Standpoint

in competition for the educational and scientific degree "Doctor"
in Professional field: 4.2.Chemical Sciences, specialty Electrochemistry
with candidate: Marina Hristova Arnaudova, Section "Electrochemistry and Corrosion", IPC - BAS
Title of the PhD thesis:
PREPARATION AND CHARACTERIZATION OF ELECTROCHEMICAL COATINGS ON NICKEL BASED Ni-M, where M = W, Mo, TiO_x
Chairman of the scientific jury: Prof. Dr. Maria Petrova, IPC - BAS

1. General characteristics of the research and applied activities of the candidate's

Marina Arnaudova graduated in 2001 from the University of Chemical Technology and Metallurgy in Sofia with a Master's degree in Materials Technology and Materials Science from the Department of Electrochemistry and Corrosion Protection. Her professional career began in 2002 as a chemist in the section "Electrochemistry and Corrosion" at the IPC - BAS and went through respectively chemist, research assistant III degree and again chemist. Between 2020-2023 she was a free PhD student at the same section. The topic of her dissertation is: "PREPARATION AND CHARACTERIZATION OF ELECTROCHEMICAL COATINGS ON NICKEL BASED Ni-M, where M = W, Mo, TiO_x" with scientific advisor Assoc. Prof. Dr. Rashko Rashkov.

The dissertation of eng. Marina Arnaudova is dedicated to some of the most common electrode materials based on nickel and its alloys. In many cases, coatings made of pure metals cannot meet the high-performance requirements demanded of them. This has necessitated the search for coatings with the required properties that could be achieved through deposition of binary or more complex alloys. One possible solution to this problem is alloys of nickel with the transition elements - tungsten, molybdenum, as well as its composites with titanium oxides. In this regard, the aim of this dissertation is related to the electrochemical deposition of alloys and composites of nickel with W, Mo, TiO_x, as well as the determination of their electrocatalytic and corrosion properties with a view to their potential application as electrode material for the hydrogen evolution reaction.

To achieve this goal, the conducted research can be divided into two groups:
1. Preparation of alloy and composite nickel coatings on **copper substrate**.
Electrolytes containing different contents of tungsten, non-stoichiometric titanium oxides and molybdenum were used under different conditions of the electrolysis process (potential, hydrodynamics regime, concentration of the reactants, pH).

The obtained materials were electrochemically characterized by investigating:

- The electrocatalytic activity for the hydrogen evolution reaction of nickel coatings with W, Mo and TiO_x on a copper plate compared to pure nickel
- Corrosion resistance - it was found that:

- The NiW and NiWTiO_x coatings showed the best corrosion resistance in 0.5MH_2SO_4, which is due to the formation of a stable tungstate phase on the surface. Impedance studies provided evidence for the simultaneous processes of diffusion, new layer formation and nickel dissolution.
- In 6MKOH, all investigated coatings showed significant corrosion resistance due to the formation of a protective layer of different types of mixed hydroxides of the NiMeO$(OH)_x$ type,

where Me = Mo or W. In this environment, NiMoW alloys stood out with the highest value of polarization resistance.

2. Preparation and characterization of alloy and composite coatings on **modified and plain carbon fibers.**

Electrochemically deposited NiW, $NiWTiO_x$, NiMo and NiMoW type coatings on oxidized and unoxidized carbon fibers. The layers obtained on the oxidized substrate possessed a more developed surface due to the formation of a gel-like layer and are characterized by better electrocatalytic activity in terms of hydrogen evolution reaction.

2. Main scientific and applied contributions

The dissertation is written in 98 pages, contains 40 figures, 14 tables and 80 references are cited. The abstract accurately reflects the main results of the thesis.

The listed scientific and applied contributions adequately reflect the achievements of the dissertation and can be formulated as follows:

- Alloy and composite nickel-based materials with W, Mo, and TiO_x were electrochemically deposited on various substrates. The dependence of the composition of the coatings on the parameters of the electrolysis process was established and the optimum conditions for obtaining coatings with the required characteristics were identified.
- The electrocatalytic activity of the obtained materials with respect to the hydrogen evolution reaction (HER) was studied. It was found that all the coatings exhibited better electrocatalytic behaviour compared to pure nickel coating. The alloys containing molybdenum showed the best electrocatalytic activity for HER compared to the other systems studied in alkaline media.
- In-depth corrosion studies were conducted in two model environments using different electrochemical methods. It was found that in acidic media ($0.5MH_2SO_4$), the NiW alloy and the $NiWTiO_x$ composite exhibited the best corrosion resistance, attributed to the formation of stable tungstate phase ($H_{0.33}O_3W$ and H_2O_4W) in the form of filamentary crystals on the surface. In alkaline media (6MKOH), all studied coatings demonstrated significant corrosion resistance. Along with good catalytic activity in this environment, they could be effectively used as electrode material for hydrogen production.

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

The main part of the results in the dissertation work have been formalized and published in five scientific publications, including one with Q1, one with Q2 and three in conference proceedings (she is first author on one of them). Some of the results have been presented at national and international scientific forums. Eng. Marina Arnaudova has participated in seven national and international research projects.

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

I have a question: what is the difference between oxidized, unoxidized, modified and plain carbon fibers?

Conclusion:

Eng. Marina Arnaudova has demonstrated to have mastered specific electrochemical and physical methods, which she has successfully applied to characterize new alloy and composite coatings on two types of substrates.

According to the attached reference on the minimum requirements of the IPC for the scientific activity of Eng. Marina Arnaudova for the acquisition of the formation and scientific degree "Doctor" (according to the Regulations of the PhD, IPC-BAS) it is shown that with a minimum required 30 points, the PhD student has an asset of 45 points (two publications with IF) and 41 citations on these two publications.

In conclusion, I would like to emphasize that the volume, the quality of the scientific contributions and the scientific metrics presented by the Ph.D. student give me reasons to recommend with confidence and pleasure to the members of the Honorable Scientific Jury to vote for the award of the educational and scientific degree "Doctor" in the professional field 4.2. Chemical Sciences, scientific specialty "Electrochemistry" to Chem. Marina Arnaudova.

08.07.2025

Signed:
(Prof. Maria