Ushchapovskyi, D. Yu. (2024). The influence of the working cell geometric parameters on electrochemical 3D printing accuracy. *Actual Issues of Modern Science. European Scientific e-Journal, 29*, 70-75. Ostrava: Tuculart Edition, European Institute for Innovation Development.

DOI: 10.47451/inn2024-04-05

The paper is published in Crossref, ICI Copernicus, BASE, Zenodo, OpenAIRE, LORY, Academic Resource Index ResearchBib, J-Gate, ISI International Scientific Indexing, ADL, JournalsPedia, Scilit, EBSCO, Mendeley, and WebArchive databases.

Dmytro Yu. Ushchapovskyi, Candidate of Technical Sciences, Associate Professor, Department of Electrochemical Production Technology, National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute". Kyiv, Ukraine.
ORCID 0000-0002-2809-2774

The influence of the working cell geometric parameters on electrochemical 3D printing accuracy

Abstract: The main technological parameters of electrochemical 3D printing are the rate of metal deposition and resolution. Electrochemical 3D printing resolution can be characterized by the ratio between the estimated metal deposition area width and the working electrode-anode diameter. In this work, the influences of the diameter of the working electrode-anode and the inter-electrode distance on electrochemical 3D printing accuracy have been investigated. The purpose of the study was to establish the influence of electrochemical cell geometric parameters' ratio on electrochemical 3D printing resolution. The author used the sources of Ukrainian scientists such as R. Babchuk, V. Vorobyova, O. Linyucheva, M. Kotyk, G. Vasyliev and foreign researchers such as K. Bouzek, K. Borve, O. Lorentsen, K. Osmundsen, I. Rousar, J. Thonstad, M. Rafiee, R. Farahani, D. Therriault and others. It was shown that the smaller the diameter of the anode (dielectric capillary) and the greater the distance from the anode dielectric housing edge to the surface of the cathode (interelectrode distance), the wider the metal deposition area. It was found that the larger the working electrode diameter, the larger the inter-electrode distance can be used to ensure the required electrochemical 3D printing resolution.

Keywords: electrochemical 3D printing, resolution, anode diameter, interelectrode distance.

Дмитро Юрійович Ущаповський, кандидат технічних наук, доцент кафедри, кафедра технології електрохімічних виробництв, Національний технічний університет України «Київський політехнічний інститут імені Ігоря Сікорського». Київ, Україна.
ORCID 0000-0002-2809-2774

Вплив геометричних параметрів робочої комірки на точність електрохімічного 3Д друку

Анотація: Основними технологічними параметрами електрохімічного 3Д друку є швидкість нашарування металу та роздільна здатність. Роздільна здатність електрохімічного 3Д-друку може бути охарактеризована співвідношенням між шириною оціночної області осадження металу та діаметром робочого електрода анода. У даній роботі досліджено вплив діаметром робочого електрода анода та міжелектродної відстані на точність електрохімічного 3Д друку. Метою дослідження було встановити вплив співвідношення геометричних параметрів електрохімічної комірки на роздільну здатність електрохімічного 3D друку. Автор використав джерела українських вчених, таких як Р. Бабчук, В. Воробйова, О. Лінючева, М. Котик, Г. Васильєв, та зарубіжних дослідників, таких як К. Бузек, К. Борве, О. Лоренцен, К. Осмундсен, І. Русар, Дж. Тонстад, М. Рафіє, Р. Фарахані, Д. Терріо та ін. Показано, що чим меншим є діаметр анода (діелектричного корпусу) і більшою відстань від краю діелектричного корпуса анода до поверхні катода (міжелектродна відстань), тим ширшою є область осадження металу. Встановлено, що чим більшим є діаметр робочого електрода, тим більшою може бути використана величина міжелектродної відстані з метою забезпечення необхідної роздільної здатності електрохімічного 3Д друку.

Ключові слова: електрохімічний 3Д друк, роздільна здатність, діаметр анода, міжелектродна відстань.

