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REVIEW

**of the doctoral dissertation by M.Sc. Muhammad Jahangir KHAN,
entitled: “Hot corrosion behaviour of a new type of thermal barrier coating materials”
– basis for the preparation of the review – Resolution of the Council of the Discipline of
Materials Engineering at the Silesian University of Technology dated 17 February 2026
(letter dated 17 February 2026)**

General characteristics of the dissertation

At present, aircraft turbojet engines are designed in such a way as to meet both economic and environmental requirements (reduction of greenhouse gas emissions). The main direction of efforts in this area is work aimed at increasing the efficiency of these engines. Based on the Carnot cycle, the simplest (apparently) solution is to increase the operating temperature at the inlet of the hot turbine. However, such an approach has caused the operating temperature of aircraft engines to dangerously approach the limiting values of their allowable operating temperatures. Therefore, so-called thermal barrier coatings (Thermal Barrier Coatings – TBCs) have been applied. These consist mainly of three basic components, namely: a substrate, most often nickel-based superalloys responsible for carrying mechanical loads; a bond coat serving as a reservoir of Al forming a protective Al_2O_3 oxide layer and Cr in order to counteract sulfur corrosion; and a ceramic coating acting as a thermal insulator between the exhaust gas atmosphere in the engine and the substrate. Thanks to the application of TBC systems, it has become possible to increase the operating temperature of turbine engines. For the production of ceramic coatings in TBC systems, ZrO_2 stabilized with Y_2O_3 in an amount of 6–8 wt.% is most commonly used, commonly referred to as YSZ – yttria-stabilized zirconia. This material exhibits excellent stability and thermal properties; however, when the stabilizing agent responsible for the tetragonal polymorphic form of ZrO_2 , i.e., Y_2O_3 , participates in reactions with the environment, a polymorphic transformation from the tetragonal to the monoclinic form

of ZrO_2 occurs during cooling. This results in an increase in the unit volume of ZrO_2 , leading to the disintegration of dense ceramic coatings. An additional dangerous aspect in the operating environment of thermal barrier coatings is the sintering of the outer layers of YSZ coatings. These processes often occur via so-called hot corrosion, i.e., the reaction of materials used in the hot section of a gas turbine with sulfur compounds. These compounds may originate from various sources, such as fuel impurities or volcanic dust. The latter also causes the introduction of magnesium and vanadium compounds into the engine, actively participating in corrosion reactions. Therefore, research is currently being conducted on the development of new materials for ceramic coatings in TBC systems characterized by increased resistance to broadly understood hot corrosion. The subject matter of the reviewed dissertation fits perfectly into this research trend, and therefore I assess it as highly relevant and worthy of investigation.

The basis for the research plan adopted in the work was an analysis of available literature data concerning thermal barrier coatings for applications under high-temperature and highly corrosive atmospheric conditions. In the dissertation, the Author described the concept and significance of thermal barrier coatings, then characterized the components of TBC systems and briefly presented their manufacturing methods. Subsequently, the reader was introduced to the mechanisms of degradation of thermal barrier coatings caused by thermal loads, differences in coefficients of linear thermal expansion of the individual components of TBC systems, concluding with a specific mechanism of degradation of thermal barrier coatings, namely as a result of hot corrosion. The Author then presented the state of the art regarding hot corrosion of thermal barrier coatings containing two-phase ceramic coatings based on rare-earth zirconates, with particular emphasis on $La_2Zr_2O_7 + 8YSZ$, $Gd_2Zr_2O_7 + 8YSZ$, and $Sm_2Zr_2O_7 + 8YSZ$. In the following part, the doctoral candidate summarized the existing literature data in the scope of the research topic of this doctoral work and indicated significant gaps in knowledge concerning the resistance of already studied composite ceramic coatings from TBC systems to hot corrosion, namely the lack of systematic studies on resistance to hot corrosion under different deposit configurations, which was identified as the aim of the work. The formulated research hypothesis assumes that $Nd_2Zr_2O_7$, $Nd_2Zr_2O_7 + 8YSZ$, and $Nd_2Ce_2O_7 + 8YSZ$ systems may exhibit higher durability under high-temperature corrosion conditions than traditional single-phase systems, which is associated with their ability to more effectively relax stresses and limit the propagation of microcracks. A key role is played here by complex degradation mechanisms, leading, among others, to the formation of non-stoichiometric phases and fine voids in the microstructure.

In order to verify this hypothesis, studies were planned including corrosion tests in molten salt environments, phase composition analysis, and evaluation of the microstructure of the coatings. The expected result is the identification of factors affecting TBC durability,

determination of structural and phase changes occurring during operation, and clarification of degradation and corrosion mechanisms. According to the doctoral candidate, the obtained results are intended to contribute to the development of more resistant coating systems and to deepen knowledge on high-temperature corrosion of materials based on rare-earth compounds.

The main focus of the experimental part of the work was the study of resistance to hot corrosion of thermal barrier coatings containing $\text{Nd}_2\text{Zr}_2\text{O}_7$, $\text{Nd}_2\text{Zr}_2\text{O}_7 + 8\text{YSZ}$, and $\text{NdCe}_2\text{O}_7 + 8\text{YSZ}$ under high-temperature conditions and in the presence of sulfate salt deposits of different chemical compositions. The obtained results made it possible to determine the resistance to hot corrosion of the studied ceramic composites and their classification. It was found that all tested ceramic coatings exhibited the best resistance to hot corrosion in contact with Na_2SO_4 . The introduction of additional MgSO_4 salt resulted in a deterioration of this resistance, whereas for the Na_2SO_4 and V_2O_5 mixture, significantly greater degradation of the tested ceramic coatings was observed.

I would like to note that the above conclusions were formulated on the basis of analysis of results obtained using X-ray diffraction (XRD) and scanning electron microscopy, including backscattered electron imaging (BSE) and energy-dispersive spectroscopy (EDS), i.e., methods limited in number, yet sufficient to support the conclusions drawn.

In summary of this part of the review, I can state that the doctoral dissertation by M.Sc. Muhammad Jahangir KHAN contains valuable results of a cognitive nature, which may in the future contribute to the development and implementation of composite materials as ceramic coatings used in thermal barrier coatings characterized by increased resistance to hot corrosion.

Detailed characteristics of the dissertation

The doctoral dissertation by M.Sc. Muhammad Jahangir KHAN entitled “Hot corrosion behaviour of a new type of thermal barrier coating materials” concerns comprehensive studies of innovative ceramic materials based on the single-phase $\text{Nd}_2\text{Zr}_2\text{O}_7$ system and composite systems based on $\text{Nd}_2\text{Zr}_2\text{O}_7 + 8\text{YSZ}$ and $\text{NdCe}_2\text{O}_7 + 8\text{YSZ}$ under hot corrosion conditions at a temperature of 920°C for up to 224 hours in contact with deposits: Na_2SO_4 , $\text{Na}_2\text{SO}_4 + \text{MgSO}_4$ (50%–50%), and $\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5$ (50%–50%). It can be inferred that the doctoral dissertation was prepared on the basis of a set of six published and thematically related scientific articles indicated on page iii. Nevertheless, the Author supplemented it with an extensive original study (106 pages), in which he presented: a literature review in the area of the work’s subject matter, the scope, methodology and selected research results, and a systematic description of the

obtained results under hot corrosion conditions for different chemical compositions of the deposit for three different ceramic coatings, namely: $\text{Nd}_2\text{Zr}_2\text{O}_7$, $\text{Nd}_2\text{Zr}_2\text{O}_7 + 8\text{YSZ}$, and $\text{NdCe}_2\text{O}_7 + 8\text{YSZ}$. This study is concluded with final remarks and an outline of further work in the field addressed in this doctoral dissertation. In my opinion, this part of the dissertation comprehensively characterizes the undertaken problem, against which the Author appropriately justified the scope of his research. Moreover, he skillfully presented and discussed the results published in the attached series of scientific articles, demonstrating their thematic coherence.

The content of the reviewed doctoral dissertation by M.Sc. Muhammad Jahangir KHAN was divided into eight chapters, excluding abstracts, lists of abbreviations used in the work, and references (the number of which is difficult to define due to repetitions). This part includes 38 figures and 4 tables.

Chapter I: Introduction presents the idea and importance of thermal barrier coatings, the types of materials used, and outlines the problem of hot corrosion.

Chapter II contains a literature review, including a brief discussion of TBC coatings, their applications, modern materials used, methods of their production, and mechanisms leading to their degradation.

Chapter III: Materials and Methods presents the materials used and the research procedures applied to analyze the properties, structure, and degradation processes of thermal barrier coatings.

Chapter IV: Thesis and Objectives presents the main research assumptions and objectives, indicating gaps in knowledge regarding two-phase composite TBC coatings. The hypothesis of increased resistance to hot corrosion of $\text{Nd}_2\text{Zr}_2\text{O}_7 + 8\text{YSZ}$ and $\text{Nd}_2\text{Ce}_2\text{O}_7 + 8\text{YSZ}$ systems was formulated. The plan of corrosion tests and phase analyses was also described, and key objectives related to durability, microstructural changes, and degradation mechanisms were defined.

Chapter V discusses the effect of molten sulfate and vanadate salts on high-temperature corrosion of single-phase $\text{Nd}_2\text{Zr}_2\text{O}_7$ coatings. Phase transformations, microstructural changes, and degradation processes in the presence of Na_2SO_4 , $\text{Na}_2\text{SO}_4 + \text{MgSO}_4$, and $\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5$ deposits were described.

