REVIEW

on the competition for **associate professor**,
Scientific direction **4.2. Chemical Sciences**, specialization **Electrochemistry (incl. Chemical power sources)** at the **Institute of Physical Chemistry**,
Bulgarian Academy of Sciences,
announced in **SG № 62/27.07.2021**,
Candidate (s): **assist. prof. Nelly Dimitrova Boshkova, PhD**,
Reviewer: **prof. DSc Assen Angelov Girginov, PhD**

1. GENERAL CHARACTERISTICS AND BRIEF BIOGRAPHICAL DATA OF THE CANDIDATE

In 1992 assistant prof. Boshkova, PhD graduated from the Technical School of Chemical Industry and Biotechnology "Prof. A. Zlatarov", Sofia, majoring in "Technology of Organic and Inorganic Substances".

In 1997 she graduated as a Master student at the Faculty of Chemistry of Sofia University "St. Kliment Ohridski" with a degree in "Chemistry" and a qualification "Chemist. Teacher of chemistry and chemical technology".

In the period 2003 - 2008 she worked as a chemist in the "Electrochemistry and Corrosion" section at the Institute of Physical Chemistry "Acad. Rostislav Kaishev" (IPC), BAS.

She became a doctoral student in the same section in 2015.

In 2017 she acquired the educational and scientific degree "Philosophical Doctor" in the scientific specialty Electrochemistry (incl. Chemical sources of electricity).

Since 2017 she has been working consecutively as an assistant professor and chief assistant professor in the "Electrochemistry and Corrosion" section in IPC-BAS.

In the period 2016 - 2020 Dr. Boshkova was a part-time lecturer in the Department of Chemistry at the Technical University of Sofia.

2. DESCRIPTION OF THE SUBMITTED MATERIALS

2.1. Scientific papers and presentations

In the announced competition Dr. Bozhkova participates with a scientific production of 41 titles:

37 scientific publications and 4 chapters in monographs, of which 14 are referenced and indexed in world-famous databases of scientific information;

48 reports and presentations at scientific conferences, of which 25 at international and 23 at national;

Abstract of the dissertation "*Zinc composite coatings with embedded polymer particles - preparation and protective ability*", for which she received the educational and scientific degree "Philosophical Doctor".

Monograph "*Zinc alloys and composites enhancing the protective and anti-corrosion properties of low carbon steel*" (ISBN 978-619-245-154-7);

Patent "*Anti-corrosion hybrid galvanic zinc coatings containing nano-dispersed polyaniline particles, electrolyte composition and electrodeposition method of coatings*" (№ 67266 B1, 15.03.2021).

2.2 Participation in research projects

Dr. Boshkova has actively participated in the implementation of 14 research projects, she is the leader of one of them: "*Innovative environmentally friendly protection systems against corrosion of metal-based structural materials*", BNSF КП-06-Н37/16 2019-2022). In the other projects assigned by NSF-MES, National Innovation Fund, Various Operational Programs, Bilateral Cooperation, External Organizations, Scientific Plan of BAS, respectively, assistant professor Boshkova also took an active part.

3. GENERAL CHARACTERISTIC OF THE RESEARCH AND APPLIED RESERARCH ACTIVITIES OF THE CANDIDATE

In general, the research activity of Dr. Boshkova is homogeneous. The main interests of her research are in the field of electrochemistry, electrodeposition of metals and alloys, protective ability of galvanic coatings, nano-composite and hybrid coatings, corrosion processes and corrosion resistance, inhibitors, characterization of materials and corrosion protection. The main direction in her research interests is the creation of new galvanic, composite, conversion and multilayer zinc coatings for corrosion protection of low carbon steel.

4. MAIN SCIENTIFIC AND APPLIED SCIENTIFIC CONTRIBUTIONS

The analysis of the presented materials gives an opportunity to classify the main scientific and scientific-applied contributions:

4.1. Zinc and zinc alloy galvanic and composite (hybrid) coatings with embedded polymer nanoparticles

The electrodeposition conditions (electrolyte composition, pH, current density, temperature) of Zn and its double alloys Zn/Mn and Zn/Co are optimized. The corrosion behavior of these zinc and zinc alloy galvanic coatings was studied in a model corrosion medium (5% NaCl) by determining the polarization resistance, acquiring potentiodynamic (polarization) and electrochemical impedance dependences. It was found (X-ray diffraction analysis, X-ray photoelectron spectroscopy) that coatings on double zinc alloys have improved protective properties compared to those of pure zinc. Depending on the alloying component (Mn or Co), the coatings have a different decorative appearance: matte or glossy. Based on these three main coatings, zinc and zinc alloy composite (hybrid) layers and systems with incorporated polymer nanoparticles (PM) have been developed.

