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Prof. dr hab. inż. Agata Dudek
Department of Materials Science and Engineering
Faculty of Production Engineering
and Materials Technology
Częstochowa University of Technology
42-202 Częstochowa
ul. Armii Krajowej 19

Review of the Doctoral Dissertation

M.Sc. Muhammad Jahangir Khan

entitled: "Hot corrosion behaviour of a new type of thermal barrier coating materials"

prepared under the supervision of:

Prof. dr hab. inż. Grzegorz Moskal (Silesian University of Technology)

and assistant supervisor:

dr inż. Marta Mikuskiewicz

Basis for the Review

The present review has been prepared at the request of the Materials Engineering Discipline Council of the Silesian University of Technology, in accordance with the resolution of 17 February 2026.

The legal basis is Article 187 of the Act of 20 July 2018 – Law on Higher Education and Science (consolidated text: Journal of Laws 2024, item 1571).

The review includes three main components:

- an assessment, with justification, of whether the dissertation demonstrates the Candidate's general theoretical knowledge in the discipline of materials engineering;
- an assessment, with justification, of whether the dissertation demonstrates the Candidate's ability to conduct independent scientific research;
- an assessment, with justification, of whether the dissertation constitutes an original solution to a scientific problem.

Characteristics and Description of the Dissertation

The reviewed doctoral dissertation entitled "Hot corrosion behaviour of a new type of thermal barrier coating materials", written in English, comprises 119 pages. The preliminary part is numbered with Roman numerals, whereas the main body of the dissertation uses Arabic numerals. The dissertation has been prepared in a format typical of experimental research works in the field of materials engineering. Its structure is clear and consists of eight main chapters, preceded by an introductory section containing, among other elements, a list of abbreviations, a list of six publications authored by the Doctoral Candidate, and abstracts in both Polish and English.

Chapter 1, "Overview", provides an introduction to the issue of thermal barrier coatings (TBCs), with particular emphasis on their importance in high-temperature applications such as gas turbines and energy systems. This chapter discusses the basic mechanisms of material degradation and the role of protective coatings in limiting these phenomena.

Chapter 2, "Introduction", takes the form of a literature review and covers a broad range of issues related to the structure of TBC systems, the properties of ceramic materials used for top-coat layers, bond coat materials, as well as coating deposition techniques (including APS, EB-PVD, SPS, and PS-PVD). An important part of this chapter is also devoted to the discussion of coating degradation mechanisms, including thermal fatigue and high-temperature corrosion, as well as a review of studies concerning composite systems based on rare-earth zirconates.

Chapter 3, "Materials and Methods", contains a detailed description of the materials used in the study and the experimental methods applied. This chapter presents the method of coating preparation, the parameters of the atmospheric plasma spraying (APS) process, the conditions of the corrosion tests, and the material characterization methods, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and chemical composition analysis by means of EDS. This chapter provides the basis for the interpretation of the results presented in the following parts of the dissertation.

Chapter 4, "Thesis and Objectives of the Work", is devoted to the formulation of the research objective and the research assumptions. It points to the need to improve the corrosion resistance of TBC coatings through the use of composite systems based on $Nd_2Zr_2O_7$ and $Nd_2Ce_2O_7$ with the addition of YSZ.

The main part of the dissertation is formed by Chapters 5–7, in which the results of the author's own research are presented. Chapter 5, "Effect of Molten Sulfate and Vanadate Salts on the Hot Corrosion Behaviour of Single-Layered $Nd_2Zr_2O_7$ Thermal Barrier Coatings", concerns single-phase $Nd_2Zr_2O_7$ coatings and their behaviour in Na_2SO_4, Na_2SO_4–$MgSO_4$, and Na_2SO_4–V_2O_5 environments.

Chapter 6, "Complex sulphate vanadate salt induced hot corrosion of $Nd_2Zr_2O_7$ + 8YSZ composite thermal barrier coating system", includes an analysis of the $Nd_2Zr_2O_7$ + 8YSZ composite coating system under analogous corrosive conditions.
Chapter 7, "Hot Corrosion Behavior of $Nd_2Ce_2O_7$ + 8YSZ Thermal Barrier Coatings in Sulfate and Vanadate Environments", is devoted to the second composite system, based on $Nd_2Ce_2O_7$ + 8YSZ.
Each of these chapters has a similar structure, including an introduction, a presentation of the research results (including XRD and SEM/EDS analyses), as well as their interpretation in the context of material degradation processes.
Chapter 8, "Conclusion and future work", contains a summary of the obtained results and indicates potential directions for further research.
When analysing the structure of the dissertation, it should be stated that it is logical and consistent with the accepted standards for doctoral dissertations in the discipline of materials engineering. At the same time, it is noticeable that Chapters 5–7 are, to a large extent, autonomous studies, resembling the structure of scientific publications. At the same time, it is noticeable that chapters 5–7 are largely autonomous studies, similar to the publication layout, which in effect gives the impression of a collection of thematically related research studies.

Justification of the Topic Selection and Its Relevance

The topic undertaken by the Doctoral Candidate falls within a current and intensively developing area of research in materials engineering, concerning the durability of materials operating under high-temperature conditions and in chemically aggressive environments. The problem of degradation of structural materials, particularly nickel-based alloys used in gas turbines, power generation systems, and aerospace applications, constitutes one of the key challenges of modern engineering.
In this context, thermal barrier coatings (TBCs) play a particularly important role, as they serve a protective function by limiting both thermal effects and the impact of corrosive agents. In the literature, yttria-stabilized zirconia (YSZ) has long been the dominant material used for ceramic top-coat layers. However, its limitations—especially at temperatures exceeding 1200°C and in the presence of aggressive compounds such as sulfates and vanadium-based species—are well documented. Consequently, there is a need to develop new materials with higher phase stability and improved resistance to chemical degradation.
The dissertation focuses on materials from the group of rare-earth zirconates and cerates, in particular $Nd_2Zr_2O_7$ and $Nd_2Ce_2O_7$, as well as their composite systems with the addition of YSZ. The selection of these materials can be considered well justified, as compounds

with a pyrochlore structure are currently being intensively investigated as potential alternatives to conventional TBC systems, due to their favourable thermal properties and high-temperature stability. At the same time, their behaviour under high-temperature corrosion conditions, especially in the presence of molten sulfate salts and vanadium compounds, remains an issue requiring further investigation.

Particular emphasis should be placed on the fact that the Candidate does not limit the study to a single material but attempts to compare several coating systems, including both single-phase ($Nd_2Zr_2O_7$) and composite systems ($Nd_2Zr_2O_7$ + 8YSZ and $Nd_2Ce_2O_7$ + 8YSZ). Such an approach allows for a broader assessment of the influence of material composition on corrosion resistance and enables the identification of potential directions for optimization of TBC systems.

The relevance of the topic is also driven by increasing industrial demands related to improving the efficiency of energy systems and reducing emissions. The pursuit of operation at higher temperatures is directly associated with the need for more advanced protective materials, resistant not only to oxidation but also to complex high-temperature corrosion processes, including so-called hot corrosion types I and II. In this context, studies on the influence of environments containing Na_2SO_4, $MgSO_4$, and V_2O_5 are of significant practical importance.

In light of the above, the selection of the dissertation topic should be considered appropriate and well justified from both scientific and application-oriented perspectives. The scope of the work corresponds to current research trends in the field of high-temperature materials. It should be noted, however, that despite the appropriate choice of topic, the dissertation places relatively limited emphasis on clearly defining the research gap, which somewhat reduces the clarity of the scientific justification for the undertaken research.

Literature Review and Its Evaluation

The literature review is presented in Chapter 2, entitled "Introduction", and constitutes an extensive part of the dissertation, covering fundamental issues related to the structure, properties, and degradation mechanisms of thermal barrier coatings (TBCs). At the end of the chapter, a list of references comprising 63 literature items is provided, indicating a broad range of sources used and forming the basis for the presented analysis. The chapter discusses both the general characteristics of TBC systems and more detailed aspects concerning materials used for ceramic top coats and bond coats, as well as coating deposition techniques.

In the introductory part, the structure of TBC systems is described, indicating that such systems consist of a metallic substrate, a bond coat, a thermally grown oxide (TGO) layer, and a ceramic top coat. Subsequently, the properties of materials used for ceramic layers are discussed, emphasizing that yttria-stabilized zirconia (YSZ) serves as the reference material for TBC applications due to its low thermal conductivity, phase stability, and high melting temperature.

An important part of the review is devoted to alternative materials, particularly rare-earth zirconates ($RE_2Zr_2O_7$), which are considered potential substitutes for conventional YSZ-based systems. It is noted that these materials are being investigated due to their improved stability at high temperatures and favourable thermal properties. The chapter also presents various coating deposition techniques, such as atmospheric plasma spraying (APS), EB-PVD, SPS, and PS-PVD.

A significant portion of the chapter is dedicated to degradation mechanisms, including high-temperature corrosion. It is highlighted that environments containing aggressive chemical compounds accelerate material degradation, with particular emphasis on the role of molten salts, which contribute to coating degradation through chemical reactions and destabilization of protective layers. In this context, previous studies on composite systems, such as $La_2Zr_2O_7$ + 8YSZ and $Sm_2Zr_2O_7$ + 8YSZ, are also discussed.

The scope of the presented literature review can be considered broad and encompassing the key issues related to the topic of the dissertation. The Candidate demonstrates knowledge of fundamental physicochemical mechanisms and current research trends in the field of TBC materials.

However, the review is largely descriptive in nature. The cited information is primarily presented as a compilation of literature data, without clear structuring in relation to the research problem addressed in the dissertation.

It is also noticeable that there is no explicit identification of a research gap that would directly justify the selection of the specific materials analysed in the study, namely $Nd_2Zr_2O_7$ and $Nd_2Ce_2O_7$. As a result, the connection between the literature review and the experimental part of the work is not entirely clear.

Additionally, the text contains repetitions of general information regarding the significance and applications of TBC systems, which slightly reduces the conciseness of this section.

Overall, the literature review provides a solid introduction to the subject of the dissertation; however, its scientific value could be enhanced through a more critical approach to the discussed issues and a clearer identification of the research problem addressed by the Candidate in the subsequent parts of the work.

Methodology of the Author's Own Research

The research methodology is presented in Chapter 3, entitled "Materials and Methods", and includes both the preparation of coating materials and the description of the experimental methods used for their characterization and evaluation of corrosion resistance.

The dissertation indicates that the investigated coating systems were produced using atmospheric plasma spraying (APS), which is a standard and widely applied method for the fabrication of TBC coatings. The study presents the general experimental procedure and the basic process parameters, allowing for an overall assessment of the applied technology.

This chapter also describes the chemical composition of the substrate material (IN-625 alloy), as well as the properties of the powders used for coating deposition, including $Nd_2Zr_2O_7$, $Nd_2Ce_2O_7$, and 8YSZ. An analysis of particle size distribution is also provided, indicating that appropriate methods were employed to control the input parameters of the spraying process.

An important component of the methodology is the description of high-temperature corrosion tests. The experiments were conducted in environments containing Na_2SO_4, Na_2SO_4 + $MgSO_4$, and Na_2SO_4 + V_2O_5, which, as stated by the Candidate, correspond to conditions encountered in real industrial applications. Test parameters such as temperature and exposure time are specified and summarized in the dissertation, allowing for an evaluation of the adopted experimental conditions.

In terms of material characterization, standard and appropriate analytical techniques were employed, including X-ray diffraction (XRD) for phase analysis and scanning electron microscopy (SEM) combined with EDS analysis for the assessment of microstructure and chemical composition of the coatings. The selected set of research methods can be considered adequate for achieving the objectives of the study.

The methodology is presented in a clear and well-structured manner, and the scope of the applied techniques is consistent with the standards used in research on TBC coating systems. The selection of methods should be regarded as appropriate and sufficient for the realization of the research objectives.

At the same time, it should be noted that the description of the methodology is largely general in nature, and in some places lacks more detailed information regarding process parameters, particularly the spraying conditions and the repeatability of the experiments. The dissertation does not include a broader analysis of measurement uncertainties or information on the number of experimental repetitions, which could enhance the reliability of the obtained results.