Chapter VI concerns studies on complex high-temperature corrosion induced by sulfate and vanadate salts in the composite system $\text{Nd}_2\text{Zr}_2\text{O}_7 + 8\text{YSZ}$. Corrosion behavior, phase composition, and microstructural changes were presented.



Chapter VII describes corrosion behavior of $\text{Nd}_2\text{Ce}_2\text{O}_7 + 8\text{YSZ}$ coatings in molten salt environments.

Chapter VIII contains final conclusions and proposals for further research directions.

The work constitutes an original approach, among other reasons due to the fact that Chapters V, VI and VII are provided with separate abstracts, literature reviews, and lists of references, which undoubtedly demonstrates both positive and, unfortunately, negative features, as will be discussed later.

In summarizing the detailed characteristics of the dissertation, I can state that the scope of research adopted by the doctoral candidate and its implementation made it possible to achieve the objective formulated in Chapter IV. The effort invested by the Author in preparing the dissertation resulted in a very good outcome in the form of a coherent monograph, despite the adopted form of a collection of selected scientific articles. It should be emphasized that M.Sc. Muhammad Jahangir KHAN is the first author in 4 out of the 6 listed publications.

The manner in which the discussion of results is conducted in the text of the dissertation demonstrates a good understanding of the issues addressed. Despite this, however, the Author did not avoid errors in preparing his dissertation. I will cite some of them and ask the doctoral candidate for comments:

1. On page 4, the doctoral candidate stated: “The TBCs eliminate or lower the operating temperature of the underlying metallic component by providing a thermal insulation layer between the hot gas stream and the metal”. I would like to ask what the doctoral candidate meant by stating that the application of thermal barrier coatings “eliminates temperature”?
2. On page 16, the doctoral candidate wrote chemical reaction No. (4) as follows:
$$\text{Al}_2\text{O}_3 + 2\text{Cr} \rightarrow \text{Cr}_2\text{O}_3 + \text{Al} \quad (4)$$

I kindly request a detailed discussion of whether the cited chemical reaction is thermodynamically feasible at all. In the discussion, please take into account the formation energies of the individual oxides as well as their dissociation pressures (Ellingham–Richardson diagram) and the affinity of both elements mentioned in the reaction for oxygen.

3. Page 16: The doctoral candidate stated: “The selection of coating–substrate systems with minimal aluminium activity differences, combined with the use of reactive element doping (Hf, Y, Zr), can suppress both oxidation and interdiffusion, thereby extending the coating lifetime under severe cyclic conditions [46–47].”. In modern nickel-based superalloys, usually used as substrate materials in thermal barrier coatings, the Al content does not exceed 6 wt.%. In MCrAlY-type bond coats, its content ranges from 8–12 wt.%, while in aluminide coatings the Al content reaches 30 wt.%. Therefore, please comment on this statement in light of the above information.
4. Page 34: Table 3.1 provides the chemical composition of the substrate material, i.e., the nickel-based superalloy IN 625. However, no information is given as to whether this is a nominal or measured composition. No concentration ranges are provided, thus it may be inferred that the chemical composition is measured. Please specify which analytical methods were used to determine the chemical composition and the uncertainty of the measurements.
5. Page 34: The type of material used for the bond coat, i.e., NiCrAlY, is mentioned, but its exact chemical composition is not specified. At the same time, no information is provided on the method used to produce the bond coat. Please comment.
6. Page 37: In the description of the methodology for producing materials for testing, the doctoral candidate declared that the thermal barrier coatings for hot corrosion tests were produced on an IN 625 nickel-based superalloy substrate in the form of rectangular specimens with dimensions of 40×20×2 mm. Meanwhile, Table 3.2 specifies “Rotation [RPM]” at a value of 120. What was the purpose of applying substrate rotation during the thermal spraying process of thermal barrier coatings onto rectangular specimens? How did this procedure affect the thickness distribution of the produced coatings?
7. Page 40: The doctoral candidate, describing the particle size distribution analysis, stated: “Each sample was measured 100 times to enhance accuracy and reproducibility, and the procedure was repeated three times in each powder batch.”. Was the number of 100 repetitions really necessary? What was the reason for performing 100 repetitions of particle size distribution analysis on the same powder sample? How long did a single measurement take?
8. Pages 49 and 50: The doctoral candidate, describing the condition of the ceramic coating after the hot corrosion test, stated: “Low magnification 5.3 (a, b) surface morphology shows that there is severe degradation with a porous and cracking structure with granular and globular corrosion deposits that occupy significant parts of the coating.”. Cracks in the ceramic coating were already visible in the “as-sprayed” state. Was the observed effect actually the result of hot corrosion? Please comment.

