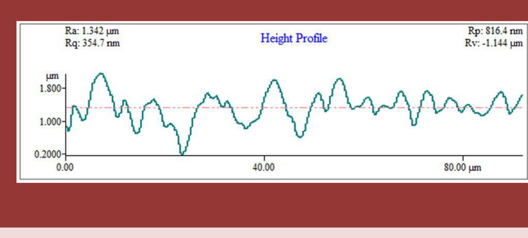
Si(111) cathode; 40 μm

electrolyte (I)

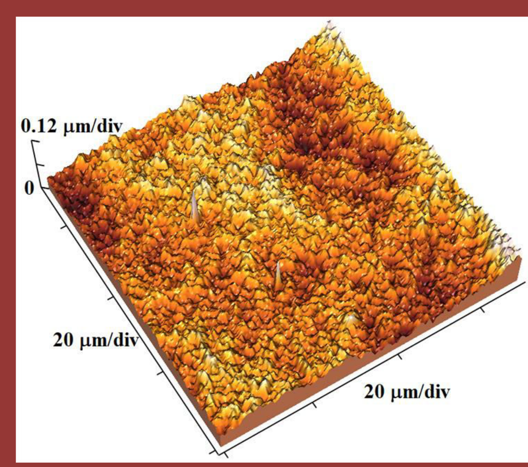


R_a = 317.20 ± 8.9 nm

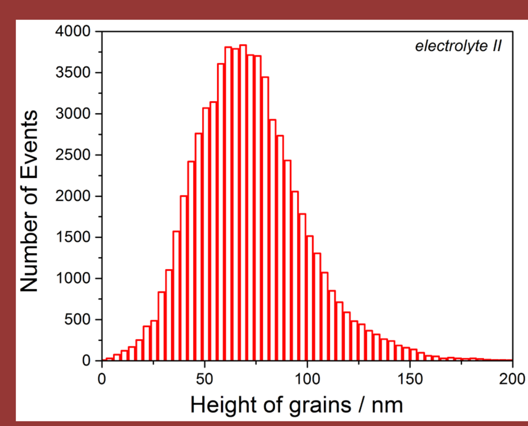


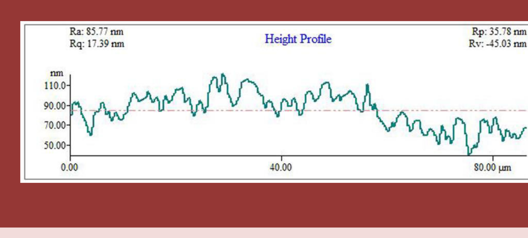


electrolyte (II)

