Centre for Functional and Surface Functionalized Glass
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Title of thesis: **Characterization of destruction processes in two phase thermal barrier coatings – model investigations in conditions of high temperature oxidation and corrosion in liquid salts deposits**
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The main objective of this PhD work is the development of advanced thermal barrier coatings (TBCs) by modifying the top ceramic layer and exploring new degradation mechanisms. TBCs play a critical role in enhancing the performance, durability, and lifespan of industrial components operating under high temperatures and corrosive environments.
Plasma Spray (PS) technology was employed to deposit the bond coat (BC) and top coat (TC) layers due to its wide industrial use and equipment accessibility. A key innovation introduced in this study is the incorporation of **dual-phase systems** into the ZrO_2-based top ceramic layer. This dual-phase approach, which involves materials like pyrochlore- and fluorite-structured zirconates and cerates, is designed to achieve lower thermal conductivity and greater thermal stability—key requirements for next-generation ceramic materials.
The degradation behavior of three advanced dual-phase systems was investigated under hot corrosion (molten sodium sulphate) and oxidation at **920°C and 970°C**:

1. Gadolinium Zirconate + YSZ ($Gd_2Zr_2O_7$ + Y_2O_3-stabilized ZrO_2)
2. Lanthanum Zirconate + YSZ ($La_2Zr_2O_7$ + Y_2O_3-stabilized ZrO_2)
3. Lanthanum Cerate + YSZ ($La_2Ce_2O_7$ + Y_2O_3-stabilized ZrO_2)

The study found that degradation occurred via multiple mechanisms such as phase decomposition, formation of new rare-earth-rich/poor phases, non-equilibrium diffusion, and inter-phase interactions. Despite prolonged exposure, visual analysis revealed that the ceramic layers remained largely intact, with only minor edge spallation.

Positive Aspects & Strengths:

- **Innovation**: The introduction of dual-phase systems in the TBC top layer is a novel and impactful approach, addressing both thermal and chemical stability.
- **Practical Relevance**: The use of industrially common Plasma Spray technology ensures the applicability of findings to real-world systems.
- **Scientific Depth**: The detailed analysis of degradation pathways—including chemical and phase interactions—adds fundamental knowledge to high-temperature coatings.
- **Comprehensive Testing**: The work includes exposure to harsh conditions (hot corrosion + oxidation) at high temperatures, demonstrating the coatings' resilience. However, additional supplementary tests—such as CMAS infiltration, extended oxidation resistance, thermal shock, and rig testing—are recommended to further validate the coatings' long-term performance.
- **Material Selection**: The use of rare-earth-based ceramics (pyrochlores and cerates) reflects advanced understanding of modern TBC design.

Conclusion and Recommendation:

The submitted doctoral report presents a well-structured investigation into the development and degradation behavior of advanced dual-phase thermal barrier coatings under high-temperature oxidation and molten salt corrosion conditions. The candidate has demonstrated a comprehensive understanding of material selection, coating deposition techniques, and degradation mechanisms, particularly with regard to the role of rare-earth zirconates and cerates in improving thermal and chemical stability.

Based on the presented work, the candidate shows clear potential for fulfilling the requirements of a doctoral degree. However, it is recommended that the candidate, based on the discretion and guidance of the supervising committee, addresses the raised questions and incorporates relevant suggestions into the final version of the dissertation where appropriate.

General comments and questions:

1-In the context of hot corrosion studies on turbine blades, it is well-documented that the mixture of Na_2SO_4 and V_2O_5 creates a highly corrosive molten salt environment due to their eutectic reaction, which significantly lowers the melting point to around 540–620°C—well below the operational temperatures of gas turbines (~800–950°C). Considering that Na_2SO_4 alone has a relatively high melting point (~884°C) and V_2O_5 melts at ~690°C, and that their combination results in a more aggressive and realistic corrosive scenario due to the formation of low-melting vanadates (e.g., $NaVO_3$, $Na_4V_2O_7$), what was the rationale behind studying Na_2SO_4 alone in your project? Was there a specific reason for excluding the synergistic effects of V_2O_5, or were there experimental limitations that led to this choice? You did it only for LZO and why you add only 10 mol percentage?

2- cross-sectional SEM images of the coatings after the hot corrosion test should be provided, as such images could significantly strengthen the analysis by illustrating the depth of salt infiltration. Moreover, it provides valuable insights into the development of porosity, crack initiation, and the extent of microstructural damage resulting from hot corrosion test.

3-Why were 920°C and 970°C chosen as the test temperatures? Are they representative of real operating environments?

4-Could the dual-phase approach be extended to other ceramic systems beyond zirconates and cerates? For other applications.

5-Considering that these new dual-phase ceramics utilize rare-earth elements in their composition, has a cost analysis been performed to compare the production expenses of these TBCs with conventional coatings? From an economic standpoint, is it justifiable to use such materials on a larger scale?

6- Please make sure to include the thickness of the ceramic coatings.

7-Part of your work was conducted on ceramic plates; however, the experimental section does not provide any data regarding the fabrication of these plates. For instance, several parameters—from mixing to sintering—can significantly influence the final properties of the plates, yet no information about these steps is included in the thesis.

8-What unique challenges or advantages particularly regarding the rate of degradation, are associated with using the dual-phase approach in comparison to the single phase system?

From text:

1-In page 4, it was mentioned" Other materials like alumina (Al2O3), due to its high melting point and good resistance to thermal shock, and silicon carbide (SiC), which has excellent thermal stability and low thermal expansion coefficient, are also promising TBCs materials" despite its thermal stability, SiC is generally unsuitable for conventional TBCs due to its severe oxidation behavior at high temperatures and its low thermal expansion mismatch with metal substrates, which can lead to surface degradation and cracking.

2- In Page 5 it was mentioned "Atomic layer deposition (ALD) and chemical vapor deposition (CVD) are two methods that can be used to deposit it." do you think we can deposit TBC with ALD and CVD?are they conventional?

3-In pages 28 and it was mentioned that "The two layers are designed to work together to provide a number of benefits." it would be better to clearly mention what those benefits are. In scientific writing, it's best to avoid general words and explain things more specifically.

4- There are several pages, such as pages 19, 21 24 and 28 , where no references are provided. Since these sections belongs to introduction and literature review section, it is essential to conduct a thorough revision and ensure that appropriate references are included throughout.

5-In page 38 Fig 3.1 need revision it is not complete.

6-In page 44, it was mentioned "these materials demonstrate good influencing characteristics, including flowability, packing density, and sintering behavior." How you can understand mentioned properties based on the SEM images.

7-various figures such as Figures 6.4, 6.7, 6.8, and 6.9 show SEM images with EDS spot analyses, where elemental atomic/weight percentages are provided for different points. While this is a valuable approach, the overall purpose of these measurements is not entirely clear. What are these selected points intended to demonstrate? In some cases, the variations in atomic percentages are minimal. It would be beneficial if, based on the combined results from EDS and XRD, a brief summary or conclusion was provided to clarify which phases are being identified and how they correspond to the points marked in the images?

8-Page 71. Figure 5.1 c and d I think it is still top surface not cross-sectional view of powders.

9-Page 102 Fig 6.8. what is the source of Mo.

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Best Regards

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