9. Page 68: In equations (3) and (4), the doctoral candidate gave the unit of enthalpy as $[\text{KJmol}^{-1}]$. K is a unit of temperature (Kelvin). Presumably, the doctoral candidate intended to denote the prefix kilo, i.e., “kJ”.
10. Chapter 6: In this chapter, the doctoral candidate made an error in figure numbering, namely, in the figure captions the number 6.2 was used twice, which resulted in the numbering of subsequent figures being shifted back by 1, i.e., the figure that should have been numbered 6.4 was labeled 6.3, figure 6.5 was labeled 6.4, etc. At the same time, the numbering in the text remained correct. This led to a situation in which the text at the end of the chapter referred to Figure 6.10, which, according to the captions, did not exist. This situation causes confusion for the reader.
11. Figures 6.6 and 6.7 (according to the incorrect numbering in the dissertation): element distribution maps are presented, but SEM/BSE images of the areas from which the maps were obtained are not shown, making it difficult to assess the correctness of the Author’s interpretation.
12. Figures 7.5 and 7.8: The figure captions read: “Cross-sectional SEM and EDS analysis of the...”. While SEM/BSE microstructure images are shown, there is not a single SEM/EDS result presented.
13. According to Table 3.3, three types of TBC systems were tested at the same temperature of 920°C , for three identical deposit compositions: Na_2SO_4 , $\text{Na}_2\text{SO}_4 + \text{MgSO}_4$ (50/50), and $\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5$ (50/50), but for different durations. What was the reason for varying the exposure time? Is a duration of 224 h representative in terms of real operating conditions of TBC systems? Please comment.
14. The APS method was adopted as the method for producing the bond coat. In the indicated SEM images after corrosion, e.g., 6.4a or b, the phenomenon of separation of individual sprayed particles is visible. Please justify the choice of the bond coat manufacturing process. Was the doctoral candidate not concerned about the phenomenon known in the literature as the “separated cell effect”? And did this effect have a potential influence on the selection of the duration of the hot corrosion test?
15. Throughout the experimental part, the doctoral candidate indicated the formation of the monoclinic form of ZrO_2 ; however, apart from XRD results, no other evidence confirming the presence of this phase was provided. Can the doctoral candidate indicate a method or methods for the quantitative/qualitative identification of the monoclinic phase of ZrO_2 ?
16. The aforementioned use of separate abstracts, introductions, and references in Chapters V, VI, and VII undoubtedly exhibited positive features, as it introduced the reader to the issues discussed in the individual chapters; however, it also resulted in the repetition of content already presented in earlier parts of the work, as well as duplication of some



references, which made the editorial assessment of the doctoral dissertation more difficult.

In addition, the doctoral candidate did not avoid editorial errors. The most striking of these is the failure to use subscripts in chemical formulas throughout the work. This could be attributed to final text formatting, were it not for the fact that within the same page some formulas are written correctly, while in subsequent lines they are not. This suggests hurried and careless editing of the doctoral dissertation.

Nevertheless, in my opinion, the identified shortcomings do not significantly reduce the scientific level of this dissertation.

Final assessment

The doctoral dissertation of M.Sc. Muhammad Jahangir KHAN undoubtedly constitutes an original solution to a scientific problem. It is based on well-planned and systematically carried out research work. The Author defined a research objective which, in my opinion, has been achieved—it has been demonstrated that composite materials based on $\text{Nd}_2\text{Zr}_2\text{O}_7$, $\text{Nd}_2\text{Zr}_2\text{O}_7 + 8\text{YSZ}$, and $\text{NdCe}_2\text{O}_7 + 8\text{YSZ}$ exhibit increased and differentiated resistance to hot corrosion under the applied conditions.

The dissertation has been prepared in an orderly and well-considered manner, which facilitates the evaluation of the presented scientific achievements. It is based on a series of six thematically related publications, which form a coherent whole and demonstrate the consistent implementation of the research program adopted by the doctoral candidate. The presented results are characterized by significant cognitive value.

In view of the above, I conclude that the doctoral dissertation entitled “*Hot corrosion behaviour of a new type of thermal barrier coating materials*”, despite the submitted remarks, meets at a satisfactory level the requirements set for doctoral theses, as specified in Article 187 of the Act of 20 July 2018 “Law on Higher Education and Science” (as amended). Consequently, I recommend to the Council of the Discipline of Materials Engineering at the Silesian University of Technology that M.Sc. Muhammad Jahangir Khan be admitted to the subsequent stages of the proceedings for the award of the doctoral degree in the discipline of materials engineering.

Podpisał: dr hab. inż. Wojciech Nowak, prof. PRz

