REVIEW

of a dissertation for obtaining a scientific and educational degree
***"DOCTOR"**, in a professional field*
4.2 Chemical sciences, Sc.. spec. "Electrochemistry"

Dissertation topic: *Obtaining and characterization of nickel-based electrochemical coatings Ni-M, where M = W, Mo, TiOx*

Scientific organization: *IPC "Acad. R. Kaishev", at the Bulgarian Academy of Sciences – Sofia*

Candidate: *Marina Hristova Arnaudova, Master eng. – chemist, s.r. III degree, assistant professor and now chemist at IPH – BAS*

Reviewer: *Ludmil Borisov Fachikov, PhD, Eng., Associate Professor, UCTM - Sofia*

1. General provisions and brief biographical data of the candidate

Marina Hristova Arnaudova was born in Sofia. In 1996, she was admitted as a student at the University of Chemical Technology and Metallurgy - Sofia, specialty „Technology of Metals and Materials Science“, specialization „Electrochemistry and Corrosion Protection“, which she successfully completed in 2001 with an educational and scientific degree of Master Engineer-Chemist. The following year she started working as a chemist at the Institute of Physical Chemistry – BAS.

At the IPC, she held the positions of chemist, research assistant III degree, and assistant in succession until 2024. Since 2024, she has been a chemist at the institute again. During the same period, she was a post graduate student in independent study in the Electrochemistry and Corrosion section.

I know Marina Hristova Arnaudova as a student in the department of „Inorganic and electrochemical productions“, but I have no direct observations

about her scientific and professional growth at IPC. Indirect and persuasive proof of its development is the work presented for the dissertation and its overall scientific production (co-authored with members of the scientific team in which she works) – published works in renowned specialized journals, participation in national and international scientific forums, 119 – quotes, the very good presentation of the pre-protection of the dissertation, etc.

2. Description of the materials presented

All minimum national, BAS and IPC Scientific Council requirements for submitting documents to the competition are precisely formatted and presented by the candidate:

1. Dissertation work
2. Autoreferrat
3. Certificate of fulfillment of the minimum requirements
4. Certificate of contributions to the dissertation
5. List of works included in the dissertation
6. List of all scientific works
7. List of noticed quotes
8. Separation protocol
9. Imprints of the works included in the dissertation
10. Curriculum vitae according to the European model
11. Diploma for educational and qualification degree "master"
12. Protocol of the meeting of the IPC colloquium „Acad. Rostislav Kaishev" for disclosure of the pre - defense procedure and selection of the composition of the scientific jury.

The dissertation submitted to me for review is printed in 100 pages and contains 40 figures, 14 tables and 2 appendices. The bibliographic reference is on 80 literary sources.

Structurally, the dissertation consists of the following sections: Introduction, Theoretical part, Purpose and tasks, Experimental part, Results and discussion, Contributions and Literature. Physicochemical and electrochemical characterization of obtained coatings, Results and discussion.

In the Theoretical part, the most – important questions related to the topic of the dissertation are discussed, and the candidate shows in-depth knowledge of theoretical electrochemistry and its applied directions, which allows her to easily comment on the results obtained during the research. In the Experimental Part, the many physic-analytic (SEM, EDX, XRF, XRD, XPS) and electrochemical methods (CVA, PPM, EIS) used to characterize deposited coatings are described. The obtained results and conclusions are presented and interpreted in depth, with accurate and accessible scientific language for non-specialists.

The scientometry of the dissertation includes five published works, and in four of them the candidate is in first place, which speaks of her personal contribution: 1- in Q1, 1- in Q2, 3 – unindexed, a total of 45 points. The citations observed for the works, included in the dissertation work, so far are 36 - for a total of 72 points.

Today, humanity is under the threat of several global changes – increase in temperature; release, because of human activity, of huge amounts of CO_2-greenhouse gas; accelerated melting of glaciers; environmental pollution; migration, etc. All this necessitates urgent solutions to reduce and eliminate the causes that led to the appearance of these problems – for example: development of new and improvement of existing technologies in material production, energy, creation of new materials, economical and nature-friendly sources of energy, etc.

Obtaining „green hydrogen" by electrolysis of water is one of the promising methods for obtaining „clean" energy. For its implementation, among other things, stable and highly efficient electrodes are also needed, which is also the goal of the dissertation work. In this sense, the topic of the dissertation is relevant, and the results obtained matter, both theoretically and practically.

3. General characteristics of the candidate's research and scientific-applied activity

The candidate in the competition has taken an active part in many national and international scientific forums:

national with a report – 11 participations, and in works she is in first place in 8 of them.

national with international participation and at international – 14 participations, as in 7 of the reports, it is in first place.

contracts and projects – NNP „New technologies in energy", „Building scientific potential", „E-Plus", „INFRAMAT" of IPC, to FNI and in teams with IEES-BAN, UZU, IEES, PU, UAN – with active participation of the candidate in their performance and presentation.