Zinc and zinc alloy composite coatings are electrochemically formed using four types of polymer particles (PP). After their stabilization, their size and shape were determined by transmission and scanning electron microscopy. Corrosion tests have shown that composite coatings definitely show increased corrosion resistance. Mixed films (identified by XRD, XPS and AFM) were found to form in the hybrid coatings in the presence of PP. These films are resistant to the model corrosion environment and their presence results in the transformation of local corrosion (characteristic of galvanic zinc in this environment) into a general one. The influence of the presence of PP in zinc (Zn/Mn and Zn/Co) alloy coatings has been studied and analyzed.

4.2. Zinc composite coatings containing nanocontainers with corrosion inhibitor

Zinc hybrid coatings containing embedded polymer nano-containers with cores of different substances (hematite, kaolinite and ZnO) were formed using two types of inhibitors (benzotriazole and safranin). Studies have shown that due to the sensitivity of the polymer shell to pH, at some point in the corrosion process it breaks, the inhibitor is released and the corrosion rate slows down in the area around the nano-containers. The electrochemical

characteristics of this type of coatings were studied by the PDP, Rp and EIS methods. The obtained results clearly showed that in the model environment these composite coatings (after a 30-day exposure period) demonstrate improved corrosion characteristics. The results obtained by electrochemical methods were further confirmed by XRD and XPS studies. It has been found that the improved protective ability of this type of coatings is largely due to the corrosion products formed.

4.3. Composite coatings with embedded particles of inorganic (ZnO, CuO) and organic (polyaniline) particles, as well as those of modified carbon spheres and carbon nano-tubes

• The preliminary studies of zinc hybrid coatings with embedded polymer-modified ZnO and CuO particles have shown encouraging results in terms of their corrosion protection. Composite coatings with polymer-modified ZnO particles are embedded directly in the coating. In turn, zinc hybrid coatings with embedded polymer-modified CuO particles are particularly promising for use in biocorrosion conditions.

• Zinc hybrid coatings with embedded polyaniline particles (PANI) have been systematically studied. Polyaniline is known to be a good corrosion inhibitor due to its active adsorption on metal surfaces. In this sense, the aim of the research is the direct use of its inhibitory properties to protect against corrosion in environments containing chlorine ions. PANI particles are incorporated into the coatings by oxidative polymerization in the presence of stabilizers (polyvinylpyrrolidone or colloidal SiO_2). The composition of the formed layer of corrosion products, in which the PANI particles exhibit their inhibitory action, was determined by XRD and XPS. Studies have shown that the presence of PANI particles definitely affects the cathodic and anodic behavior of coatings. A strong depolarization is observed in the cathodic zone, and in the anodic a delay of the corrosion process is registered in comparison with that in zinc.

• Zinc hybrid coatings with embedded polymer-modified carbon spheres and carbon nanotubes have been synthesized. The conditions for preparing a stable suspension of carbon sphere particles for electrodeposition on low carbon steel samples are described in detail. After stabilization of the suspension, the particles are incorporated into the zinc coating by co-polarization. The influence of carbon spheres on the cathodic and anodic processes was evaluated by cyclic voltammetry. The performed PDP, Rp and EIS measurements in the model corrosive environment have definitely confirmed the higher protective ability of the coatings compared to those of pure zinc.

Electrochemically synthesized composite coatings with embedded carbon nanotubes have also shown very good decorative, physico-mechanical properties, as well as increased corrosion resistance in other environments (0.5M Na_2SO_4 and 0.5M H_3BO_3). Their surface morphology was studied by means of SEM. The perspectives for their practical application are presented.

4.4. Corrosion inhibitors

Nitrogen-containing heterocyclic di-cation compounds have been synthesized for possible use as inhibitors in hybrid zinc galvanic coatings. These compounds were characterized by NMR spectroscopy. The study of their inhibitory action against corrosion of steel and galvanized steel was performed by electrochemical methods. The results obtained from long-term exposure (70 days) in the model medium (5% NaCl) have shown that these compounds show a pronounced protective effect against corrosion of low-alloy steel. This presents them as promising for future use as inhibitors in various hybrid zinc galvanic coatings.

