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Thermal Barrier Coatings

Failure Mechanisms and Life Prediction

Krishna Praveen Jonnalagadda

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During the course of research underlying this thesis, Krishna Praveen Jonnalagadda was enrolled in Agora Materiae, a multidisciplinary doctoral program at Linköping University, Sweden.

Cover:

Heavily modified SEM image showing the top view of yttria stabilized zirconia thermal barrier coating when exposed to mixed-gas atmosphere containing SO₂ at 780 °C.

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Abstract

Thermal barrier coatings (TBCs) use in the hot sections of gas turbine engine enables them to run at higher temperatures, and as a consequence, achieve higher thermal efficiency. For full operational exploitation of TBCs, understanding their failure and knowing the service life is essential. The broad objective of the current research is to study the failure mechanisms of new TBC materials and deposition techniques during corrosion and thermal cycling and to develop life models capable of predicting the final failure during thermal cycling.

Yttria-stabilized zirconia (YSZ) has constraints such as limited operation temperature, despite being the current industry standard. Pyrochlores of $A_2B_2O_7$ type have been suggested as a potential replacement for YSZ and were studied in this work. Additionally, improvements to the conventional YSZ in the form of nanostructured YSZ were also explored. The requirement for the new deposition process comes from the fact that the existing low-cost deposition processes, like atmospheric plasma spray (APS), generally exhibit lower strain tolerance. A relatively new technique, suspension plasma spray (SPS), known to be promising with better strain tolerance, has been studied in this work.

At the gas turbine operating conditions, TBCs degrade and eventually fail. Common failure observed in gas turbines can be due to corrosion, thermal mismatch between the ceramic and the metallic layers, and bond coat oxidation during thermal cycling. SPS and APS TBCs were subjected to different test conditions to understand their corrosion behavior. A study on the multi-layered SPS TBCs in the presence of $V_2O_5+Na_2SO_4$ showed that YSZ based SPS coatings were less susceptible to corrosion damage compared to $Gd_2Zr_2O_7$ SPS TBCs. A study on the influence of a sealing layer in multi-layered SPS TBCs in the presence of Na_2SO_4+NaCl showed that the sealing layer is ineffective if the material used for sealing is inert to the molten salts. A new study on the influence of corrosion, caused by a mixed-gas atmosphere, on the thermal cycling fatigue life of SPS TBCs was conducted. Results showed that corrosive products grew inside the top coat close to the bond coat/top coat interface along with accelerated growth of alumina. These, together, reduced the TCF life of corrosion exposed samples significantly. Finally, a study on the influence of salt concentration and temperature on a thin (dense) and a thick (porous) coating showed that thick and porous coatings have lower corrosion resistance than the thin and dense coatings. Additionally, a combination of low temperature and high salt concentration was observed to cause more damage.

Thermal cycling studies were done with the objective of understanding the failure mechanisms and developing a life model. A life model based on fracture mechanics approach has been developed by taking into account different crack growth paths during thermal cycling, sintering of the top coat, oxidation of the bond coat and the thermal mismatch stresses. Validation of such a life model by comparing to the experimental results showed that the model could predict the TCF life reasonably well at temperatures of 1100 °C or below. At higher temperatures, the accuracy of the model became worse. As a further development, a simplified crack growth model was established. This simplified model was shown to be capable of predicting the TCF life as well as the effect of hold times with good accuracy.