Introduction

The electrochemical type of the latest additive 3D printing technology is characterized by energy efficiency and environmental safety and makes it possible to obtain metal products with unique properties (*Rafiee et al., 2020*; *Chen et al., 2017*). The main technological parameters of this process are metal deposition rate and the accuracy or resolution. Electrochemical 3D printing resolution is determined by the characteristic size of the metal deposition zone directly under the working electrode-anode. The resolution (*Babchuk et al., 2024*) is determined by the properties of the electrochemical system regarding the redistribution of the current on the surface of the cathode on which electrodeposition is performed. In particular, when the electrolyte is supplied under pressure (*3D printing apparatus…, 2024*), it causes an expansion of electric current distribution area on the cathode surface contributing to the expansion of metal electrochemical deposition area and a decrease in the resolution of 3D printing. A decrease in the throwing power of the electrolyte, on the contrary, contributes to an increase in the localization of metal deposition and, as a result, to an increase in resolution (*Vasyliev et al., 2021a*). To limit current spreading area during electrochemical 3D printing, the working electrode-anode arrangement is often used in the dielectric capillary.

Most often, the current distribution in the electrolyte is secondary and depends both on the cell geometric parameters and the electrode reaction characteristics, namely, first of all, the cathode polarizability – the value corresponding to the cathodic polarization curve slope (*Bouzek et al., 1995*; *Electrode growth…, 2015*). During copper electrodeposition, the current efficiency approaches 100%, so the metal distribution is consistent with the current distribution on the cathode surface. This, accordingly, makes it possible to conduct model studies with greater accuracy (*Vasyliev et al., 2021a*). If the same electrolyte with fixed known physicochemical parameters is used in research, electrochemical 3D printing resolution will be affected by such system geometric parameters as the working electrode-anode diameter and the distance between the edge of the anode dielectric capillary and the cathode surface (interelectrode distance). Establishing these parameters' correlation influence on electrochemical 3D printing resolution is a significant scientific and technical task.

Thus, the purpose of this work, based on model studies, is to establish the influence of electrochemical cell geometric parameters' ratio on electrochemical 3D printing resolution.

Based on the purpose, the following tasks were identified:

- conduct modeling of the metal electrodeposition process during electrochemical 3D printing;
- investigate the electrochemical cell geometric parameters influence on electrochemical 3D printing accuracy.

The considered literary sources are devoted to the basic technological principles of the implementation of metal products electrochemical 3D printing method. In particular, the influence of the electrochemical cell geometric parameters and the electrochemical system properties on the metal distribution uniformity during electrodeposition have been considered. An analysis of factors influencing the resolution of electrochemical 3D printing was performed. The author used the sources of Ukrainian scientists such as R. Babchuk, V. Vorobyova, O. Linyucheva, M. Kotyk, G. Vasyliev and foreign researchers such as K. Bouzek, K. Borve, O. Lorentsen, K. Osmundsen, I. Rousar, J. Thonstad, M. Rafiee, R. Farahani, D. Therriault and others.

Research methodology

The COMSOL Multyphysics 4.3 software was used to model the influence of the 3D printer electrochemical cell geometric parameters on the locally electrodeposited fragment profile and, accordingly, electrochemical 3D printing resolution. Long-term copper deposit growth model was used (*Electrode growth…, 2015*). Based on the model's geometric parameters modification, electrochemical 3D printer working cell model (*Vasyliev, et al., 2022*; *Vasyliev, et al., 2023*; *Ushchapovskyi et al., 2022*; *Vasyliev et al., 2021b*) was developed in the appropriate software, presented in Appendix (*Figure 1*).

