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Evaluation

of the doctoral dissertation of MSc Eng Amjad Iqbal entitled "*Characterization of destruction processes in two-phase thermal barrier coatings – model investigations in conditions of high-temperature oxidation and corrosion in liquid salts deposits*"

1. Characteristics of the doctoral thesis

The doctoral thesis submitted for review by Mr. MSc Eng. Amjad Igbal is mainly devoted to the development of a new type of thermal barrier coatings (TBC) by modifying the external ceramic layer. Ceramic TBCs are currently considered to be one of the best solutions for protecting metallic materials exposed to high-temperature oxidation (above 500 °C), especially in aggressive work environments - i.e. molten salts, hot gases and vapors. The problem of degradation of metallic materials due to broadly understood high-temperature corrosion is particularly current in some of the fastest developing industries, i.e. energy industry, automotive and aviation. Of course, many different solutions have already been developed to limit the effects of high-temperature corrosion, but so far this problem remains largely unsolved and unfortunately generates billions of losses each year related to the need to replace degraded elements of various devices.

As I have already mentioned, ceramic TBCs, especially those based on ZrO_2 stabilized with Y_2O_3 oxide – YSZ for short, are often used to protect metallic elements. Such widespread use of ZrO_2-based materials is of course related to its specific physicochemical properties, the most important of which are high melting point, low thermal conductivity and coefficient of thermal expansion (CTE) adapted to the metallic substrate. All this means that TBCs based on ZrO_2 (in tetragonal variety) guarantee low thermal conductivity, resistance to thermal shock and high thermal and chemical stability. Considering the previously mentioned working environment (high temperatures, aggressive working environment), these are of course key parameters from the point of view of the functional properties of TBCs. However, to make things less rosy, the use of ZrO_2-based materials has its limitations, primarily related to thermo-chemical stability, especially during cyclic temperature changes.

That is why we are constantly looking for new solutions that will eliminate or at least reduce the obvious disadvantages of these materials. In connection with this, the Author in the dissertation proposed the use of three two-phase systems based on ZrO_2 and gadolinium zirconate ($Gd_2Zr_2O_7$+Y_2O_3(ZrO_2) – GZO-YSZ), lanthanum zirconate ($La_2Zr_2O_7$+Y_2O_3(ZrO_2) – LZO-YSZ) and lanthanum cerate ($La_2Ce_2O_7$+Y_2O_3(ZrO_2) – LCO-YSZ). The presence of two phases is primarily intended to improve the thermo-mechanical resistance of the layers due to the presence of interphase boundaries.

To sum up, I consider taking up such a topic as well as the selection of materials and methods of solving the noticed problems to be most justified and extremely interesting from both the scientific and ultimately utilitarian point of view.

Nowadays, when most doctoral dissertations are presented in the form of a series of thematically related publications, the submitted doctoral dissertation should be classified as unusual, as it was presented in the "old" form, i.e. in the form of a monograph. Layout thesis is classic and apart from the Summaries in English, Portuguese and Polish, it consists of four main chapters, i.e. Introduction, Literature Review, Experimental Part and Conclusions. The dissertation is also accompanied by a short Supplement.

2. Substantive evaluation of the work

The dissertation begins with a presentation of abstracts and a brief introduction to the issues related to the subject of the thesis, including a discussion of problems related to high-temperature corrosion and a review of currently used TBCs. Each TBC coating consists of two layers, i.e. a bonding layer (Bond Coat - BC) and a top layer (Top Coat - TC) providing appropriate insulating properties. Under operating conditions, BC oxidation additionally forms a layer called thermally generated oxide (TGO) consisting mainly of BC alloying elements, ideally α-Al_2O_3. Individual TBC layers are most often deposited using various thermal spraying methods, the most popular of which are atmospheric plasma spraying (APS) and electron beam physical vapor deposition (EB-PVD). These methods allow obtaining high-quality (tight) TBC coatings of controlled thickness. Thus, improving the functional properties of TBC coatings can be achieved both by modifying the chemical composition, structure and microstructure of individual layers as well as by improving the process of their application. With this in mind, the Author reviewed the literature mainly for materials used as bonding layers and top layers. The material for the BC layer must provide adequate adhesion and protection of the substrate against oxidation. In turn, the material for the TC layers must provide low thermal conductivity, low thermal diffusivity of oxygen and molten salts, phase stability at high temperatures, high resistance to thermal shock and good adhesion to the BC layer.

