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REVIEW OF THE DOCTORAL DISSERTATION OF HAFIZ MUHAMMAD SHOAIB

The doctoral dissertation entitled "Electrodeposition of ternary zinc–iron–molybdenum and zinc–iron–tungsten alloy coatings designed for corrosion protection of steel", prepared by Mr Hafiz Muhammad Shoaib, has been conducted under the supervision of Prof. Juliusz Winiarski and Dr Anna Mazur-Nowacka at the Faculty of Chemistry, Wrocław University of Science and Technology.

The dissertation takes the traditional form of a monograph, comprising 132 pages, 30 figures, 11 tables, and 132 references. It consists of five main chapters, as well as abstracts, a list of abbreviations, a table of contents and a bibliography. It should be noted that, even at a formal level, the structure of the work is clear, logical and consistent with the standards adopted for doctoral dissertations. The author effectively guides the reader from a general overview of the problem and the state of the art, through a description of the methodology, to the chapter on results and discussion, and finally to the conclusions.

This thesis addresses a timely topic that aligns well with current research trends in surface engineering. Finding alternatives to traditional Zn–Ni systems that maintain high corrosion resistance and good coating quality is one of the most important areas of development in protective coating technologies. For this reason, Zn–Fe–Mo and Zn–Fe–W systems are a justified choice for both scientific and practical reasons. This dissertation forms part of a broader research trend focusing on nickel-free materials, co-deposition processes for hard-to-reduce metals and controlling coating properties by selecting appropriate electrochemical parameters. This topic is important not only from the perspective of basic research, but also with regard to potential industrial applications.

Chapter one is an introduction to the thesis and outlines its basic framework, including the background to the research problem, the hypothesis, the research questions and the scope of the dissertation. The doctoral candidate correctly points out that, while traditional zinc coatings are effective, they require further modification to improve their performance characteristics. The rationale for choosing molybdenum and tungsten is logical and grounded in current knowledge. However, the thesis objective has been formulated rather broadly. Rather than presenting a single, clearly defined scientific problem, a set of specific

objectives concerning the relationship between bath composition, current density, coating structure and corrosion resistance are presented instead. While this approach is appropriate from the perspective of experimental work, it somewhat weakens the thesis's focus on the core problem.

Chapter two provides a comprehensive literature review and serves as an introduction to the experimental section. The author discusses applications of electrodeposition and zinc coatings and alloys, as well as the factors that influence the process and fundamental issues related to corrosion. The scope of the bibliography is notable. Analysis shows that more than half of the 122 references are from the last 10 years, attesting to the topicality of the subject matter. This is a notable strength of the work, demonstrating that the doctoral candidate is up to date with the latest research. However, it should be noted that the literature review is primarily descriptive in nature. While the author cites numerous publications, they rarely compare them critically. There is a lack of clear indication of which elements of the literature remain controversial and which are well established. Consequently, while the literature review lays the groundwork for the author's own research, it does not fully exploit the potential of critical synthesis.

Chapter three covers materials and research methodology. This section has been carefully prepared with great attention to detail. The doctoral candidate describes how the steel and copper substrates were prepared for the structural analysis, how the surfaces were cleaned and activated, the composition of the baths, how electrodeposition was carried out, and the parameters of the individual research techniques. The electroplating baths were prepared at a pH of 5.7 and deposition was carried out at current densities ranging from 10 to 25 mA/cm^2. The combination of methods employed, including CV, UV–Vis, SEM, EDX, profilometry, FIB/SEM, TEM/STEM, XRD, polarisation measurements and EIS, enabled multi-level analysis of the studied system. This is one of the dissertation's clear strengths. However, the lack of systematically presented information on the number of repetitions and the standard deviation of the results is disappointing. For a study based on extensive numerical data, explicitly considering aspects of repeatability and measurement uncertainty would strengthen the credibility of the conclusions further.

Chapter four forms the core of the dissertation. Here, the doctoral candidate presents the most important experimental data, which is what determines the value of the work most significantly. In subsection 4.1, the author analyses the CV results and demonstrates that the galvanic bath composition significantly impacts the course of the reduction processes. For zinc, the reduction potential shifts from approximately −1.12 V to approximately −1.25 V for iron, the shift is from approximately −0.40 V to approximately −1.25 V. Interpreting these results as manifestations of changing degrees of ion complexation and metal reduction conditions is correct and consistent with electrochemistry fundamentals. It is also noteworthy that the PhD candidate does not merely observe the final

coatings, but also attempts to capture the process at the level of the electrolyte and cathodic reactions. However, this section remains primarily qualitative. Including quantitative elements in the analysis could significantly enhance its cognitive value.

In subsection 4.2, which focuses on UV–Vis spectroscopy, the author identifies bands around 480 nm and a broad band in the 650–880 nm range. They attribute these bands to iron complexes and to molybdenum and tungsten, respectively. Incorporating spectroscopic analysis into the description of the electrodeposition process is valuable because it enables the plating bath to be viewed as a chemically active system that changes over time. These results clearly demonstrate that the chemistry of the solution directly impacts the subsequent deposition process. However, it seems that this potential was not fully exploited in the discussion. Stronger integration of UV–Vis data with CV results, as well as with the subsequent composition and structure of the coatings, would lend the work a more coherent interpretive character.