According to the corresponding model, calculations and the profile of the copper deposit long-term growth on the working cathode surface were performed (*Figure 1*, position 1). Calculations were performed to achieve a maximum height of the deposit growth profile of 100 μm. The simulation was performed for the following values of the relevant parameters. The distance between the cathode surface and the anode dielectric capillary edge (l), mm: 0,1; 0,5; 1. Anode diameter (D), mm: 1; 4; 6. The parameters of the selected electrochemical system were as follows. A copper sulfate electrolyte was chosen for modeling, for which the slope of the cathodic and anodic polarization curves corresponded to 1000 $mA \cdot cm^{-2} \cdot V^{-1}$; the electrical conductivity of the electrolyte was 0,08 S/cm.

Research results

To achieve the idealized maximum electrochemical 3D printing accuracy, locally electrodeposited object model profile should be rectangular (*Ushchapovskyi et al., 2022*). However, due to the peculiarities of the current distribution in the electrochemical cell, as was shown earlier (*Vasyliev et al., 2021a*; *Vasyliev, et al., 2022*; *Vasyliev, et al., 2023*), it approaches the parabolic one. The results of model studies on the influence of the working electrode-anode dielectric capillary width and the distance from the corresponding capillary edge to the cathode surface on the metal local electrodeposition area width are shown in the Appendix (*Figure 2*). As can be seen from this figure, the smaller the diameter of the anode (dielectric capillary) and the greater the distance from the anode dielectric capillary edge to the cathode surface, the wider is metal deposition area and the larger is the metal deposit growth profile deviation from the idealized (rectangular) shape.

For the purpose of quantitative assessment and establishment of relevant regularities, the following was adopted in this work. The metal deposition area estimated width (W) was determined under the condition that the deposit growth profile height corresponds to 10% of the maximum height of the profile of the locally electrodeposited fragment of the metal deposit and in this case is 10 μm. For convenience, the ratio between the metal deposition evaluation region width and the anode diameter – W/D – was adopted in this work as a criterion that allows for a quantitative assessment of geometric parameters influence on electrochemical 3D printing resolution. The W/D dependences on the distance between the working electrode-anode dielectric capillary edge and the cathode surface l for different values of working electrode-anode diameters D are presented in the Appendix (*Figure 3*).

Thus, the following can be summarized from the studies presented in *(Figure 2*; *Figure 3*). To focus the electric field and narrow metal deposition region, the distance *l* between the anode dielectric capillary edge and the cathode surface during local electrochemical deposition must remain constant and acquire the minimum possible value. Based on the data shown in the Appendix (*Figure 3*), the dependence of the minimum possible values of W/D depending on the working electrode-anode diameter D was obtained under the condition that $l \rightarrow 0$ (*Figure 4*). If it is assumed that the value $W/D = 1.25$ corresponds to the maximum value of the relative error permissible for engineering calculations of 25%, the dependence of the optimal distance between the dielectric capillary edge and the cathode surface *l* on the working electrode-anode diameter D corresponds to the following in the Appendix (*Figure 4*). Thus, it can be concluded that the larger the value of D, the larger the value of l can be applied to provide the necessary electrochemical 3D printing resolution.

Discussion

Electrochemical 3D printing resolution determines the characteristic size of the created object, just like its quality and compliance with geometric parameters. With electrochemical 3D printing in an electrolyte solution, the resolution will be increased by focusing the electric field in the interelectrode space. For this, the electrolyte composition selection, just like the variation of the working electrode geometric parameters, can be used. Further research in this direction may be aimed at investigating the influence of the current mode, and in particular, the pulse mode, on metal product electrochemical 3D printing accuracy and quality.

Conclusion

The effect of the main electrochemical cell geometric parameters on electrochemical 3D printing resolution has been investigated. A regularity describing the correlation between the working electrode diameter and the interelectrode distance was established. It has been shown that the larger the working electrode-anode diameter and the smaller the inter-electrode distance, the smaller the metal deposition area relative expansion and the higher electrochemical 3D printing resolution.