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Praveen

Linköping, Feb 2019

Appended papers

- I. *K.P. Jonnalagadda, S. Mahade, N. Curry, X-H. Li, N. Markocsan, P. Nylén, S. Björklund and R. L. Peng, “Hot Corrosion Mechanism in Multi-Layer Suspension Plasma Sprayed $\text{Gd}_2\text{Zr}_2\text{O}_7/\text{YSZ}$ Thermal Barrier Coatings in the Presence of $\text{V}_2\text{O}_5 + \text{Na}_2\text{SO}_4$ ”, Journal of Thermal Spray Technology, vol. 26, pp. 140-149, 2017
- II. K.P. Jonnalagadda, S. Mahade, S. Kramer, P. Zhang, N. Curry, X-H. Li and R.L. Peng, “Failure of Multilayer Suspension Plasma Sprayed Thermal Barrier Coatings in the Presence of Na_2SO_4 and NaCl at 900 °C”, Journal of Thermal Spray Technology, vol. 28, pp. 212-222, 2019
- III. K.P. Jonnalagadda, P. Zhang, M. Gupta, X-H. Li and R.L. Peng, “Hot Gas Corrosion and Its Influence On The Thermal Cycling Performance Of Suspension Plasma Spray TBCs”, Submitted and accepted for presentation at ASME Turbo Expo Conference, Phoenix, Arizona, USA, 2019
- IV. K.P. Jonnalagadda, R. Eriksson, R.L. Peng, X-H. Li and S. Johansson, “Factors Affecting the Performance of Thermal Barrier Coatings in the Presence of V_2O_5 and Na_2SO_4 ”, Journal of Ceramic Science and Technology, vol. 07, pp. 409-416, 2016
- V. K.P. Jonnalagadda, R. Eriksson, K. Yuan, X-H. Li, X. Ji, Y. Yu and R.L. Peng, “A study of damage evolution in high purity nano TBCs during thermal cycling: A fracture mechanics based modelling approach”, Journal of the European Ceramic Society, vol. 37, pp. 2889-2999, 2017
- VI. K.P. Jonnalagadda, R. Eriksson, K. Yuan, X-H. Li, X. Ji, Y. Yu and R.L. Peng, “Comparison of damage evolution during thermal cycling in a high purity nano and a conventional thermal barrier coating”, Surface & Coatings Technology, vol. 332, pp. 47-56, 2017
- VII. K.P. Jonnalagadda, R. Eriksson, X-H. Li and R.L. Peng, “Thermal Barrier Coatings: Life model development and validation”, Surface & Coatings Technology, <https://doi.org/10.1016/j.surfcoat.2019.01.117>
- VIII. K.P. Jonnalagadda, R. Eriksson, X-H. Li and R.L. Peng, “Fatigue life prediction of thermal barrier coatings using a simplified crack growth model”, Journal of the European Ceramic Society, vol. 39, pp. 1869-1876, 2019

Author's contribution: In all the above papers, I performed all analysis and testing except for: Mixed-gas corrosion tests (conducted at Swerea KIMAB, Sweden), Iso-thermal oxidation tests (conducted at Siemens Industrial Turbomachinery AB, Sweden). I was the main contributor to the manuscripts for all the articles.

Co-author Robert Eriksson wrote the basic modeling script used in the papers. V-VII. He also partly contributed to the basic model formulation used in paper. VIII along with Fig. 15, 16 used in this thesis. Robert Eriksson also contributed to Fig. 9a-e, 11a, 14a-b (in the paper. V), Fig. 11 (in the paper. VI), Fig. 1 (in the paper. VII) and Fig. 1 (in the paper. VIII). Co-author Pimin Zhang contributed to Fig. 7 and 12 (in the paper. III). All the other co-authors helped in discussions and editing the articles.