Overall, the adopted research methodology is correct and consistent with the standards of materials engineering; however, its description could be supplemented with more detailed information concerning the experimental conditions and their repeatability.

Objective of the Work and Research Assumptions

The objective and scope of the dissertation are presented in Chapter 4, entitled "Thesis and Objectives of the Work". It is indicated that the subject of the study is the analysis of the high-temperature corrosion resistance of selected TBC coating systems, particularly those based on materials such as $Nd_2Zr_2O_7$, $Nd_2Zr_2O_7$ + 8YSZ, and $Nd_2Ce_2O_7$ + 8YSZ.
The content of the dissertation shows that the main direction of the research is to determine the influence of corrosive environments on the durability of coatings. As stated in the descriptive part of the work, one of the objectives is to understand the mechanisms of degradation, microstructural changes, and the influence of phase composition on the durability of TBC systems. Elsewhere, the Candidate emphasizes the need to improve the overall durability of TBC systems through the use of composite coatings, which constitutes one of the main assumptions underlying the conducted research.
The scope of the study includes the analysis of coating behaviour in environments containing aggressive chemical agents, such as Na_2SO_4, Na_2SO_4 + $MgSO_4$, and Na_2SO_4 + V_2O_5. This is also clearly stated in the abstract of the dissertation, where the Candidate notes that the work is devoted to the issue of high-temperature corrosion resistance in environments containing molten sodium and magnesium sulfate salts, as well as vanadium pentoxide.
The analysis of the presented information indicates that the objective of the work has a cognitive and experimental character and focuses on identifying relationships between material structure and resistance to high-temperature corrosion. It should be noted, however, that these objectives are presented in a descriptive and somewhat dispersed manner throughout different parts of the dissertation.
The Candidate does not formulate a clear research hypothesis nor explicitly define verifiable assumptions that would be consistently addressed in the subsequent chapters. It should be emphasized that current regulations do not require the formal formulation of a research thesis in a doctoral dissertation; however, its clear definition would significantly facilitate the assessment of the coherence of the work and the degree to which the assumed objectives have been achieved.
From the analysis of the dissertation, it can be inferred that one of the main assumptions is the improvement of corrosion resistance of coatings through the use of composite systems, particularly those containing a YSZ phase. This is indicated, among others, by the statement that the introduction of composite systems was intended to enhance coating

durability under aggressive corrosive environments. However, this assumption is not explicitly formulated.

The objective of the work is consistent with the chosen topic and has a sound scientific basis; however, its formulation could be more precise, particularly through a clearer definition of research assumptions and their explicit linkage to the scope of the conducted research.

Research Results and Their Interpretation

The results of the original research are presented in Chapters 5–7, which constitute the core part of the dissertation. In these chapters, the Candidate analyses the behaviour of three coating systems: single-phase $Nd_2Zr_2O_7$ and composite systems $Nd_2Zr_2O_7$ + 8YSZ and $Nd_2Ce_2O_7$ + 8YSZ, exposed to environments containing Na_2SO_4, Na_2SO_4 + $MgSO_4$, and Na_2SO_4 + V_2O_5.

Chapter 5 is devoted to the analysis of single-phase $Nd_2Zr_2O_7$ coatings. The Candidate presents the results of phase and microstructural studies, indicating that in a pure Na_2SO_4 environment the coatings exhibit relatively good corrosion resistance. At the same time, it is noted that the introduction of additional components, such as $MgSO_4$ and V_2O_5, leads to a significant deterioration of coating properties. In particular, the presence of V_2O_5 results in the intensification of degradation processes, which the Candidate associates with the formation of neodymium vanadates and the destabilization of the material structure. As a result, cracking of the coating and its delamination are observed.

Chapter 6 presents the results for the $Nd_2Zr_2O_7$ + 8YSZ composite system. The Candidate indicates that the use of a composite system leads to improved coating durability compared to the single-phase material. In particular, no coating delamination was observed under the analysed conditions. At the same time, phase transformations were identified, involving the transition from a pyrochlore structure to a fluorite-type structure with a modified chemical composition. These phenomena are associated with the interaction with the corrosive environment and the migration of chemical species within the coating.

Chapter 7 concerns the second composite system, $Nd_2Ce_2O_7$ + 8YSZ. In this case, the Candidate indicates higher phase stability of the material and lower susceptibility to degradation compared to the previously analysed systems. The observed structural changes are less pronounced and mainly involve the formation of reaction products, such as neodymium oxysulfates. It is emphasized that this material does not undergo significant structural transformations leading to the loss of coating integrity.

The presented results are supported by XRD and SEM/EDS analyses, enabling the assessment of both phase and microstructural changes. The obtained results are coherent and logically related to the applied experimental conditions. The Candidate consistently compares the behaviour of the individual coating systems, allowing for the identification of differences in their corrosion resistance.

However, it should be noted that the interpretation of the results is, in many places, predominantly descriptive. The Candidate focuses mainly on presenting the observed changes, such as the formation of new phases or microstructural degradation, while providing a less developed, in-depth analysis of the mechanisms responsible for these phenomena. In particular, there is a lack of broader reference to physicochemical models and a more detailed comparison of the obtained results with literature data.

It is also noticeable that the individual chapters follow a similar structure and partly replicate the scheme of results presentation, which may suggest their relatively independent character, resembling the format of scientific publications (abstract, introduction, results and discussion, conclusion, references). Consequently, the integration of results into a single, coherent analysis covering all investigated material systems is somewhat limited.

Despite the above remarks, it should be emphasized that the obtained results have clear scientific value and allow for the assessment of the influence of material composition on the corrosion resistance of TBC coatings. Particularly important is the identification of the beneficial effect of composite systems, including $Nd_2Ce_2O_7$ + 8YSZ, which demonstrates the highest stability under the analysed conditions.

Discussion Remarks

The analysed doctoral dissertation constitutes a study of significant scientific and application-oriented value; however, several issues can be identified within its content that would benefit from further clarification.

First, it is worth referring to the formulation of the research assumptions. The objective of the dissertation has been defined correctly and is consistent with the undertaken topic; however, it remains relatively general in nature. A more explicit definition of the research assumptions and their clearer linkage to the scope of the conducted studies could further enhance the transparency and coherence of the work.

With regard to the literature review, it should be emphasized that it covers a broad range of issues related to TBC coatings. At the same time, in certain sections, it gives the impression of being predominantly descriptive. Supplementing this part with a clearer identification of research gaps and their direct connection to the subsequent parts of the dissertation could strengthen its analytical dimension.

The experimental part has been prepared correctly, and the applied research methods are consistent with the standards adopted in materials engineering. The description of the methodology is clear; however, in selected areas it could be supplemented with more detailed information regarding process parameters and the organization of the experiments, particularly in terms of their repeatability.

Regarding the presentation of results, their coherence and logical relationship with the scope of the conducted research should be emphasized. At the same time, the interpretation of the obtained results is, in many places, primarily descriptive. A more extensive discussion of the mechanisms responsible for the observed phenomena, as well as a more comprehensive reference to literature data, could further strengthen the scientific value of this part of the work.

A noticeable feature of the dissertation is the structure of Chapters 5–7, which exhibit a largely autonomous character. On the one hand, this reflects the potential for presenting the results in a publication-oriented format; on the other hand, it somewhat limits the overall coherence of the dissertation as a unified study.

The dissertation also contains minor editorial shortcomings, such as inconsistencies in the numbering of subsections or repetitions of certain information. However, these are of a technical nature and do not significantly affect the substantive evaluation of the work.

These remarks are of a supplementary nature and do not affect the overall assessment of the dissertation, which constitutes a reliable experimental study and provides valuable insights into the behaviour of TBC coatings under high-temperature corrosion conditions.

Questions for Discussion

1. The dissertation demonstrates varying corrosion resistance of the investigated coating systems, with particularly favourable properties observed for composite systems containing YSZ. In this context, please explain which mechanisms, in your opinion, are primarily responsible for the improved durability of these systems compared to single-phase coatings.
2. The results indicate a significant impact of V_2O_5 on the intensification of degradation processes. What factors determine the particularly aggressive nature of this environment, and how does it affect the phase stability of the analysed materials?
3. Phase transformations involving the transition from a pyrochlore structure to a fluorite-type structure were observed in the study. Please comment on the significance of these transformations from the perspective of the functional properties of the coatings, particularly their durability under service conditions.
4. The experiments were conducted under specific laboratory conditions. To what extent can the obtained results be extrapolated to real operating conditions of components used in turbines or energy systems.

5. The study employs atmospheric plasma spraying (APS) for coating deposition. In your opinion, could the use of alternative methods, such as EB-PVD or SPS, significantly influence the corrosion resistance of the analysed systems?
6. In the context of the obtained results, please indicate which of the analysed coating systems has the greatest application potential and what further research would be necessary before its implementation in industrial conditions.

Final Evaluation of the Dissertation and Conclusion

Assessment of Compliance with Formal Requirements

Assessment of the Candidate's Theoretical Knowledge

The submitted doctoral dissertation demonstrates that the Candidate possesses a well-established and broad theoretical knowledge in the discipline of materials engineering, particularly in the field of high-temperature materials and thermal barrier coatings (TBCs). This is reflected both in the presented literature review and in the manner in which the experimental results are interpreted. The Candidate shows a sound understanding of issues related to the structure and functioning of coating systems, degradation mechanisms under high-temperature corrosion conditions, and the properties of ceramic materials, including those from the group of rare-earth zirconates and cerates.

Assessment of the Ability to Conduct Independent Research

The scope of the conducted research and the manner of its implementation indicate that the Candidate is capable of independently planning and carrying out scientific work. This applies both to the preparation of coating materials, the selection of research methods, and the analysis of the obtained results. The Candidate has demonstrated the ability to perform experimental research using modern analytical techniques, such as XRD, SEM, and EDS, as well as the ability to interpret the observed phenomena in the context of processes occurring in materials under the influence of aggressive high-temperature environments.

It is also worth emphasizing the connection between the research results and scientific publications, which confirms the Candidate's research activity and ability to present results within the scientific community.

Assessment of Originality and Scientific Value

The doctoral dissertation constitutes an original study addressing a scientific problem related to the high-temperature corrosion resistance of TBC coatings. In particular, it focuses on the analysis of systems based on $Nd_2Zr_2O_7$ and $Nd_2Ce_2O_7$, including composite systems with YSZ, exposed to environments containing molten sulfate salts and vanadium compounds.

The originality of the work is primarily reflected in the comparative analysis of several material systems and in the identification of their degradation mechanisms under complex corrosive conditions. The obtained results provide valuable insights, contributing to a better understanding of the behaviour of coating materials under high-temperature conditions, and may also have potential application significance in the design of more durable TBC systems.

Final Conclusion

The doctoral dissertation by M.Sc. Muhammad Jahangir Khan, entitled "Hot corrosion behaviour of a new type of thermal barrier coating materials", prepared under the supervision of Prof. Grzegorz Moskal and assistant supervisor Dr Marta Mikuskiewicz, constitutes a valuable scientific contribution in the field of materials engineering.

The work addresses a relevant and important issue related to the corrosion resistance of thermal barrier coatings under high-temperature conditions, taking into account both material and technological aspects. The presented research has been properly designed and conducted, and the obtained results have been subjected to logical analysis and interpretation.

The dissertation confirms that the Candidate possesses the appropriate theoretical knowledge in the discipline of materials engineering, the ability to conduct independent scientific research, and the capability to solve experimental research problems.

Taking into account the scope of the conducted research, its methodological correctness, the scientific value of the obtained results, and their cognitive and application-oriented significance, it is concluded **that the reviewed dissertation meets the requirements specified in Article 187 of the Act of 20 July 2018 – Law on Higher Education and Science (as amended).**

Therefore, I recommend that the dissertation be admitted to the further stages of the doctoral procedure leading to the award of the PhD degree in the field of engineering and technical sciences, in the discipline of materials engineering.

Podpisała: prof. dr hab. inż. Agata Dudek