4.5. Conversion surface passive films

In the same model corrosion medium (5% NaCl) the protective ability of different types of chromatic passivating films (based on conversion solutions containing Cr^{3+} compounds) on galvanic and composite zinc coatings was evaluated. Similar studies have also been performed on conversion films of alloy (Zn/Mn and Zn/Co) zinc coatings. It has been found that, depending on the conditions, conversion films of different colors (transparent, gray-black and light green) can be obtained. The corrosion properties (in environments of 3% and 5% NaCl) of this type of coatings were evaluated by classical methods (PDP, Rp, EIS, Salt spray tests, etc.). The surface morphology of the coatings was determined by SEM, and the compounds present in the mixed layer were identified by XPS and XRD. To some extent this layer fills the pores of the film, thus preventing penetration of the corrosive environment. The so formed barrier layers formed inhibit corrosion processes.

4.6. Protective coatings based on sol / gel technology

Systematic studies have been performed on the preparation of multilayer systems based on sol/gel coatings containing ZrO_2 and TiO_2 on low carbon steel samples. The zirconium precursor used has a constant composition, while the TiO_2 solution is modified with two types of polymers. These polymers have been found to increase the protective properties of coatings under external polarization conditions compared to the unmodified titanium layer. Detailed studies were also performed on multilayer systems composed of the same starting components (ZrO_2 and TiO_2), made in different variations (ratios). The protective ability of the coatings so formed was tested in the same corrosive medium (5% NaCl). The coatings have shown good corrosion resistance (PDP method). In addition, their phase composition (XRD, EDX and XPS), surface morphology (SEM and AFM) were analyzed, and also their hydrophobicity (contact angle measurement) was assessed. The result is amorphous and dense coatings that clearly demonstrate increased corrosion resistance of low carbon steel in a medium containing chlorine ions. In conclusion, it is worth noting that the multilayer coatings obtained by this method are very promising for increasing the corrosion resistance of low carbon steels in this type of corrosion media.

4.7. Other papers

• Research and corrosion monitoring of austenitic and low-carbon steels used in the facilities of "Kozloduy" NPP in model environments typical for the plant's heat exchangers have been carried out. The corrosion products formed on the inner walls of the heat exchangers were analyzed. The beneficial effect of mono-ethanol-amine as a mixed inhibitor was established.

• Apparatus and methodology for obtaining metal and oxide nano-particles, as well as for adjusting their dimensions have been developed. The facility allows effective control of various parameters related to the nucleation and growth of nanoparticles.

The experimental techniques used, the large number of analytical methods and the reasonable calculation procedures are a guarantee for the high reliability of the obtained results.

I would like to pay special attention to the monograph "*Alloys and composites of zinc increasing the protective and anti-corrosion characteristics of low carbon steel*" presented by Dr. Boshkova and accepted for publication (Publishing House of BAS "Prof. Marin Drinov"). It should be noted that the subject of the presented monographic work is both very relevant and very important. It provides a thorough analysis of a serious problem related to the corrosion of products and equipment made of low carbon steel. In this sense, it is of particular interest to present the various possibilities and approaches for improving the protective and

anti-corrosion properties of this type of construction materials. The described studies have shown the possibility of applying galvanic coatings based on zinc and some of its alloys as protective coatings on this type of steel. Methods for forming zinc composite (hybrid) coatings with embedded various polymer particles have been developed and presented. Models are proposed explaining the process of incorporation of polymer particles into zinc coatings. The monographic work is of undeniable interest both for the expansion of fundamental knowledge and for the application of a number of innovative solutions in this extremely important field of materials science. In addition, the presented monograph will undoubtedly be very useful for all specialists working in the field of corrosion and corrosion protection.

5. IMPACT OF THE CANDIDATE'S SCIENTIFIC PUBLICATIONS IN THE BULGARIAN AND FOREIGH LITERATURE

Dr. Boshkova's literary awareness leaves no doubt. Many of the literary sources cited in her works have been published in recent years. Her research is well known to other scientists in the field of theory and application of multilayer zinc coatings for the protection of low carbon steel. In the presented materials for seven of the scientific works 58 citations are noticed (excluding those of the works included in the dissertation). It is worth noting that 57 of them are by foreign authors. The materials presented for participation in the competition by assistant professor Boshkova are analyzed and evaluated in accordance with the Regulations of IPC-BAS for holding the academic position "Associate Professor" and are summarized in the following table:

Group of indicators:	Indicator №:		Total number of points:	Requirements of IPC-BAS:
А	**1.** Dissertation:		**50**	**50**
	Q_1:	*1 x 25 = 25 p.*		
	Q_4:	*2 x 12 = 24 p.*		
	SJR:	*2 x 10 = 20 p.*		
	Book chapters:	*1 x 15 = 15 p.*		
В	**4.** Scientific publications:		**100**	**100**
	Q_2:	*5 x 20 = 100 p.*		
Г	**5.** Monographs :	*1 x 30 = 30 p.*	**235**	**220**
	7. Publications:			
	Q_2:	*4 x 20 = 80 p.*		
	Q_3:	*3 x 15 = 45 p.*		
	SJR:	*1 x 10 = 10 p.*		
	8. Book chapters:	*3 x 15 = 45 p.*		
	9. Patents:	*1 x 25 = 25 p.*		
Д	Citations:	*58 x 2 = 116 p.*	**116**	**60**
Sum:			**501**	**430**

The presented data clearly show that assistant professor Dr. Boshkova fulfills the necessary requirements set out in these regulations. In addition, a reference on the SCOPUS website showed the presence of an additional article in the journal "*COATINGS*" (Q2, IF 2.881): Boshkova N., Kamburova K., Radeva T., Boshkov N., "Hybrid zinc- based multilayer systems with improved protective ability against localized corrosion incorporating polymer-modified ZnO or CuO particles", *Coatings* **11**, (2021), 1223. All this clearly demonstrates that Dr. Boshkova continues her active work on the subject.

6. CRITICAL REMARKS AND RECOMMENDATIONS TO THE SCIENTIFIC PAPERS OF THE CANDIDATE

I have essentially no objections to the presented materials. However, I allow myself to make two recommendations for the future scientific work of Dr. Boshkova:

• I believe that she has the necessary experience and knowledge to write a review article on "*Zinc composite coatings containing nano-containers with corrosion inhibitors*".

• Future results should be presented for publication mainly in international specialized journals with Impact Factor.

7. PERSONAL IMPRESSIONS OF THE REVIEWER ABOUT THE CANDIDATE

Unfortunately, I have no immediate personal impressions of the scientific activity of assistant professor Boshkova. However, my acquaintance with the presented materials convinces me that she is a very good and knowledgeable researcher, with a wide range of interests and high competence in the application of modern electrochemical and analytical methods in the elaboration and research of various types of protective zinc coatings. Her scientific works undoubtedly present Dr. Boshkova as an established researcher with in-depth knowledge in the field of research and application of new coatings for corrosion protection of low-carbon steels.

A very good impression is made by the fact that Dr. Boshkova has presented her vision for her future research work: It is planned to form environmentally friendly protective films, selection of suitable particles for obtaining composite zinc coatings, as well as such, based on sol/gel technology. Various effective inhibitors for exposure of the formed coatings in model corrosive media, as well as their possible incorporation into the protective coatings, will also be investigated.

8. CONCLUSION

The field in which the main scientific and applied results of assistant professor Boshkova is a leading and promising for science and technology. The formation and study of protective coatings based on composite zinc alloys open wide opportunities for basic research. On the other hand, the coatings obtained as a result of these studies are finding and are about to find even more practical application for the corrosion protection of low-carbon steel products.

The research activity of Dr. Boshkova fully meets the thematic priorities of IPC-BAS, related to the development of new functional materials based on electrochemically formed metal, alloy and modified polymer coatings with protective, decorative and electrocatalytic properties.

Dr. Boshkova's scientific development is harmonious. She consistently goes through academic degrees and titles. At the present stage of her activity, she is an already established researcher with very good theoretical and experimental training in the field of electrochemical technologies and the formation of protective coatings.

Her scientific contributions are definitely important, and they have received a good international evaluation. These contributions have been achieved through significant research on complex systems and phenomena. The conducted research is largely aimed at solving a number of applied tasks.

Given the above, I have no doubt that we have before us the successful work of a trained researcher and scientist. Her scientific activity, contributions, scientometric indicators

and competence fully meet the requirements of the Regulations for acquiring scientific titles and holding academic positions at IPC "Acad. Rostislav Kaishev", BAS. Therefore, I can confidently recommend to the esteemed Scientific Jury to propose to the Scientific Council at IPC to present the scientific title and the academic position of ASSOCIATE PROFESSOR, in Chemical Sciences (code 4.2) scientific specialty Electrochemistry (incl. Chemical power sources) of assistant professor Dr. Nelly Dimitrova Bozhkova.

18.11.2021

Reviewer: