O P I N I O N

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Concerning the competition for the academic position of "Associate Professor" in professional field 4.2 "Chemical sciences" (Solid State Chemistry) for the needs of the Laboratory "Electron Spectroscopy of Solid Surfaces" at the IGIC-BAS, announced in the State Gazette, announced in the State Gazette issue 46 of 26.05.2023.

One candidate has submitted documents for participation in the announced competition, namely Ch. assistant professor, Dr. Alexander Svetoslavov Tsanev from IONH-BAN

1. General characteristics of the presented materials

Ch. Assistant Professor Dr. Alexander Tsanev, obtained his master's degree in 2001 from the Faculty of Chemistry of Sofia University "St. Kliment Ohridski majoring in "Inorganic and Analytical Chemistry". The candidate started working as a chemist in the Laboratory "Electron Spectroscopy of Solid Surfaces" at the IGIC-BAS in 2004. In 2017, he defended his doctoral dissertation at the IGIC-BAS on the topic "Obtaining and characterization of mixed oxide films of Zr with rare earth elements Ce and Y for catalytic application". In 2019, Dr. Tsanev was elected Chief Assistant Professor. The total number of articles of the candidate is 29, on which 56 citations have been noticed. Ch. Assistant Professor Dr. Alexander Tsanev participated in the competition with 21 publications, of which 8 were presented as habilitation work (129 points) and 13 – outside of it (230 points). Of these articles, 2 are in journals falling in the Q1 quartile, and 9 in Q2. The citations on the articles submitted for participation in the competition are 38. The candidate participated in 8 international, foreign, and national conferences. He is also a member of the collectives of 3 national projects. The candidate's Hirsch index is 5. The scientometric indicators presented by Ch. Assistant Professor Dr. Alexander Tsanev's materials exceed the national minimum requirements (according to Art. 29b of the Law for the development of the academic staff in the Republic of Bulgaria), those of the BAS (Art. 2 of the Regulations for the conditions and procedure for acquiring scientific degrees and for holding academic positions at the BAS) and of the additional requirements of IGIC (art. 3, paragraph 13, art. 28, paragraph (6) a, of the Regulations on the conditions and procedures for acquiring scientific degrees and for holding academic positions in IGIC).

2. Principal scientific and/or applied contributions

The main scientific contributions of the candidate included in the habilitation report are related to the application of photoelectron spectroscopy methods to the study of the growth mechanism of conversion anti-corrosion coatings, as well as to the study of the corrosion processes of the already obtained coatings. In papers B.4.1, B.4.2, B.4.3, B.4.4, B.4.6, and B.4.8, the influence of preliminary alkaline activation, acid de-oxidation, as well as anodizing of the surface of aluminum alloy Al-1050 on the processes of immersion formation of protective films of cerium oxide on it were investigated. The influence of cerium and phosphate ions in the process of corrosion protection of an aluminum alloy was studied. By means of an analysis of the XPS spectra obtained from different depths of the sample (XPS-profiles), a dependence was established between the method of surface treatment and the chemical composition and

thickness of the obtained surface layer, which are a prerequisite for a different rate of formation and homogeneity of the formed on them cerium oxide layers. XPS analyses have registered the changes in the surface composition of the investigated samples as a function of the different processing procedures carried out and have shown that under conditions close to the appearance of pitting corrosion, changes in the chemical composition occurred during the corrosion process in favor of an increase the concentration of $Al(OH)_3$, which improve the corrosion behavior of the Al/Al_2O_3 system. During the conversion, the cerium oxide layer was not affected by the corrosive effects of the aggressive environment. It is shown that the corrosion processes of aluminum are expressed mainly in an increase in the concentration of the formed corrosion products of AlOOH and $Al(OH)_3$. Due to the low solubility of these products, the corrosion resistance of the $Al/Al_2O_3/Ce_2O_3$ system has increased, including the occurrence and development of pitting corrosion. These studies have enabled the optimization of the processing processes of aluminum alloys, with the aim of obtaining maximally protective cerium conversion coatings, the main factor of which is the presence of slightly soluble Ce^{4+}.

In papers C.4.6. and C.4.8. by XPS, the role of the deposition of phosphate coatings on cerium oxide conversion layers was investigated. It is shown that the surface of the layers is completely covered with slightly soluble and insoluble PO_3 and P_2O_5/P_4O_{10} groups, which play an essential role in the corrosion resistance of aluminum alloys. During this treatment, the concentrations of aluminum and cerium oxides in the conversion coatings are significantly reduced due to the formation of phosphates in them, which determines the increased resistance of these layers to the diffusion of chloride ions and pitting.

In papers B.4.5 and B.4.7, the role of silver ion incorporation on the surface properties of aluminum alloys and how these properties affected the corrosion resistance of these alloys was established. It was found that the presence of silver ions leads to an increase in the hydroxide and oxide-hydroxide component on the surface, and that silver is incorporated into the pores of the aluminum alloys, at a depth of more than 9-10 nm, that is why it is not registered in the analyses.

The silver in the pores is in the form of Ag^+, which suggests the presence of an oxidation process before it enters the pores. As a result, the mechanism of its incorporation was established - the oxidation of Ag probably occurred with the migration of O^{2-} ions inward from the electrolyte through the surface of the bottoms and the walls of the pores of the aluminum alloy.

The candidate's publications other than the habilitation report are classified into three main areas:

1. Investigation by XPS of electrochemical corrosion and processes taking place in electrolytes.
2. Investigation by XPS of processes of catalysis, photocatalysis, and electrocatalysis.
3. Identification and proof by XPS of oxide phases resulting from chemical synthesis.

Point 1: Surface modification of aluminum and its alloys with oxide layers of Ce, P, Cu, Ni, and other elements has been shown to result in increased corrosion resistance of the treated alloys, as the formed surface layer serves as an effective barrier against diffusion of corrosive chloride ions. XPS investigation of the effects of electrochemical modification of the zinc surface has resulted in samples with improved corrosion protection and can be used as Zn-based functional layers and optically active sensing elements. A synergistic effect of electrodeposited zinc-cerium oxide coatings was found for increased corrosion protection of low-carbon steels. (D.7.2, D.7.3, D.7.4, D.7.5, D.7.6, D.7.11, D.7.12)

Point 2.: The relationship between the composition of the obtained electrocatalysts, the oxidation state of the active components in them, and their electrocatalytic application was studied. (D.7.1., D.7.7., D.7.8., D.7.9.)
Point 3. The processes of preparation by ion sputtering and subsequent thermal treatment of nanocrystalline boron nitride (G.7.10.) were investigated by XPS.

I know Dr. Tsanev personally and I have a very good impression of his work.

3. Conclusion

Everything stated so far presents Dr. Tsanev as a well-established specialist with knowledge and skills in the field of X-ray photoelectron spectroscopy and its application in the study of materials. **This gives me reason with great conviction to recommend to the esteemed jury to elect Ch. Assistant Professor, Dr. Alexander Svetoslavov Tsanev, for academic position "Associate Professor" in the professional field of "Chemical Sciences" (Solid State Chemistry).**

Sofia 05.09.2023 Signature:

(Prof. Dr. Daniela Kovacheva)