

REVIEW

On a thesis for the scientific and educational degree "DOCTOR" of (Philosophy Doctor, PhD), professional field, 4.2 Chemical Sciences, scientific specialty "Electrochemistry" (incl. chemical sources of current)

Scientific organization: Institute of Physical Chemistry, Bulgarian Academy of Sciences, "Acad. R. Kaishev".

Reviewer: Professor Dr. Branimir Ivanov Banov IEES-BAS, member of the Scientific Jury, appointed by Order of the Director of Institute of Physical Chemistry - BAS.

1. General information and brief biographical data about the candidate

Veselina Petrova Chakarova was born on 27.11.1979 in the city of Sofia. In 1994, she entered the University Chemical Technological and Metallurgical UCTM-Sofia, where she successively acquired the following degrees of education as follows: 1998 "Chemical Technologist", and in 2011. "Bachelor in the Department of "Inorganic Chemical Technologies". In the period 2012-2014, she acquired the "Master" degree in the Department of "Electrochemistry and Corrosion" of the Chemical-Technological and Metallurgical University. Meanwhile, while still a bachelor; in 2011, she entered the Institute of Physical Chemistry-BAS, as a chemist. In the period 2011-2017, she was promoted to the rank of assistant professor, which she held until 2019. For the period 2019-2024, she set herself the task of her academic growth, applied for and started her doctoral studies under the supervision of Prof. M. Petrova and Assoc. Prof. M. Monev.

I do not know Chem. Eng. Vesselina Chakarova personally and I have no direct observations of her work and scientific growth, so in my judgment I will base my assessment only on the documents and materials provided to me for this purpose. The very good basic theoretical education that chem. eng. Vesselina Chakarova received the University, as well as her fluent English language skills, have allowed here not only to develop interesting and achieve excellent results on the topic, but to present them at national and international forums in the best possible way to the scientific community around the world. The recognition of the world scientific community for her work is reflected in 50 citations noted so far. Of course, this is the fruit of the entire team, but the leading role of Chakarova can be boldly attributed to the thesis applicant. The achieved results are natural and are due to the very good theoretical background from the UCTM and the extensive practical experience of the applicant, who started his creative process in the early 2011.

2. Description of the materials presented and relevance of the topic of the thesis

The materials submitted by the candidate include the documents required by the procedure, namely:

- PhD Thesis, (Thesis)
- Abstract,
- Reference to the Contributions of the thesis,
- List of scientific works included in the thesis,
- List of participation in conferences with reports and poster presentations, as well as participation in other scientific events,
- List of all scientific works of the thesis candidate to date,
- List of noted citations,
- Curriculum Vitae (CV)

All presented documents correspond exactly to the requirements set by law and allow the evaluation of the thesis to be complete, accurate and fully justified, thanks to the comprehensive information provided.

The thesis is written on 111 pages and contains 64 figures and 35 tables. 120 literary sources are cited. The thesis itself is based on five (5) publications, as follows: two (2) Q2, one (1) Q3 and two (2) Q4. The works arranged in this way carry a total of 79 points with a required minimum of 30 points, which shows that the candidate has tried hard enough for a very good performance, exceeding the required minimum by more than 2 times. The number of citations noted for the moment is 8. It should be noted also that in only one of the works from the Q2 segment, the thesis candidate chem. eng. V. Chakarova is in second place, while in all other presented publications she occupies the leading first place, which confirms her competence, diligence and quality of work done.

Participation in national and international forums, as well as national ones with international participation, can only be praised for the high activity. Participation in national scientific forums with oral reports - 4 pcs., presentation of posters at national scientific forums - 12 pcs., delivery of oral reports at international forums - 5 pcs., and participation in international forums with poster presentations - 29 pcs.

Participation in Contracts. Several groups can be formed here, as follows: DAAD -2 pcs., CC Electrochemical Surface Technology -1 pc., Ministry of Education, NSF-4 pcs., INFRAMAT (2019-2023) -6 pcs., "Young Scientist" (2020-2023) 1 pc. The results presented above are more than impressive and confirm the activity, ambition and competence of the thesis candidate.