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- IX. S. Mahade, K.P. Jonnalagadda, N. Curry, X-H. Li, S. Björklund, N. Markocsan, P. Nylén and R.L. Peng, “Engineered architectures of gadolinium zirconate based thermal barrier coatings subjected to hot corrosion test”, *Surface & Coatings Technology*, vol. 328, pp. 361-370, 2017
- X. *R. Eriksson, Z. Chen and K.P. Jonnalagadda, “Bending fatigue of Thermal Barrier Coatings”, *Journal of Engineering Gas Turbines Power*, vol. 139, pp. 122101-122106, 2017
- XI. K.P. Jonnalagadda, K. Yuan, X-H. Li, X. Ji, Y. Yu and R.L. Peng, “Influence of Top Coat and Bond Coat Pre-Oxidation on the Corrosion Resistance of Thermal Barrier Coatings in the Presence of SO₂” from the proceedings of ASME Turbo Expo 2018: Turbomachinery Technical Conference and Exposition, Oslo, Norway, 2018
- XII. R. Eriksson and K.P. Jonnalagadda, “A Study on crack configurations in Thermal Barrier Coatings”, from the proceedings of ASME Turbo Expo 2017: Turbomachinery Technical Conference and Exposition, Charlotte, North Carolina, USA, 2017
- XIII. K. Yuan, K.P. Jonnalagadda, Y. Yu, R.L. Peng, X-H. Li, X. Ji and J. Shen, “Thermal fatigue of thermal barrier coatings with a high Cr-MCrAlY bond coat”, from the proceedings of International Thermal Spray Conference, Beijing, China, 2016
- XIV. K.P. Jonnalagadda, K. Yuan, X-H. Li, Y. Yu and R.L. Peng, “Modelling the diffusion of minor elements in different MCrAlY-Superalloy coating/substrates at high temperature”, In: Liu X. et al. (eds) *Energy Materials 2017. The Minerals, Metals & Materials Series*. Springer, Cham

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Acronyms

APS	Atmospheric Plasma Spray
BC	Bond Coat
CTE	Coefficient of Thermal Expansion
CMAS	Calcia-Magnesia-Alumino-Silicate
DGZ	Dense Gadolinium Zirconate
EB-PVD	Electron Beam Physical Vapor Deposition
EDS	Energy Dispersive X-ray Spectroscopy
FEM	Finite Element Method
GZ	Gadolinium Zirconate
HVAF	High-Velocity Air Fuel
HVOF	High-Velocity Oxy-Fuel
SEM	Scanning Electron Microscope
SPS	Suspension Plasma Spray
TBC	Thermal Barrier Coatings
TC	Top Coat
TCF	Thermal Cycling Fatigue
TGO	Thermally Grown Oxide
XRD	X-ray Diffraction
YSZ	Yttria-Stabilized Zirconia

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Part A

Background and Theory

1 Introduction

1.1 Background

World energy consumption, in million tonnes of oil equivalent, during the period 2000-2017 has increased by about 41 % [1] and is set to increase steadily in the future as a result of a growing population. The power sector is by far the single biggest market for energy consumption; absorbing over 40 % of primary energy in 2017 and is also the single most important source of carbon dioxide emissions (by combustion of fossil fuels), accounting for over a third of emissions in 2017 [2]. Electricity generated from non-renewable fossil fuels still accounts for a significant share (over 50%) in the global power generation [3]. The important question now to be asked is “how can we provide the energy service demanded by a growing population, yet reduce the total consumption from non-renewable energy sources?”. One of the solutions that have been suggested is to increase the energy conversion efficiency by technological advancements [4]. By this way, the power generation, to an extent, can become efficient in the near future.

Gas turbines, making use of non-renewable energy sources, for power generation and aero engines, have become both reliable and widespread in today's society. The global gas turbine market size is projected to reach USD 30.08 billion by 2025 [5]. The market growth is likely to be driven by technological advancements to meet the growing energy demands. In order to accomplish this, the turbines have to be operated at higher temperatures, and this puts an enormous demand on the high temperature properties of materials used in gas turbines. Furthermore, there is a significant interest in the use of alternative (sustainable) fuels such as bio-fuels [6]. Use of such fuels may also require stricter requirements (likely related to corrosion) on the materials. Furthermore, putting more demands on the fatigue properties of the materials is the increase in the frequent start and stop of gas turbines used in the power grids of solar energy and wind power.

The present research was started at Linköping University, Sweden, in close collaboration with Siemens Industrial Turbomachinery AB, Sweden, and Beijing General Research Institute of Mining and Metallurgy, China, to address partly the challenges faced by the gas turbine industry.

To improve the efficiency of gas turbines, thermal insulation of the components in the form of coatings is the most practical approach. In line with this, the objective of the present research is to provide the industry with new coating material systems along with their knowledge of failure mechanisms, new deposition processes along with optimizing the existing deposition processes, and provide appropriate life models for estimating the final failure.