References:

3D printing apparatus using selective electrochemical deposition. (2024, February 15). *Jastia*. https://patents.justia.com/patent/20240052512

Babchuk, R., Uschapovskiy, D., Vorobyova, V., Linyucheva, O., Kotyk, M., & Vasyliev, G. (2024). Additive concentration and nozzle moving speed influence on local copper deposition for electrochemical 3D-printing. *Journal of Electrochemical Science and Engineering*, *14*(2), 265-273. https://doi.org/10.5599/jese.2291

Bouzek, K., Borve, K., Lorentsen, O. A., Osmundsen, K., Rousar, I., & Thonstad, J. (1995). Current distribution at the electrodes in zinc electrowinning cells. *Journal of Electrochemical Society*, *142*(1), 64-69. https://iopscience.iop.org/article/10.1149/1.2043939

Chen, X., Liu, X., Childs, P., Brandon, N., & Wu, B. (2017). A low-cost desktop electrochemical metal 3D printer. *Advanced Materials Technology*, *2*(10), 1700148. https://doi.org/10.1002/admt.201700148

Electrode growth next to an insulator. (2015, October 19). https://www.comsol.com/model/electrode-growth-next-to-an-insulator-10212

Rafiee, M., Farahani, R. D., & Therriault, D. (2020). Multi-material 3D and 4D printing: A survey. *Advanced Science*, *7*(12), 1902307-1902324. https://doi.org/10.1002/advs.201902307

Ushchapovskyi, D. Yu., Vorobyova, V. I., Plivak, O. A., Motronyuk, T. I., & Vasyliev, G. S. (2022). Limitations of copper nitrate electrolyte for fast electrochemical 3D-printing. *Bulletin of Cherkasy State Technological University. Technical Science*, *4*, 77-87. https://doi.org/10.24025/2306-4412.4.2022.265832

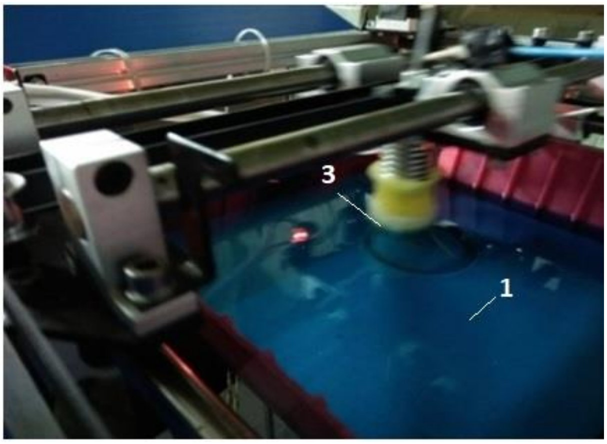
Vasyliev, G. S., Uschapovskyi, D. Yu., Vorobyova, V. I., & Linyucheva, O. V. (2021a). Modelling approach in the development of electrochemical 3D-printing systems. *KPI Science News*, *2*, 97-105. https://doi.org/10.20535/kpisn.2021.2.233716

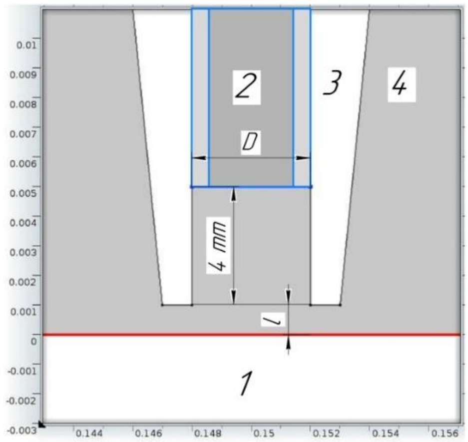
Vasyliev, G. S., Ushchapovskyi, D. Yu., Vorobyova, V. I., Motronyuk, T. I., & Linyucheva, O. V. (2021b). Development of additive technology – improvement of electrochemical 3d printing system. In *Electrochemistry today: achievements, problems and prospects*. Kyiv: MPBP Gordon. (In Ukrainian). http://ionc.com.ua/PDF/Book-IX-EX-2021.pdf