The most commonly used BC layer is the so-called MCrAlY type coating where M = Co, Ni or Co/Ni. Currently, work on these materials is mainly focused on doping them with noble metals, which allows for significant improvement in resistance to high-temperature oxidation. Among the materials used for the TC layer, the ever-popular YSZ reigns supreme. Of course, there are many proposals in the literature for the use of other materials (e.g. rare earth oxides, SiC), but so far the work carried out has not led to the development of coatings that could constitute real competition for YSZ, taking into account functional properties and price. The main disadvantages of YSZ-based coatings are: 1) limited resistance to cracking resulting from phase transformations occurring at high temperatures 2) insufficient matching of the thermal expansion coefficient to the substrate 3) often unsatisfactory resistance to aggressive working environments. Currently, research focuses mainly on modifying the chemical composition and microstructures of the YSZ-based TC layer. In this context, it is proposed to obtain multi-layer (several ceramic layers) or multi-phase TBCs. From the point of view of eliminating defects of YSZ-based coatings, the design and production of multi-phase layers seems particularly interesting. The presence of an appropriately selected additional phase with low thermal conductivity allows for a significant reduction in the thermal conductivity of the entire coating and, no less importantly, a reduction in the always existing stresses.

With all this in mind, the PhD candidate proposed appropriate two-phase materials and in this context posed three research questions: 1. Are two-phase systems (phase with pyrochlore structure and YSZ) stable at high temperatures? 2. How will two-phase systems degrade in the Na_2SO4 environment? and 3. How does the presence of two phases, including interphase boundaries, affect the stability of the coating at high temperatures with exposure to Na_2SO_4?

The next part of the dissertation, which is a literature review, presents detailed information on high-temperature corrosion, rare-earth zirconates and two-phase TBCs. The information contained in these three subsections on the mechanisms of high-temperature corrosion, the structure of selected chemical compounds and the structure and operation of two-phase ceramic coatings is crucial from the point of view of interpreting the research results presented in the experimental part.

To sum up, reading the issues raised in the introduction and during the analysis of the literature allows one to easily understand what the Author was guided by both when choosing the type of protective layers and the materials from which they were made.

The main part of the work, covering about 70% of the volume of the entire material, consists of chapters 3-6 presenting the procedure of obtaining (chapter 3) and the characteristics of the obtained TBCs (chapters 4-6). A nickel-based superalloy (Inconel 625) was selected as the substrate, on which NiCrAlY layers constituting the bonding layer (BC) and ceramic coatings constituting the top layer (TC) were applied by plasma spraying (ASP). Three types of two-phase systems with YSZ were proposed for the TC layer, i.e. based on lanthanum zirconate (LZO + YSZ), gadolinium zirconate (GZO + YSZ) and lanthanum cerate (LCO + YSZ), which were also applied by ASP. The TBCs obtained in this way were subjected to oxidation and high-temperature corrosion tests. In order to facilitate the determination of changes occurring in two-phase coatings, it was also decided to carry out corrosion tests in the presence of Na_2SO_4 on appropriately prepared model powders with compositions corresponding to the proposed TC.