The aim of the dissertation work is the electrochemical deposition of alloy and composite coatings of Ni with W, Mo and TiOx, determination of their chemical composition, structure, morphology, electrocatalytic properties and corrosion resistance, in view of their potential application as electrode materials in hydrogen evolution.

To achieve this goal, the following tasks have been defined:

1. Obtaining nickel alloy and composite materials with W, Mo and non-stoichiometric TiOx:

• Selection of electrolytes and conditions of the electrochemical process.

• Physical characterization of the resulting coatings.

2. Study of the catalytic activity in relation to the hydrogen release reaction of the resulting coatings (on different substrates).

3. Corrosion resistance assessment in two model environments (0.5 M H_2SO_4 and 6 M KOH).

To realize the set tasks, systematic studies were carried out for: selection and preparation of the samples, selection of electrolytes and the conditions for obtaining the coatings (temperature, pH, concentration, stirring, current indicators, deposition time). The obtained results are presented clearly in graphical and tabular form, which facilitates their perception and analysis.

4. Main scientific and applied scientific contributions

The scientific and scientifically applied contributions presented by the candidate sufficiently reflect the most important achievements of the dissertation work. In short, I would summarize them as follows:

Suitable electrolytes have been selected, and the environmental conditions and parameters of the electrolysis process have been determined to obtain alloy and composite coatings of Ni with W, Mo and TiOx, on a copper and carbon base, with optimal electrochemical characteristics, by means of a variety of physicoanalytical and electrochemical methods.

It has been found that the coatings have a higher electrocatalytic activity (especially NiMo), compared to a single nickel coating, when H_2 is released on them.

The corrosion resistance of the resulting coatings is determined in two model environments. It has been proven that in 0.5M H_2SO_4, the highest resistance is the NiW alloy and the NiWTiOx composite, as a result of the tungsten phase ($H_{0.33}O_3W$ and H_2O_4W). In 6M KOH, all coatings are highly corrosion-resistant, i.e., they can be used as electrodes in the production of hydrogen.

5. Reflection of the candidate's scientific publications in bulgarian and foreign literature

As noted in **2.** of my review, 5 works and 36 citations were published on the candidate's dissertation work. The quantitative dimension is 117 p. – the minimum requirements are fulfilled. In addition, she has presented the complete list of all publications with her participation and the 119 citations noticed so far.

All this, in addition, shows that Eng. Him. Marina Hristova Arnaudova is a recognizable and established name among the international scientific community.

6. Critical remarks and recommendations to the candidate's scientific works

I have no significant critical remarks about the candidate's dissertation and scientific works.

I recommend refining some terminological definitions:

- in the title of the dissertation „....*electrochemical coatings*....". Electrochemical is the method of obtaining the coatings, as correctly written in V.1 - ....electrochemical deposition.., or in V.1.4 .....electrolysis process....;

- in III. Purpose and tasks „..... *and corrosion properties*.....". It is correct „corrosion behavior or resistance", as written in 3. of Purpose and tasks.

Question: How are the model media selected to determined the corrosion resistance of the coatings – nature, concentration? - according to literature data, from preliminary tests, from the composition of the coatings, etc.

7. Personal impressions of the reviewer about the candidate

Ing. Chemist Marina Hristova Arnaudova completed her higher education at UCTM – Sofia, specialty "Technology of Materials and Materials Science" (specialization "Electrochemistry and Corrosion Protection"). I have been her

teacher in the field of corrosion and material protection. During her studies, she was distinguished by responsibility and diligence in the learning process. She was correct and responsive to her colleagues and enjoyed their respect, as well as that of the lecturers from the department and the University. He has a good fundamental background in electrochemistry, corrosion, and general chemistry. She has mastered a variety of electrochemical, corrosion and physicoanalytical methods and techniques for research and analysis. He can skillfully present and comment on the results obtained during the development of the dissertation.

CONCLUSION

In conclusion, I believe that the dissertation submitted to me for review, in terms of volume, methodological level, scientific and scientific-applied contributions and publications in the specialized scientific literature, Law on ZRASRB and fully meets the requirements of the minimum requirements set by the SC of IPC "Acad. R. Kaishev" - BAS, for acquiring scientific degrees and occupying academic positions.

From the above and starting, first of all, from the scientific and applied contributions of the dissertation work, the importance of the obtained results for the creation of new materials and coatings for high catalytic and energy efficiency, stability and environmental protection, as well as the successful implementation of the educational goals of the doctoral studies, I express my positive assessment and recommend to the members of the Scientific Jury at IPC - BAS to conduct the public defense of the above dissertation work, to vote for the award of the educational and scientific degree "doctor" in professional direction 4.2 Chemical sciences, scientific specialty „Electrochemistry" of eng. – chemist Marina Hristova Arnaudova.

София

12.07.2025

Рецензент: