Институт по ФИЗИКОХИМИЯ при БАН
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REVIEW

on the dissertation for the acquisition of the educational and scientific degree "Doctor" in a professional field 4.2. Chemical Sciences "Electrochemistry"

Author of the dissertation: Eng. Vesselina Petrova Chakarova

Topic of the dissertation: "Obtaining and characterization of Ni-P coatings on different types of substrates"

Reviewer: Rashko Stefanov Rashkov, Ph.D., Associate Professor, Institute of Physical Chemistry - BAS

1. General information and brief biographical data about the candidate.

One of the important advantages of chemical metallization of products compared to electrochemical deposition is the uniformity of the coating, which makes them a preferred material for coating various elements in aircraft construction, shipbuilding, for coating pipes for the gas and oil industry, etc. In addition, these coatings have good corrosion resistance. For example, chemically deposited Ni-P coatings are distinguished by better tribological properties and corrosion protection ability than galvanically obtained nickel coatings. The co-deposition of dispersed particles to chemically obtained Ni-P coatings leads to increased wear resistance, low friction coefficient, for which they are widely used in the manufacture of abrasive tools. Recently, there have even been studies of chemically deposited Ni-P alloys as a catalytic material for electrodes in the hydrogen production. Another important advantage of chemical metallization is the conducting of dielectrics. One of the disadvantages, however, is the large number of pre-treatment operations before the actual metallization. Therefore, the efforts of scientists are aimed at facilitating the process by developing technological schemes for direct metallization. Part of these problems and in particular the conditions for obtaining chemical Ni and Ni-P coatings on various substrates, their characterization and the possibility of various applications are the subject of the current doctoral thesis, prepared by Eng. Vesselina Chakarova. She graduated with a Bachelor's degree, Department of Inorganic Chemical Technologies at Chemical Technology and Metallurgy University in 2011. In 2012-2014, she obtained a Master's degree in Electrochemistry and Corrosion Protection at the same university on the topic: "Chemical Deposition of Composite Nickel-Phosphorus Coatings on Flexible Substrates" with scientific supervisor Assoc. Prof. Dr. M. Petrova and consultant Assoc. Prof. Dr. Il. Gadzhov. It is obvious that the doctoral thesis prepared by Eng. Vesselina Chakarova is a continuation of the research underlying her diploma work. For the period 2011 – 2017, 2019-2024 she was appointed as a chemist at the Institute of Physical Chemistry at the Bulgarian Academy of Sciences, and in 2017 - 2019 she was an assistant at the same institute. On 01.01.2020 she was enrolled as a PhD student in independent training at the Institute of Physical Chemistry-BAS and was enrolled with the right to defend on 01.12.2022.

2. Description of the submitted materials.

The scientific output of PhD student Vesselina Chakarova includes 13 papers in refereed international journals, 2 papers in non-refereed international journals and one patent. During her appointment at the Institute of Physical Chemistry, she participated in 14 projects, one of which she was the supervisor. These projects largely correlate with the topic of her PhD. The doctoral thesis of PhD student Vesselina Chakarova is structured on 5 publications – one in *Archives of Metallurgy and Materials* with quartile Q2, one in *Trans. Inst. Met. Finish.*, with quartile Q2, 2 in *Bulg. Chem. Commun* with quartile Q4 and one in *Electrocatalysis* with quartile Q3, which is a total of 79 points with a minimum of 30. The main part of the results was reported at 12 national and 22 international scientific forums. Obviously, the PhD student has not only fulfilled, but also exceeded the required minimum according to the current regulations on the conditions and procedure for acquiring scientific degrees and for occupying academic positions at the Institute of Physical Chemistry.

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

The dissertation submitted to me for review is written on 110 pages, contains 64 figures and 35 tables. 120 references are cited, distributed in the relevant sections. The main sections are: Introduction, Theoretical part, covering a brief historical overview and literature review, Experimental part, Experimental results and discussion. The introduction outlines the advantages of chemically deposited Ni-P coatings over galvanically deposited ones, relating to better layer uniformity, better tribological properties and better corrosion resistance. The wide range of applications of these coatings is also mentioned, including their use as a catalytic material in the production of hydrogen as well as for the conducting of dielectrics. A detailed description of the properties of chemically deposited Ni-P coatings and the influence of the components of the solutions for their preparation as well as the preliminary preparation processes are clearly presented in the theoretical part. An in-depth review of the used diamond particles, boron nitride particles and silicon carbide, as suitable dispersoids for co-deposition in the nickel matrix and their application as abrasive materials, is made. Based on a critical analysis of the literature review, conclusions are drawn that the reasons for the anti-corrosion properties of Ni-P coatings are still not fully understood. In addition, very few studies have addressed the electrocatalytic activity of these coatings. Based on these conclusions, the goal of the dissertation is clearly formulated, namely: chemical deposition of Ni-P and composite Ni-P coatings on different types of substrates (flexible and solid) and their characterization in terms of abrasiveness, corrosion resistance and electrocatalytic activity. The main tasks for achieving the goal of the dissertation are identified:
1. Establishing the optimal composition and operating mode of a solution for chemical deposition of Ni-P coatings. The determining factors are stability and productivity of the solution, appearance and adhesion of the coating.
2. Chemical deposition of composite Ni-P coatings on polyethylene terephthalate (PET) using microdispersed particles differing in composition and size.
3. Investigation of the corrosion behavior of Ni-P and composite Ni-P coatings on acrylonitrile-butadiene-styrene (ABS) in sulfate and chloride environments.