The thesis is very well structured, being divided into separate parts, followed by conclusions and cited literature. This arrangement makes it much easier for the reviewer to compare the literature data with the obtained results, if necessary. Thus, at each separate stage of the conducted research, the progress achieved is clearly visible. The thesis contains the following parts: Introduction, Historical review, Literature review, Goals and resulting tasks, Experimental part, Experimental results, Abrasive properties of composite Ni-P coatings, Corrosion behavior of chemical and composite Ni-P coatings, Electro-catalytic properties of chemical Ni-P on steel and Chemical deposition of Ni on ABS not containing a reducer. As already mentioned, after each study, conclusions and literature follow.

Topic relevance. Electroplating is an extremely important part of the electrochemistry of metals and deals with the application (deposition) of one metal on another (substrate) in order to improve the mechanical, electrical and mainly corrosion characteristics of the first. Corrosion protection of various structural elements is of essential importance, both for the safety of the structural elements and from a financial point of view. The deposition of metal (protective coatings) is a complex multi-step process that hides pitfalls at every step. In addition, when it comes to coating non-metallic samples, the problems increase many times over. It is in this direction that a series of studies have been conducted on various non-metallic samples such as PET and ABS. The formed coatings are made of Ni-P, or Ni-P matrix with various dispersion systems such as BN, SiC or Diamond embedded in it. The incorporation of such finely dispersed particles into the structure of the Ni-P matrix aims to obtain abrasive materials applied to various non-metallic substrates. Moreover, here is the big challenge in the topic. However, the thesis candidate has successfully solved and overcome the challenges and achieved excellent results. The technology thus developed for incorporating fine dispersed powders can be used as a decorative and anti-corrosion coating.

Based on the above, it can be concluded that the research conducted is more than relevant and timely. This is also evidenced by the fact that the works of the thesis have more than 50 noted citations. This fact confirms that we have not only a successful thesis preparation, but also a fully developed scientist with his own contribution to the subject. In addition, of course, the development of a method for obtaining chemical (electroless) coatings without the use of a reducer is the icing on the cake in this thesis.

3. General characteristics of the research

The aim of this thesis is the chemical deposition of pure and composite Ni-P coatings on various types of substrates, flexible and rigid, conductive and non-

conductive, and the conditions of preparation, their abrasive ability, corrosion resistance and electro catalytic activity have been studied.

The following tasks arise from the goal set thus:

- Establishment of optimal composition and operating mode of a solution for chemical deposition of Ni-P coatings. Determination of factors affecting the performance of the solution, appearance and adhesion.
- Chemical deposition of composite Ni-P on PET with the inclusion of micro dispersed particles such as BN, SiC, and diamond of different particle sizes in Ni-P matrix.
- Investigation of the corrosion behavior of pure and composite Ni-P coatings on ABS.
- Investigation of the electro catalytic properties of chemically deposited Ni-P in terms of HER and OER in alkaline and HER in acidic media.
- Investigation of the possibility and conditions for preparing the surface of ABS for metallization by chemical deposition of a Ni layer from a solution containing no reducing agent.

In order to meet the set tasks, systematic studies were conducted to determine the technological scheme of sample processing.

The appropriate solutions for the preliminary preparation of the various surfaces of the metal electrodes (steel) and the polymeric materials PET and ABS have been selected. The proposed technological scheme approaches the classical one, including the following operations: degreasing, pickling, reduction, pre-activation, activation, acceleration. For each individual subject PET, ABS or metal steel electrode, the optimal conditions for the processes have been selected, such as concentration, pH, temperature, stirring mode time of processing.

Boron nitride (BN), silicon carbide (SiC) and diamond particles (C*) with different particle size distributions, ranging from 1 to 300 μm for diamond powder, from 1-5 μm for hexagonal BN, from 50-125 μm for cubic BN and 7-70 μm for SiC, were used as micro dispersed particles.

After optimizing the composition and conditions for obtaining the chemical coatings process (electro less plating), such as concentration, temperature, pH, stirring, process time, reliability, the obtained samples were subjected to complex physicochemical studies. The coating thickness of the samples have been evaluated by X-ray fluorescence analysis, X-RAY XDAL, the surface elemental composition and morphology - with SEM and EDS, the phase composition with

XRD and TEM and the chemical surface state by XPS. Only for determining the tribological behavior was used a special self-made apparatus developed at the Institute of Physical Chemistry IPC-BAS.

The interpretation of the obtained data is very good and gives a complete and adequate picture of the conducted research and obtained results. The thesis author has tried to illustrate and explain all the steps and obtained data, both textually and support graphically. The figures presented in the thesis are unambiguous and show a deep understanding of the processes and serious theoretical background combined with excellent practical experience, which inevitably leads to excellent results.

