OPINION OF REVIWER

by Assoc. Prof. Dr. Hristo Gospodinov Kolev at the Institute of Catalysis at BAS, appointed as a reviewer by order RD-09-132/17.07.2023 of the director of the Institute of General and Inorganic Chemistry at BAS, on the materials submitted for participation in the competition announced in the State Gazette, issue 46 of 26.05.2023, for acquiring the academic position of "Associate Professor" for the needs of the Laboratory of Electronic Spectroscopy of Solid Surfaces at the Institute of General and Inorganic Chemistry at BAS, in the professional field 4.2. Chemical Sciences (Solid State Chemistry), and the decision of the Scientific Council of General and Inorganic Chemistry (Protocol No. 8 /11.07.2023).

1. General presentation of the obtained materials

The only candidate in the announced competition is Assistant Professor Dr. Alexander Svetoslavov Tsanev from the Institute of General and Inorganic Chemistry at BAS. The set of materials submitted by Dr. Tsanev are in accordance with Article 24 of the Law on the Development of the Academic Staff in the Republic of Bulgaria (ZPACPB), Article 53 and 54 of the Regulation for the Implementation of the Law on the Development of the Academic Staff in the Republic of Bulgaria, and Article 27 and 28 of the Regulation on the Conditions and Procedure for the Acquisition of Academic Degrees and the Appointment to Academic Positions at the Institute of General and Inorganic Chemistry.

The candidate has submitted a total of 29 scientific publications and all the necessary documents to participate in the competition for the academic position of "Associate Professor" at the Institute of General and Inorganic Chemistry at BAS.

2. Short candidate’s biographical data

Dr. Alexander Tsanev graduated from the Faculty of Chemistry at Sofia University "St. Kliment Ohridski," specializing in "Inorganic and Analytical Chemistry" in 2001. From 2004 to the present, he has been working at the Institute of General and Inorganic Chemistry at BAS, sequentially holding the positions of "chemist" (until 2019) and "assistant prof." (from 2019 to the present) in the Laboratory of Electronic Spectroscopy of Solid Surfaces. In 2017, he defended a

dissertation on the topic "Synthesis and Characterization of Mixed Oxide Films of Zr with Rare Earth Elements Ce and Y for Catalytic Applications" and obtained a Ph.D. degree in the field of 4.2. Chemical Sciences (Solid State Chemistry). In this way, Dr. Tsanev formally meets the requirements for participation in the competition.

3. Evaluation of scientific and applied research activities of the applicant

The candidate has a total of 29 publications, of which 21 are in journals indexed in the Q category, while the rest are in peer-reviewed journals and book chapters. In the announced competition, the candidate participates with 8 publications, one of which is in the Q1 category, 2 in Q2, 2 in Q3, 2 in Q4, and one publication in a peer-reviewed journal with an SJR index.

All of the candidate's publications have received more than 60 citations, with 20 citations of which are from publications used in the competition. Dr. Tsanev's Hirsch index (h-index) is 5, calculated in Scopus.

The candidate's scientific research work has been presented at 8 international and national scientific forums, including events such as "Electrochemistry in Ingenious Molecules, Surfaces, and Devices," "International Summer Schools on Vacuum, Electron and ION Technologies," "Workshops on Size-Dependent Effects in Materials for Environmental Protection and Energy Application," among others.

Dr. Alexander Tsanev meets the minimum national requirements as regulated in the Regulation for the Implementation of the Law on the Development of the Academic Staff in the Republic of Bulgaria and additional requirements outlined in the Regulation on the Conditions and Procedure for the Acquisition of Academic Degrees and the Appointment to Academic Positions at the Institute of General and Inorganic Chemistry - BAS for acquiring the academic position of "Associate Professor." According to the reference provided by Dr. Tsanev, it is evident that he exceeds both the minimum and additional requirements of the IGIC - BAS.

4. Scientific and applied contributions

Dr. Tsanev's scientific work is focused on the study of corrosion processes occurring in aluminium alloys and methods for their protection, using X-ray Photoelectron Spectroscopy (XPS). By combining this powerful method for studying chemical composition, the degree of oxidation of elements, and the stoichiometry of surfaces with other characterization techniques such as SEM,

XRD, TEM, gas tests, etc., he works on determining optimal process parameters and effective technologies for industrial production.

The candidate's scientific contributions can be grouped into several main areas, including: Investigation of electrochemical corrosion processes and electrolyte-related phenomena; Research on catalysis, photocatalysis, and electrocatalysis processes; Identification and characterization of oxide phases resulting from chemical synthesis.

The primary experimental method used for these studies is X-ray Photoelectron Spectroscopy (XPS).

The scientific research presented in the Habilitation work is unified by the idea of creating and studying protective coatings for aluminum alloys (AA 1050 and AA 2024) with a wide range of applications in light and heavy industries, mechanical engineering, aerospace industry, aviation systems, auxiliary parts of locomotives, and etc. Conversion coatings/layers based on cerium have been employed as protective coatings. A systematic approach has been applied to study the growth mechanism of conversion anti-corrosion coatings and the corrosion processes of the obtained protective layers when applied to aluminium alloys AA 1050 and AA 2024.

The research began by investigating the effect of pre-alkali activation and acid deoxidation on the surface of aluminum alloy AA 1050 on the immersion formation processes of protective cerium oxide films (Publication B.4.1). The study identified differences in film thickness, formation rate, and homogeneity of the layers when subjected to different pretreatments involving sodium-based treatments and sequential treatments with sodium and nitric acid. It was determined that the layers primarily consist of AlOOH and Al_2O_3, with an approximate ratio of AlOOH/Al_2O_3 of 3.6:1.

In Publication B.4.2, using XPS analysis, the impact of the processes involved in the immersion formation of protective cerium oxide films followed by anodization of aluminium layers in aqueous solutions of orthophosphoric acid was investigated, and how these processes influenced the corrosion behaviour of alloy AA 1050. The study showed that the products of the underlying reactions were incorporated into the micropores of the anodic films and blocked them. This led to increased corrosion resistance of the films.

The habilitation work further explores the effect of cerium ions on the corrosion protection of anodized aluminium alloys coated with conversion layers of cerium oxides/hydroxides (Publication B.4.3). It demonstrated an increase in the concentration of corrosion products such as

AlOOH and $Al(OH)_3$. Due to the low solubility of these products, corrosion resistance was enhanced in the $Al/Al_2O_3/Ce_2O_3$ system, including the prevention of pitting corrosion initiation and development.

In Publication B.4.4., in-depth profiles during the deposition of cerium conversion layers were studied. It was found that the pretreatment of the Al substrate, as well as the presence of Cu^{2+}, had a significant influence on the thickness, composition, and protective ability of the formed cerium and aluminium mixed conversion layers. These studies allowed for the optimization of aluminium alloy processing processes to obtain maximally protective cerium conversion coatings, with a key factor being the presence of sparingly soluble Ce^{4+}.

The role of phosphate coatings on cerium conversion layers was investigated in Publication B.4.6. It was established that the surface was entirely covered with sparingly soluble and insoluble phosphate groups, which played a crucial role in the corrosion resistance of aluminium alloys.

Phosphate post-treatments have a significant impact on the chemical composition and oxidation states of surface elements in the studied systems containing cerium conversion layers (Publication B.4.8). The predominant formation of $AlPO_4$, AlOOH, $CePO_4$, as well as compounds such as PO_3^-, P_2O_5 and P_4O_{10} has been demonstrated.

The role of incorporating silver ions on the surface properties of aluminium AA 1050 alloys has been investigated (publication B.4.5.). It has been found that in the samples that are not incorporated with silver ions, the aluminium consists entirely of Al_2O_3, whereas in those containing silver ions, aluminium is in the form of Al_2O_3, accompanied by $Al(OH)_3$ and AlO(OH).

The research also investigated the impact of incorporated silver ions on the surface corrosion properties of aluminium AA 1050 alloys during prolonged exposure to a model aggressive corrosion environment (Publication B.4.7). It was found that silver ions had penetrated the pores of the aluminium alloy, with their oxidation state being 1+. A process of oxidation before the infiltration of silver ions into the aluminium alloy pores was hypothesized.

Dr. Tsanev's scientific work is entirely focused on studying the surfaces of aluminium alloys, metal oxides, and finding effective methods to improve their corrosion resistance. His primary experimental method, X-ray Photoelectron Spectroscopy (XPS), is well-mastered and extensively used in his research. Additional analysis methods such as SEM, XPS, XRD, TEM, gas tests, and others have been employed in the publications, allowing for data collection on morphology,

structure, chemical composition, oxidation state of elements, and surface stoichiometry. These data are crucial for clarifying and optimizing the conditions for obtaining protective coatings and layers, leading to improved operational characteristics.

Participation in scientific and applied contracts and projects

Dr. Tsanev is an active participant in 8 scientific projects funded by the Research Fund. He is also a member of a national center funded by the European Union - UNION I. These projects have provided significant financial resources, which have been used for scientific research and the acquisition of tangible assets for the Institute of General and Inorganic Chemistry at BAS. This active involvement in projects and contracts reflects the dedication and importance of Dr. Tsanev's scientific work and his contribution to scientific development and research in the field of surface chemistry and materials.

CONCLUSION

Assistant Professor Dr. Alexander Svetoslav Tsanev's scientific research fully aligns with the theme of the announced competition for the academic position of "Associate Professor." Dr. Tsanev is a highly proficient specialist in the field of solid-state chemistry, utilizing X-ray Photoelectron Spectroscopy to determine the chemical composition, degree of oxidation of elements, and surface stoichiometry of materials. His research is focused on improving the quality of human life through the study of corrosion processes occurring in aluminium alloys and finding ways to protect them. His publication record, citations of published results, active scientific engagement, maintenance of scientific equipment in the "Electron Spectroscopy of Solid Surfaces" laboratory, and participation in scientific projects fully meet all the requirements of the Law on the Development of Academic Staff and the Regulations on the Conditions and Procedure for Acquiring Scientific Degrees and Taking Academic Positions at the Institute of General and Inorganic Chemistry - BAS. Therefore, I strongly recommend to the esteemed members of the Scientific Jury and the respected Scientific Council of the Institute of General and Inorganic Chemistry to award Assistant Professor Dr. Alexander Svetoslav Tsanev the academic position of "Associate Professor" in the field of 4.2. Chemical Sciences (Solid State Chemistry).

04.09.2023г. Reviewer: ……

Sofia / Assoc. Prof. Dr. Hristo Kolev /