Subsections 4.3–4.5 concern morphology, chemical composition and surface topography. The doctoral candidate demonstrates that an increase in current density leads to significant changes in layer quality. For Zn–Fe–Mo coatings, Ra roughness decreases from approximately 0.75 µm to 0.035 µm; for Zn–Fe–W coatings, it decreases from 1.25 µm to 0.20 µm. This marked improvement in topography with increasing current density is well documented and consistent with SEM observations indicating a transition from porous, heterogeneous structures to compact, fine-grained coatings. One positive aspect is that the author does not rely on a single technique, but rather builds their conclusion based on the consistency of several independent data sources.

The EDX analysis convincingly complements the morphological results. The doctoral candidate shows that the molybdenum and tungsten content generally falls within the range of 1–5% by mass, while the iron content rises to around 11–12% at higher current densities. These data suggest that the final composition of the coatings is not simply a reflection of the bath composition, but rather the result of more complex interactions between reduction processes at the cathode. This is an important conclusion because it enables electrochemical parameters to be linked to the actual nature of the coating. However, from a reviewer's perspective, this section could be strengthened by integrating the CV and UV–Vis results more closely, moving from a correct description of the phenomena to a more concise mechanistic interpretation.

The results of the FIB/SEM, TEM/STEM and XRD analyses provide a comprehensive overview of the structure of the coating. The author identifies zinc and intermetallic phases, including $Fe_{22}Zn_{78}$, and indicates that electrodeposition conditions affect the composition, structure, and microstructure of deposits. This suggests that changes in process parameters lead to restructuring of the material at multiple organisational levels. However, a deeper synthesis of how the

relationships between composition, phase structure and topography translate into final corrosion behaviour is lacking. The inclusion of such an interpretive layer could enhance the quality of the dissertation further.

Subsection 4.8 is devoted to corrosion properties. The doctoral candidate utilised both polarization measurements and impedance spectroscopy to evaluate the behaviour of the coatings from two complementary perspectives. i_{corr} values ranging from 0.27 to 1.0 μA/cm² for the Zn–Fe–Mo system and from 2.4 to 7.9 μA/cm² for the Zn–Fe–W system, with concurrent R_3 values reaching approximately 85 kΩ·cm², indicate the favourable protective properties of the selected coatings. The author is to be commended for not oversimplifying the presentation of the results and demonstrating that different measurement techniques do not always identify the same variant as the absolute best. This is a realistic situation for multi-component and microstructurally complex systems. However, a clearer organisation of the evaluation criteria would be useful here, to help the reader understand which characteristics the PhD candidate considers to be the most important: minimum i_{corr}, high charge transfer R_3, optimal morphology, or perhaps a compromise between these.

Chapter Five presents the final conclusions. These are consistent with the experimental data and summarise the most important findings of the work. The author correctly identifies the influence of current density and electroplating bath composition on the morphology, composition, structure and corrosion resistance of the coatings. However, some of the conclusions are rather general and could emphasise the novel contribution of the work more clearly. Of the sections in the reviewed dissertation, the experimental section is by far the strongest, while the synthesis section could be more selective and focused on a single central problem.

The most important strengths of the work, in my view, are the broad and well-chosen set of research methods, the high labour intensity of the experimental section, the correct correlation of morphological results with profilometry, the convincing analysis of the influence of process parameters on chemical composition, and the genuine attempt to link these results to corrosion resistance. The main areas for improvement are a more precise definition of the central scientific problem, a deeper quantitative analysis, stronger correlation of results obtained using different techniques and clearer distinction of the author's own contribution in the final conclusions. These are, however, constructive comments rather than objections that undermine the value of the dissertation as a whole.

Questions for the dissertation:

1. How would the author suggest formulating a single, overarching criterion for selecting optimal process parameters that takes into account chemical composition, surface morphology and corrosion test results simultaneously?

2. Based on the obtained data, is it possible to propose a simplified model that describes the co-deposition of molybdenum and tungsten in the studied systems?

3. Which method does the PhD candidate consider to be the most decisive in assessing the quality of the coatings, and what is the rationale for this choice?

4. How would the author interpret the differences between the conclusions drawn from impedance and polarization measurements?

5. What modifications to the experimental setup or bath composition could, in the PhD candidate's opinion, improve the reproducibility and quality of the coatings obtained further?

6. How does the author assess the potential for the studied systems to be applied in practice in relation to industrial requirements?

In summary, the reviewed dissertation is a mature piece of research, well aligned with current trends in modern coating material research and providing valuable experimental data. The author has demonstrated their ability to independently plan and carry out complex materials and electrochemical studies. The comments provided are supplementary. In my opinion, the dissertation fully meets the statutory criteria and should proceed to the next stage of the doctoral process, leading to the award of the degree (Ustawa z dnia 20 lipca 2018 r. - Prawo o szkolnictwie wyższym i nauce, tekst jednolity: Dz. U. z 2024 r. poz. 1571 z późniejszymi zmianami). I respectfully request that the Scientific Discipline Council for Chemical Engineering at Wrocław University of Science and Technology accept the thesis and admit Mr Hafiz Muhammad Shoaib to the subsequent stages of the doctoral procedure.

Signed by /
Podpisano przez:

Grzegorz Józef Lota

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