4. Main scientific and applied scientific contributions of the thesis

The main scientific and scientifically applied contributions are determined and defined by the thesis candidate, with which I completely agree and allow myself to quote verbatim, and they sound like this:

1. Abrasive materials based on composite chemical Ni-P coatings with different composition (BN, SiC, C*(diamond) and particle size (1-300 μm) on a flexible (PET) substrate were obtained. Tribological tests were conducted, which showed that the obtained materials could be successfully used for abrasive processing of rock samples.
2. Operating conditions have been established under which chemical Ni-P coatings with better electro catalytic properties are deposited compared to electrodeposited Ni with respect to HER and OER in alkaline media, as well as HER in acidic media.
3. The corrosion behavior of thin chemical Ni-P coatings with different phosphorus contents in acidic, neutral and alkaline environments has been studied. The corrosion characteristics have been determined and the changes in the composition and morphology of the coatings due to the corrosive effects of the environment have been shown.
4. An original method for wiring activated ABS is proposed by treating it in an alkaline solution containing nickel sulfate and citric acid at a temperature above 40°C. A porous oxidized nickel layer is deposited on the surface of the activated ABS with a thickness sufficient to initiate subsequent electrodeposition of copper from a classical acidic electrolyte.

5. Reflection of the candidate's scientific publications in Bulgarian and international literature

Chemical Eng. Vesselina Chakarova has provided the full list and copies of the publications included in the thesis, from which the results achieved and presented to the broad national and international scientific community are very clearly visible.

The thesis itself, as already mentioned, is based on five (5) publications, as follows: two (2) Q2, one (1) Q3 and two (2) Q4. The works selected in this way carry 79 points with a required minimum of 30 points, which shows that the candidate has made enough effort for his presentation, exceeding the required minimum by more than 2 times. The thesis candidate V. Chakarova is the leading author in four out of five publications, which is a recognition of the team for her leading role in the conducted research and processing of the results. Eight (8) citations have been noted on the submitted and included in the thesis publications. From the academic reference, according to the LDASRB and the Regulations of the Institute of Physical Chemistry, IPC-BAS, it is clear that the thesis candidate exceeds and overcome by many times the minimum requirements.

The additional materials provided, such as publications not included in the thesis and the number of citations (50!), show that Chemical Engineer Vesselina Chakarova is a fully established scientist with a reputation and an established international name.

6. Critical remarks, recommendations and questions

I have no remarks, recommendations or questions for the thesis.

7. Personal impressions

I do not know the doctoral student personally and have no common publications with her. The materials presented at the preliminary thesis presentation very pleasantly surprised me. Very good and clear professional language and expression, combined with knowledge, basic understanding of the matter and the processes that take place and comment on. The same is observed in the written thesis work document. Good Bulgarian language, precise expression, showing skill, understanding and in-depth professional knowledge of the matter.

8. CONCLUSION

Active scientific research activity defines chem. eng. Vesselina Petrova Chakarova as a young and ambitious scientist in the field of chemical coatings with a taste for challenges in the scientific field as:

- new ways for electroless coating of polymer materials (PET, ABS),
- new functional applications (abrasive, with microstructure hard solid particles embedded in a Ni-P matrix),

- simplified technologies (direct metallization of products from ABS),
- environmental protection (corrosion protection with Ni-P coating),
- improved energy efficiency (new materials for highly efficient electro catalysis of HER and OER),
- new structural materials and technology for industry.

The scientific contributions of the doctoral candidate, chem. eng. Vesselina Petrova Chakarova and the material submitted for review are up-to-date and fully cover and exceed many times the requirements of the LDASRB and the Regulations on the conditions and procedure for acquiring scientific degrees and occupying academic positions at the Institute of Physical Chemistry, Bulgarian Academy of Sciences, "Acad. R. Kaishev"

The presented materials give me full reason to recommend with conviction to the Honorable Jury to support my positive assessment for the doctoral student, chemical engineer, Vesselina Petrova Chakarova, and to vote for awarding the scientific and educational degree "DOCTOR" in the professional field 4.2 Chemical Sciences, scientific specialty "Electrochemistry" (including chemical sources of current).

Sofia

Reviewer:

29.01.2025