4. Investigation of the electrocatalytic properties of chemically deposited Ni-P coatings with respect to the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in alkaline and HER in acidic environments.
5. Investigation of the possibility of preparing the ABS surface for metallization by chemical deposition of a Ni layer from a solution containing no reducing agent.

To accomplish the tasks set, both physical and electrochemical methods were used, described in the "Experimental Part". The selection of substrates and microdispersed particles, the technological schemes for pre-treatment of the substrates, as well as the compositions and operating modes of solutions for chemical deposition of Ni and Ni-P coatings are noted here.

In the experimental results and discussion section, the main results are presented, systematized in four chapters, corresponding to the tasks set. In the first, the influence of the composition and operating mode on the speed and stability of the solution for chemical deposition of Ni-P coatings on a flexible PET substrate was studied. From the results obtained, the composition and operating conditions of a base solution were selected. Composite Ni-P coatings were deposited with it, including diamond, boron nitride and silicon carbide particles of different sizes. A huge number of experiments were performed to clarify the influence of particle size, deposition time on the mass of the composite coating, temperature and six types of hydrodynamic modes. It was established that for the incorporation of dispersed particles, their pre-wetting with a surfactant and the selection of an appropriate hydrodynamic mode are important. For example, for particles with smaller sizes, a constant air stirring mode is suitable, while for larger particles, a combined operating mode is used - a stirring period and a rest period. The abrasive properties of composite coatings have been demonstrated in limestone processing, where it was found that larger particles remove a greater amount of mass, but the effect is strongest with diamond particles. Studies on the corrosion resistance of chemically deposited Ni-P coatings have been carried out in model alkaline, neutral and acidic environments. It has been shown that chemical Ni-P coatings with a higher P content have better corrosion resistance compared to electrodeposited Ni. This fact is associated with the P content in Ni-P coatings, since Ni dissolves preferentially and the surface is enriched in P. A comparison of the corrosion resistance of chemical Ni-P and composite Ni-P coatings in the salt spray chamber has been made. Weight loss has been found for both types of coatings, with the loss being greater for composite coatings. This is attributed to corrosion of the coating around the particles and their subsequent mechanical removal.

The following chapter presents results of systematic studies on the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) on steel samples with electrodeposited Ni and chemical deposited Ni-P coatings in alkaline and acidic environments. It was found that in alkaline environments, with a decrease in the P content in the chemical Ni-P coating, the hydrogen evolution overvoltage decreases, and with electrodeposited Ni the catalytic effect is the best. In contrast to HER, chemically deposited coatings with a higher P content are distinguished by better activity for OER compared to electrodeposited Ni. In acidic environments, the catalytic activity for HER increases with increasing P content in the coating to values of about 7 wt. %, after which it decreases and at 18.1 wt. % approaches that of electrodeposited Ni. This fact is associated with the real area, the change in the intrinsic activity of the electrode due to the alloying of Ni with P, as well as the phase composition, very well illustrated by TEM and XRD analyses.

In the fourth part of the experimental results, an original method for modifying the activated ABS sample with a nickel layer is presented, in which the acceleration and classical chemical nickel plating operations are replaced by an electrolyte containing no reducing agent. A significant number of experiments have been carried out on the influence of the main components of the nickel

solution on its stability and conductivity. The studies show that copper can be electrochemically deposited from a classical acidic electrolyte on the ABS sample treated in the presence of propionic acid.

From what has been said so far, it is evident that the tasks set have been fulfilled, and the volume, analyses and discussions at a high scientific level fully satisfy the criteria for the doctoral thesis for obtaining the degree of "doctor". The abstract correctly reflects the results, conclusions and contributions of the doctoral thesis.

4. Main scientific and applied scientific contributions.

The contributions of the dissertation work could be summarized as follows:

• Abrasive materials based on composite chemical Ni-P coatings with different composition and size of dispersoids (diamond, boron nitride and silicon carbide particles) were obtained. The composite coatings were deposited on a flexible polyethylene terephthalate (PET) substrate and tribological tests were conducted. In this way, their application in the practice of abrasive processing of limestone was proven.