Vasyliev, G., Vorobyova, V., Uschapovskiy, D., & Linyucheva, O. (2022). Local electrochemical deposition of copper from sulfate solution. *Journal of Electrochemical Science and Engineering*, *12*(3), 557-563. https://doi.org/10.5599/jese.1352

Vasyliev, G., Vorobyova, V., Uschapovskiy, D., Kotyk, M., & Linyucheva, O. (2023). Influence of polarization curve slope on the accuracy of local copper electrodeposition from sulphate electrolyte. *Journal of Electrochemical Science and Engineering*, *13*(6), 971-980. https://doi.org/10.5599/jese.1899

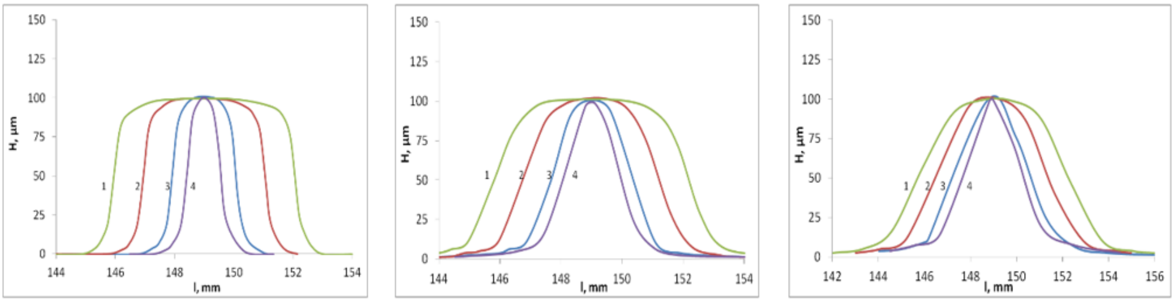
Appendix





(a) (b)

Figure 1. Image (a) and schema of model of electrochemical cell of 3D printer (b): 1 – cathode; 2 – anode; 3 – dielectric capillary; 4 – electrolyte



(a) (b) (c)

Figure 2. Influence of the distance l between the edge of the dielectric capillary of the working electrode-anode and the cathode surface on the model profile of the copper deposit. Value l, mm: a – 0.1; b – 0.5; c – 1. Diameter of the working electrode of the anode D, mm: 1–1; 2–2; 3–4; 4–6.

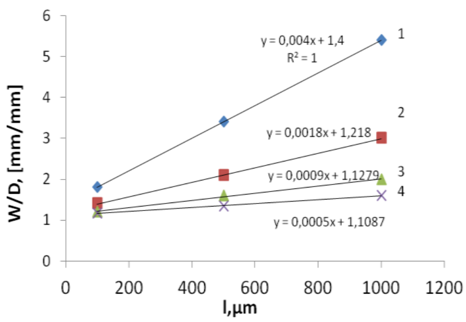


Figure 3. Dependencies of the relative expansion of the metal deposition area W/D on the distance l between the edge of the dielectric capillary of the working electrode-anode and the surface of the cathode, for the corresponding values of D, mm: 1–1; 2–2; 3–4; 4–6.

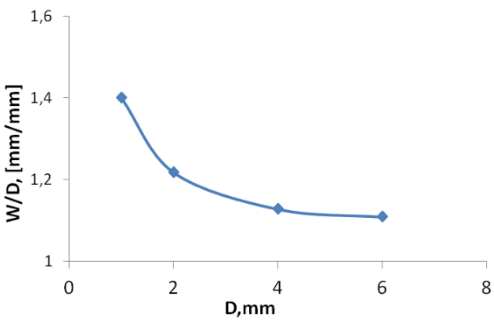


Figure 4. Dependencies of the value of the relative expansion of the metal deposition area W/D on D, provided that $l \rightarrow 0$