A brief introduction to gas turbines, their applications and the need for coatings are discussed in the sections below. The introductory section in Part A is based on my licentiate thesis “Failure mechanisms in APS and SPS thermal barrier coatings during cyclic oxidation and hot corrosion” from 2017 [7].

1.2 Gas turbines

Gas turbines are used for two purposes: 1) as land-based gas turbines for generating electricity and driving machinery such as compressors for pumping natural gas, propellers for ships, etc. and 2) as aero-engines for powering aircraft. Based on the type of application the design might vary, but the overall operation principle remains the same. Land-based gas turbines are manufactured in different sizes ranging from low- to high-power generation. For instance, the gas turbines developed and manufactured by Siemens range from 4 MW to up to 567 MW. An illustration of a gas turbine is shown in Fig. 1.

Fig. 1 A Siemens land-based gas turbine showing the hot and cold sections. Courtesy of Siemens.

The gas turbine shown in Fig. 1 has three main sections:

- a. Compressor: Air from the atmosphere is sucked into the compressor where it gets compressed. The temperature in the compressor part of the gas turbine is low relative to the other two parts, and hence it is considered a cold section.
- b. Combustor: The combustor takes air from the exit of the compressor and delivers it to the turbine at a much higher temperature. The fuel in the combustor is injected into the compressed air through the burners. The inlet temperature of air in the combustion chamber ranges from 541 °C-614 °C for a low pressure regenerative

gas turbine and 686 °C-857 °C for a high pressure ratio gas turbine. Combustion chamber exit temperatures range from 927 °C-1593 °C [8].

- c. Turbine: The turbine inlet temperature is the same as the combustor exit temperature. Here the gases (at high temperature and pressure) expand along the turbine blades and rotate them changing the form of energy from heat to mechanical. The gases flow through different turbine stages and the first stage of the turbine, which is closest to the combustor, experiences the highest temperature. The mechanical energy from the turbines is converted into electrical energy by an electric generator. Alternatively, the energy can be used to drive a fan, and the high pressure of the gases at the exhaust provides thrust to propel an aircraft forward.

The thermal efficiency (η) of a gas turbine following an ideal Carnot cycle [9] is given by

$$\eta = 1 - \frac{T_{exit}}{T_{inlet}} \quad (1.1)$$

where T_{exit} and T_{inlet} represent the exit and the inlet temperatures of the turbine. Equation (1.1) shows that increasing the turbine inlet temperature increases the thermal efficiency of the gas turbine.

Increasing the inlet temperature of the turbine puts direct demand on the materials operating in the hot sections of the gas turbine where the temperatures can exist in the range of 1600 °C [8]. This temperature is above the melting point of the best performing materials in the gas turbines today such as Ni-based superalloys. Such high turbine inlet temperatures, therefore, are only possible through surface insulation and internal cooling. The insulation of turbine components from the hot gases is offered through **thermal barrier coatings**. Along with the use of coatings, part of the air from the compressor bypasses the combustor to cool the turbine components. However, the cooling schemes are limited to the amount of air that can be used without resulting in a drop in the thermal efficiency. As a rule of thumb, if more than 8% of the air is being used for cooling, the advantage of higher operating temperature is lost [8].

To further improve the efficiency of gas turbines (and thereby reducing emissions), there are two different approaches. 1) through improvements in the design of a new class of superalloys, and 2) improvement in the durability of thermal barrier coatings. Over the past few decades, there have been advancements in the development of superalloys for use in gas turbines, and this led to the increase in turbine operating temperatures [10,11]. Further significant improvements only through the advancements in superalloys are unlikely [11]. However, major advancements can be possible through the improvements in coating reliability and performance [11,12].

Improvements in the thermal barrier coatings can lead to higher operating temperatures. However, this also implies stricter requirements on the durability and performance of thermal barrier coatings as the coating failure will expose the underlying metallic components to much harsher environments. The main challenge now is in augmenting the durability of thermal barrier coatings while increasing the turbine inlet temperature. The emphasis is, then, on understanding the failure mechanisms of thermal barrier coatings and being able to predict their final failure which is the main

focus of the present research. The tools to predict the failure of thermal barrier coatings accurately, in the form of modeling, can provide the much required factor of safety while reducing conservatism during the part design.

1.3 Aim and scope

The main aim of the present research is to study and understand the failure mechanisms of thermal barrier coatings during **corrosion** and **thermal cycling** and to develop relevant **life models** for estimating the final failure during thermal cycling.

The failure mechanisms were studied on new coating materials in addition to yttria-stabilized zirconia (YSZ), the current industry standard. The new materials that were studied included gadolinium zirconate ($\text{Gd}_2\text{Zr}_2\text{O}_7$), a composite of gadolinium zirconate and yttria-stabilized zirconia ($\text{Gd}_2\text{Zr}_2\text{O}_7+\text{YSZ}$), and a high-purity nano YSZ.

Deposition techniques that were studied included, in addition to the conventional atmospheric plasma spray (APS), suspension plasma spray (SPS).

Thermal cycling tests were conducted at Linköping University with different maximum test temperatures while keeping the minimum test temperature to 100 °C. Corrosion tests were conducted at Linköping University, Linköping, Sweden (salt deposition) and at Swerea KIMAB, Stockholm, Sweden (mixed-gas type corrosion). Iso-thermal oxidation tests were conducted at Siemens Industrial Turbomachinery, Finspång, Sweden.

A previously developed life model was improved further to understand the damage development during thermal cycling tests. The model was validated by comparing with the experimental results. A new model was developed to address the limitations of the first model.

It is strongly believed that the results of this research, to a certain extent, can be employed during the design of thermal barrier coatings. Through extensive experimental investigation on the corrosion behavior of thermal barrier coatings, suitability of specific coating material and the deposition technique combination can be addressed. By being able to predict the life of TBC during thermal cycling, the suitability of a coating for different operating conditions can be assessed.

2 Thermal Barrier Coatings

Thermal barrier coatings (TBCs) are complex material systems that are being used in the hot sections of gas turbines [13,14] and also recently considered for diesel engines [15,16]. TBCs have a two-layered structure where the top coating layer (known as the top coat) is made of a low thermal conductivity ceramic and offers thermal insulation from the hot gases. Below the top coat is a metallic coating (known as the bond coat) that offers resistance against oxidation and corrosion at high temperatures. The bond coat is applied on the surface of the turbine component made of a Ni-based superalloy, referred to as the substrate. Together, they constitute the thermal barrier coating system. There is a fourth constituent of a TBC system, a thermally grown oxide (TGO). TGO is a reaction product that forms at the bond coat/top coat interface when the coating is exposed to high temperature. When exposed to high temperature, TGO growth occurs, and diffusion of elements in the bond coat to/from the substrate takes place resulting in a change of properties of the substrate and the bond coat. At the same time, the top coat microstructure also changes. These simultaneous changes make the TBC system complex to analyze as each change may affect the performance of the TBCs.

A typical microstructure of a TBC system, deposited by atmospheric plasma spray, along with the temperature distribution is given in Fig. 2. Each layer of the TBC is discussed in detail in the subsequent sections.

Fig. 2 Temperature gradient in a TBC system across different layers.

2.1 Materials in a TBC system

2.1.1 Top coat

The top layer in TBC offers thermal insulation against the hot gases in a gas turbine. It is not difficult to realize that the performance and integrity of the top coat are critical to the performance of the entire gas turbine as spallation of the top coat will expose the underlying turbine components to the hot gases. The top coat, together with internal cooling (circulating part of the air from the compressor exit through the internal channels of the turbine component), keep the temperature of the substrate low so that it does not lose its load bearing capability. The temperature drop in the top coat can be in the range of 100-300 °C for a coating thickness in the range of 0.1-0.5 mm [13]. Naturally, the material for the top coat should have a low thermal conductivity. The thermal expansion coefficient should be close to that of the substrate to reduce the stresses caused by thermal expansion mismatch. The material should also exhibit high temperature phase stability [17].

From a materials perspective, a lot of materials have been researched for the use as TBC top coats. Among them, yttria-stabilized zirconia (YSZ) is currently the industry standard. Yttria is added to zirconia to stabilize its phase at high temperature. Pure zirconia is allotropic. It exhibits a monoclinic structure up to 1170 °C, tetragonal structure in the temperature range of 1170-2370 °C and cubic structure up to its melting point at 2690 °C. The phase transformation of zirconia from tetragonal to monoclinic is martensitic and involves a 3-5 % volume increase [11]. This is sufficient to damage the mechanical integrity of the coating and is a serious concern. Yttria (Y_2O_3), when added to zirconia in the range of 7-8 wt. %, forms a non-transformable tetragonal prime (t') phase [18]. The phase diagram of zirconia-yttria is shown in Fig. 3. This phase is stable up to 1200 °C above which the zirconia partitions into yttria-poor tetragonal and yttria-rich cubic [19,20]. It has been observed that the non-transformable tetragonal prime phase has a higher toughness relative to the cubic phase and the reason has been attributed to the ferroelastic toughening mechanism [21]. The value for the optimal range of Y_2O_3 (6-8 wt. %) has been arrived at from the durability rig testing by Stecura [22].

Yttria-stabilized zirconia has several attractive properties such as low thermal conductivity and a high coefficient of thermal expansion [18,23]. It is thermo-chemically compatible with the protective thermally grown oxide (TGO). It exhibits a high fracture toughness of $\sim 2 \text{ MPa } \sqrt{\text{m}}$ [24,25]. All these features have made YSZ the preferred choice for top coat material in TBC applications for many decades. YSZ has a functional operation limit of about 1200 °C, and for better performance at higher temperatures, YSZ has to be substituted with other materials [26].

There are other limitations with YSZ such as sintering at high temperatures (which increases the thermal conductivity and the elastic modulus) and its susceptibility to attack from certain corrosive species such as vanadium. For any new materials to be

considered as the potential replacement for YSZ, there are many requirements the material has to satisfy with thermal conductivity being the foremost.

Fig. 3 Phase diagram of $\text{ZrO}_2\text{-Y}_2\text{O}_3$ system. Taken from Ref [27].

Before discussing other potential materials for TBC applications, it is worth to mention the recently developed nanostructured yttria-stabilized zirconia coatings. These nano-YSZ coatings get their name from the nano-structure of the powder. These coatings exhibit a bimodal structure formed from the re-solidification of the agglomerates that are fully melted in the plasma spray jet and from the incorporation of the semi-molten nano-structured agglomerated particles [28]. Published research on nano-YSZ based TBCs show that they exhibit better life during both thermal shock and thermal cycling tests compared to the conventional YSZ coatings [29–31]. Work by Lima and Marple showed that it is possible to design a nano-YSZ with better sintering resistance compared to conventional YSZ coatings [28]. Nano-YSZ coatings also exhibit superior corrosion resistance compared to conventional YSZ in the presence of $\text{Na}_2\text{SO}_4\text{+V}_2\text{O}_5$ [32].

Despite all the observed improvements that nano-YSZ TBCs offer over the conventional YSZ TBC, the research to further develop these coatings does not seem to be as intensive as the research focus in finding alternative materials for replacing YSZ. The possible reasons could be due to the upper operating limit of YSZ or that the properties exhibited by other potential TBC materials outweigh the advantages offered by nano-YSZ TBCs.

In the context of research on new top coat materials, several other oxides such as CaO, MgO, Sc_2O_3 , and CeO_2 have been tested, but none of these coatings satisfy the requirement of long term stability of the resulting oxide [17]. Recent research has been aimed towards pyrochlores of $\text{A}_2\text{B}_2\text{O}_7$ type [33,34]. Pyrochlores, such as $\text{Gd}_2\text{Zr}_2\text{O}_7$, exhibit better thermal insulation (lower thermal conductivity) compared to YSZ [35,36].