The three most important chapters of the dissertation (chapters 4-6) are devoted to the description and characterization of the two-phase systems LZO+YSZ (chapter 4), GZO+YSZ (chapter 5) and LCO+YSZ (chapter 6). Before each chapter, a short introduction is presented indicating the greatest problems associated with various types of high-temperature corrosion. Undoubtedly, in the transport industry, apart from high temperature, the greatest challenges are related to the presence of various types of air pollutants (CaO, MgO, Al_2O_3 and SiO_2) and fuel (Na, S, V), which in the operating conditions of turbines, engines, etc. results in the appearance of, respectively, melted aluminosilicate deposits (so-called CMAS corrosion) and melted Na_2SO_4 and V_2O_5. Conventional YZS-based coatings interact quite easily with these types of alloys, resulting in their rapid phase decomposition. The first of the proposals for preventing this phenomenon presented by the Author is the use of a two-phase system $La_2Zr_2O_7$+$Y_2O_3(ZrO_2)$ – LZO-YSZ (chapter 4). The extremely valuable, from the point of view of high-temperature corrosion, physicochemical properties of $La_2Zr_2O_7$ are known, hence the attempt to combine the properties of YSZ and LZO should not be surprising. The obtained TBCs in the ratio YSZ/LZO = 50/50 were characterized in terms of structure (XRD) and microstructure (SEM with EBSD) and then subjected to tests in the environment of liquid sodium sulfate (Na_2SO_4) and a mixture of 90% Na_2SO_4+10% V_2O_5. Very interestingly designed tests of heating at different temperatures of model powders with compositions corresponding to the individual phases and their mixtures with different compounds (Na_2SO_4, Cr_2O_3, NiO) having a decisive influence on the course of corrosion were also carried out. All these studies allowed, on the one hand, to determine the thermo-chemical stability of the obtained layers but also to describe the corrosion mechanisms in various conditions. It has been shown that the proposed procedures allow obtaining good quality (tightness, homogeneity, thickness) of the layer from the LZO-YSZ system and these coatings are stable in various corrosive environments. The results of model tests of powders confirmed the stability of the obtained materials, especially in the stability of the tetragonal zirconium oxide variety. Importantly, the presence of Na_2SO_4 and V_2O_5 does not have a major effect on the polymorphic transformation of ZrO_2. Detailed analyses also allowed to determine the influence of NiO and Cr_2O_3 oxides, formed in the TGO zone, on the stability of TBC. The conducted studies allowed to state that the proposed layers are stable in high-temperature corrosion conditions, including aggressive environments.

A similar research procedure was used for the $Gd_2Zr_2O_7+Y_2O_3(ZrO_2)$ - GZO+YSZ system (chapter 5). This research was a continuation of the work carried out in the group of Prof. G. Moskal on the influence of the ionic radius of the rare earth element in zirconate compounds on the stability of the two-phase $X_2Zr_2O_7+Y_2O_3(ZrO_2)$ systems, where X = rare earth element. Similarly to the previous study, the structure and microstructure of both the model materials and the target systems before and after corrosion allowed to determine the thermo-chemical stability of the obtained layers and the corrosion mechanism paths under various conditions. XRD studies showed the formation of numerous phases with a lower concentration of Gd_2O_3 than in the stoichiometric $Gd_2Zr_2O_7$, which indicates the diffusion nature of the decomposition processes of the GZO+YSZ coating compounds. Nevertheless significant changes were found practically exclusively in the zirconate phase, which clearly indicates a decomposition mechanism associated exclusively with the transformation of this phase. The decomposition effect was observed only in two-phase GZO+YSZ coatings and the corresponding mixture of model powders. This allowed the PhD student to state that the driving force of the observed phenomena is the formation of thermodynamically more favorable tetragonal or cubic oxide phases based on zirconium oxide. Additionally, the decomposition of zirconate is also associated with partial evaporation of gadolinium oxide during the plasma spraying process. This of course results in deviations from the assumed composition of two-phase coatings and is certainly one of the reasons for phase instability, and therefore has a definitely negative impact on the durability of the obtained TBC coatings. Unfortunately, the presence of sodium sulfate additionally accelerates the formation of non-stoichiometric zirconate compounds through various mechanisms, including synergistic degradation and the decomposition-re-precipitation mechanism described by Rapp. All this makes the proposed GZO+YSZ system in its current form unstable and does not meet the requirements for TBC.

Studies on the GZO+YSZ system, and earlier studies with zirconates of other rare earth elements also allowed to state that the decreasing diameter of lanthanide cations from lanthanum to lutetium determines the decreasing stability of the phase composition, in the system with YSZ. The next chapter of the dissertation is devoted to the preparation and studies of the lanthanum cerate system - $Y_2O_3(ZrO_2)$ (LCO+YSZ) - chapter 6. The idea of using $La_2Ce_2O_7$ is related to its extremely favorable thermophysical properties, i.e. primarily low thermal conductivity, high coefficient of thermal expansion and high melting temperature. Nevertheless, the use of $La_2Ce_2O_7$ as a single layer in TBC coatings encounters many problems related to its reaction with alumina derived from TGO, leading to the formation of lanthanum aluminate ($LaAlO_3$). Phase transformations of the resulting lanthanum aluminate introduce significant stresses in the coating, thus increasing the risk of cracking and chipping. Hence the idea to produce two-phase layers in order to use the thermophysical properties of lanthanum cerate and simultaneously eliminate the above-mentioned unfavorable phenomenon.

The re-used research procedure, similar to that used for zirconates, allowed the Author to determine the thermochemical resistance of the obtained LCO+YSZ layers, including the description of degradation mechanisms. In the two-phase LCO+YSZ system, in the initial stages of degradation, the formation of ZrO_2, Y_2O_3, La_2O_3, CeO_2 oxides occurs, which then interact resulting in the formation of secondary products dependent on the environment. At elevated temperatures (approx. 970 °C), phase dissolution was observed, similar to that in the GZO+YSZ system. In-depth studies at higher temperatures allowed to determine the degradation mechanisms of the YSZ-LCO system, which are largely determined by the presence of nickel and chromium from the TGO layer. To sum up, it was found that the LCO-YSZ system is much more stable in pure oxidation conditions than in high-temperature corrosion tests. The conclusions in Chapter 7 briefly summarize the results of all studies, specifying the differences in the degradation paths of individual systems and stating that TBC layers based on lanthanum zirconate and YSZ are extremely promising from the point of view of high-temperature corrosion, including in aggressive environments. Nevertheless, it is still necessary to specify in detail the role of oxides from the TGO zone and their influence on the degradation process of the layer.

Assessing the entire work, it should be stated that it constitutes an original and comprehensive approach to the design, production and characterization of TBC resistance to high-temperature corrosion. The manner of presenting the research results and their interpretation indicate the good preparation of the PhD student in the field of Materials Engineering.

The reviewed work, like any work of this type, obviously contains several minor flaws and awkward formulations. From the more serious substantive and polemic comments, I would mention the following:

1. The work includes a summary in Polish, which is a classic example of using the translator in the ctrl+C – ctrl+V mode and is far from being pure Polish, including the title "Abstractive".
2. On page 2 the Author writes that TBC coatings obtained by thermal spraying methods are 200–300 μm thick. On page 5, we find information that the TC layer itself is 100–600 μm thick, and on page 10, that the BC layer itself is 100–300 μm thick – where do these discrepancies come from?
3. On page 12, we read "*Are two-phase systems (pyrochlore and zirconia) stable at high temperatures*?" Pyrochlore is a mineral. The Author does not use pyrochlore in the dissertation, but compounds with a pyrochlore structure.
4. What was the basis for determining the time intervals during corrosion tests?
5. Page 45. The caption under the drawing indicates that this is Zr_2O_7, but we are dealing with ZrO_2?
6. Page 48. What does the Author mean by EDX morphology?
7. Page 64. "*In addition, metallic elements such as Al, Cr, Mn and Ni were added, which significantly increased the resistance to oxidation...*" I did not find any studies on Al and Mn in the work?
8. Why were SEM+EBSD studies not carried out on cross-sections after corrosion tests of individual two-phase systems? This would certainly contribute greatly to the

description of corrosion mechanisms as it would enable tracking of the diffusion processes and the formation of corrosion products inside the layers.

9. There are many unnecessary repetitions in the introductions to chapters 4-6.

10. Were any attempts made to perform *in-situ* XRD studies - currently there are systems that allow for the analysis of changes in the phase composition of samples during annealing even to 1500 °C. What is more, appropriately designed measurements also allow for the estimation of stresses present in the material.

11. Please suggest other methods for assessing changes in the phase composition of multilayer materials.

12. Were the most important (from the application point of view) properties of the obtained layers tested, i.e. adhesion to the substrate, thermal conductivity, thermal expansion coefficient, porosity, etc.?

3. Final conclusion

The reviewed work meets all the requirements for doctoral dissertations specified in the Law on Higher Education and Science of July 20, 2018 (Journal of Laws of 2018, item 1668) and on this basis I am applying for admission of Mr. Amjad Iqbal to the next stages of the doctoral thesis.

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