• Working conditions have been established under which chemical Ni-P coatings with better electrocatalytic properties are deposited compared to electrodeposited nickel with respect to the hydrogen evolution reaction in alkaline and acidic environments and the oxygen evolution reaction in alkaline environments are deposited. The influence of P in the coating, its surface and phase composition on the electrocatalytic behavior of these coatings has been clarified.

• Given the practical focus of the studied materials, the doctoral thesis has paid special attention to their corrosion behavior. 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 corrosion have been shown. The studies concern not only chemical Ni-P coatings, but also composite Ni-P coatings. In the latter, the particle size has been taken into account.

• For me, undoubtedly, the most significant contribution of the doctoral thesis is the original method for conducting activated ABS by processing in an alkaline solution containing nickel sulfate and citric acid at a temperature above 40°C. In this method, the acceleration and chemical nickel plating processes are replaced by only one process. In this way, the overall chemical nickel plating process becomes more economical due to the reduction of operations, the reduction of the consumption of chemicals and of washing and wastewater. In addition, it prevents the spontaneous decomposition of the chemical nickel plating solution due to deviations in the technological regime. In the presence of propionic acid in a Ni solution for the processing of an ABS sample, a non-dense nickel layer is formed. The statement is successfully illustrated by XPS analysis. This layer is in an oxidized state with a thickness sufficient for subsequent electrodeposition of copper from a classical acidic electrolyte.

I would like to emphasize that the contributions of the dissertation are significant both scientifically and scientifically-applied and represent a further development and enrichment of knowledge in the field of chemical deposition of Ni-P coatings on various materials.

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

The doctoral thesis of the PhD student Vesselina Chakarova includes a total of 5 publications in IF journals. By the time of submission of the materials for review, a total of 8 citations from foreign authors have been presented in the articles. This fact speaks of the topicality and content of the thesis.

6. Critical notes and recommendations.

I have a few technical remarks to:
The abstract – the captions of the figure legends are difficult to distinguish.
The dissertation – the magnifications of the images in Fig. 30, 32 and 34 should be the same.
I have the following questions:
- How is adhesion assessed (p.46)?
- How do you determine the number of particles included (p.49)?
- What is the relationship with pH in Table 23 (p.62)?
These technical remarks in no way belittle the results of the dissertation work and do not affect their interpretation.

7. Personal impressions of the reviewer about the candidate.

I know Eng. Vesselina Chakarova from her appointment at the Institute of Physical Chemistry at the Bulgarian Academy of Sciences. I was impressed by her diligence and curiosity when entering a difficult subject, related to the mastery of complex and unfamiliar methodologies. She has significant experience in the field of scientific research and technological development. This experience has been quantified in the form of participation in a number of national and international projects, such as DAAD - Inter-institutional cooperation with TU Ilmenau, Germany - "Chemical preparation of metal and metal-composite coatings" and "Characterization of hydrogen storage electrodes used in alkaline electrolysis", framework contract for scientific research in the field of electrochemical technologies for surface treatment between CEST, Austria and IPC-BAS, project DFNP-17-127/31.07.17, INFRAMAT, including a beneficiary under the National Scientific Program "Young Scientists and Postdoctoral Fellows", module "Young Scientist" for the period 30.04.2020 - 28.04.2024, etc.

In recent years, she has received a number of awards at the national level, e.g. award for poster presentation - "Corrosion resistance of chemical Ni-P coatings obtained on a polymer substrate (ABS)", V Scientific Seminar on Physical Chemistry for Young Scientists and PhD Students, 19-21 April 2016, Sofia; award for poster presentation "Corrosion tests of chemical Ni-P coatings in sulphate or chloride media", 4th Interdisciplinary PhD Forum with International Participation, May 16 – 19, 2023, Sandanski, Bulgaria; award for poster presentation - "Electroless nickel oxy-hydroxide structures on different substrates", 5th Interdisciplinary PhD Forum with International Participation, 16 – 19 April 2024, Kyustendil, Bulgaria. All this gives me reason to believe that the merit in carrying out the research for the doctoral thesis is largely hers.

CONCLUSION

The logical and highly scientific presentation of the results in the doctoral thesis, as well as the analysis made, show that the material is dissertation able, and the topic is extremely relevant. The scientific contributions and scientometric data fully meet the requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria and the Regulations on the terms and procedure for acquiring scientific degrees and for occupying academic positions at the Institute of Physical Chemistry "Acad. R. Kaishev". Given the above and the achieved level of qualification of the PhD student, my assessment is positive and I strongly recommend that the members of the scientific jury vote for awarding the educational and scientific degree "Doctor" in professional field 4.2. Chemical Sciences "Electrochemistry" to Eng. Vesselina Chakarova.

Sofia, **Reviewer:**

28.01.2025 г. /Assoc