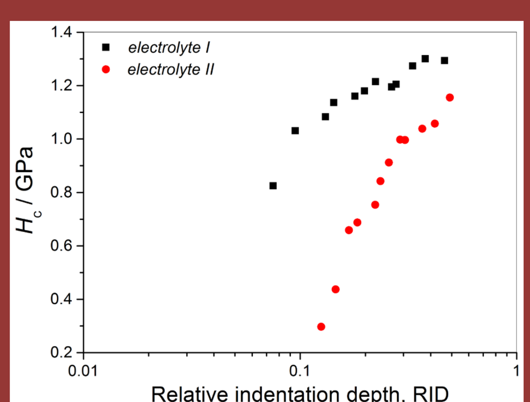


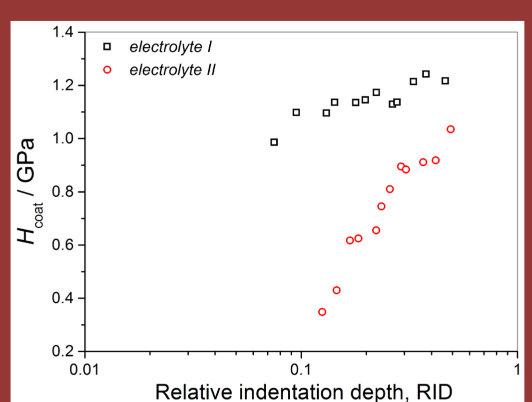
R_a = 15.36 ± 1.5 nm

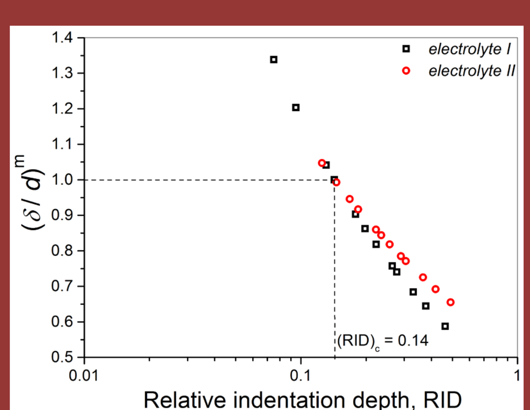




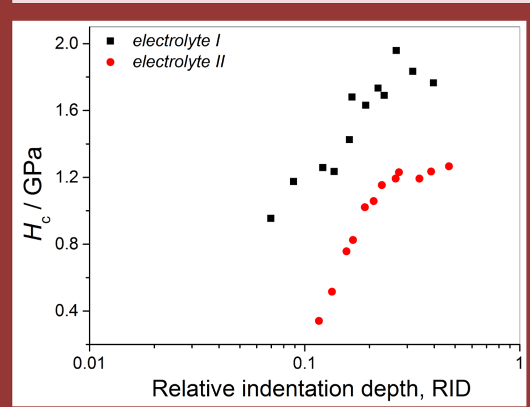
Hardness analysis

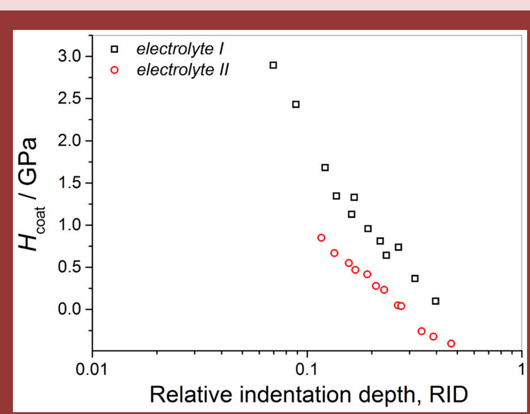


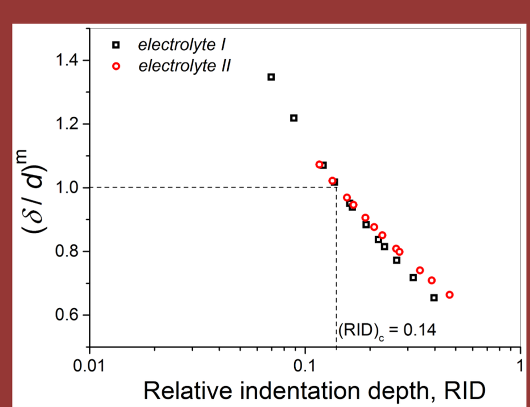


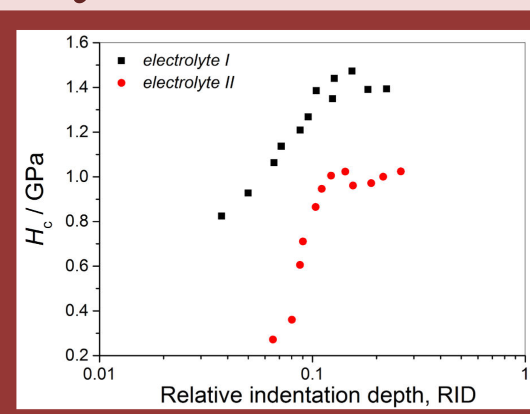


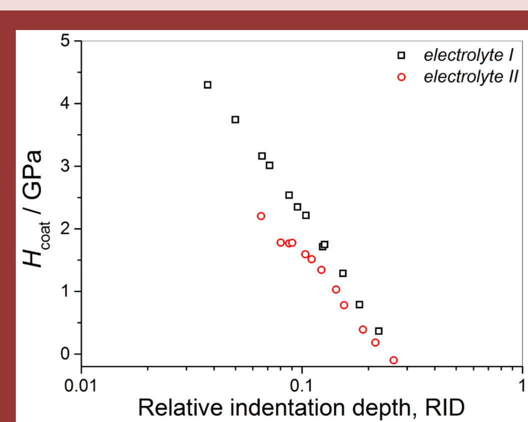
Hardness analysis*)

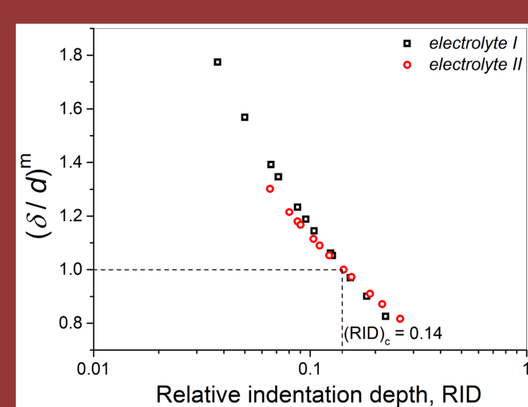












Sarajevo, B&H
June 30th June – 2nd July 2022.

CONCLUSIONS

- ✓ The roughness of the fine-grained coatings was considerably larger than the roughness of smooth coatings.
- ✓ Hardness of the mat Cu coatings was larger than that obtained for mirror bright Cu coatings. This difference can be attributed to numerous boundaries among grains in the fine-grained mat coatings.
- ✓ The shapes of the dependencies of the coating hardness calculated by the C–L model on the RID differ mutually for the Cu coatings obtained on the brass and the Si(111) cathodes. This indicated the strong effect of cathode hardness on coating hardness.
- ✓ Irrespective of conditions of electrolysis, the critical or limiting relative indentation depth (RID) of 0.14 was established for all types of the coatings. This value separates the zone in which the composite hardness can be equaled with the coating hardness (negligible effect of the cathode hardness on the composite hardness) and the zone of a necessary application of the C–L model for a determination of the absolute hardness of the Cu coatings (the strong effect of the cathode hardness on the composite hardness).

Hardness analysis:*) H_c – composite; H_{coat} – calculated by application of the Chicot-Lesage (C-L) composite hardness model; RID – Relative Indentation Depth; m –Meyer's index; d – indentation depth; δ - coating thickness.

This work was supported by Science Fund of the RS (Grant No. AdCatFC: 7739802)