An understanding of the heat transfer mechanism in ceramics is important to understand the reason for the lower thermal conductivity in pyrochlores. Thermal energy, in general, is transported by electrons (only exist in pure metals), lattice waves (phonons) which exist in ceramics and metals (at low temperatures) and electromagnetic waves (photons) [37]. At temperatures below 1200 °C, phonon transport dominates the heat conduction through zirconia [38]. Phonon transport is directly proportional to the mean free path. Thus, the addition of yttria decreases the thermal conductivity of ZrO_2 considerably from pure zirconia [38]. The reduction is due to shortening of the intrinsic mean path, due to yttria addition, in zirconia by increasing the phonon scattering, introduction of vacancies and generation of local strain fields by the dopant atoms. In summary, introducing atomic-level defects due to the inclusion of atoms of differing mass, vacancies and interstitials can reduce the thermal conductivity of the top coat [38].

The low thermal conductivity in pyrochlores is due to phonon scattering by point defects. Two types of point defects are observed in these materials: 1) substitutional rare-earth solute cations (such as Gd) that replace zirconium and 2) oxygen vacancies created by the substitution of tetravalent zirconium by a trivalent rare-earth [35]. In the case of $\text{Gd}_2\text{Zr}_2\text{O}_7$, the phonon scattering by gadolinium solute cations is effective due to the high atomic number, Z , difference between Gd and Zr ($Z(\text{Gd}) = 157$, $Z(\text{Zr}) = 91$). Note that the phonon scattering due to the same point is much lower in YSZ due to the similar atomic numbers of yttrium and zirconium ($Z(\text{Zr}) = 91$, $Z(\text{Y}) = 89$). Additionally, in the case of $\text{Gd}_2\text{Zr}_2\text{O}_7$, there exists a significantly higher amount of oxygen vacancies as a result of 33 mol. % Gd_2O_3 in gadolinium zirconate. The above two factors, together, reduce the thermal conductivity of gadolinium zirconate significantly compared to YSZ [35].

The limitations of gadolinium zirconate are that it is thermo-chemically incompatible with alumina (the thermally grown oxide) [39] and it has a lower coefficient of thermal expansion (CTE) compared to YSZ [40]. This led to the development of multi-layered coatings which were proven to have a better life during thermal cycling than the single-layered TBCs [41,42]. Gadolinium zirconate is also known to have lower fracture toughness compared to YSZ [43,44]. This makes crack propagation easier in $\text{Gd}_2\text{Zr}_2\text{O}_7$. A novel approach that was developed is to blend

gadolinium zirconate and YSZ to make a composite of $\text{Gd}_2\text{Zr}_2\text{O}_7$ +YSZ. This composite has previously shown to have a lower susceptibility to corrosion damage, in the presence of Na_2SO_4 + V_2O_5 , compared to pure $\text{Gd}_2\text{Zr}_2\text{O}_7$ [45]. Other approaches to strengthening gadolinium zirconate include adding 3 mol. % nanostructured YSZ to $\text{Gd}_2\text{Zr}_2\text{O}_7$ to toughen the material. This material was deposited on top of 4.5 mol. % YSZ. This multi-layered coating exhibited more than a 3-fold increase in the thermal shock lifetime compared to a pure gadolinium zirconate layer [25].

2.1.2 Bond coat

While the top coat material, such as YSZ, provides the required thermal insulation, it is transparent to oxygen at high temperatures. Besides, due to the pores and the micro-cracks in the top coat (see section 2.2.1), the deposits of corrosive salts can melt and infiltrate the top coat and reach the substrate. The typical elements that offer corrosion and oxidation resistance at high temperatures such as aluminum (Al) and chromium (Cr), are generally not present in sufficient quantities in the substrate as higher amounts of Al and Cr will affect its creep strength [17]. For imparting the required oxidation and corrosion resistance, and as well as to improve the bonding between the top ceramic coat and the metallic substrate, a protective metallic coating, known as the bond coat, is deposited on top of the substrate.

One of the commonly used bond coats is of MCrAlX type, where M is Ni or Co or both and X is a reactive element (yttrium is used in a majority of the bond coats). A bond coat usually has about 6-12 wt. % Al and 17-30 wt. % Cr. Oxidation resistance offered by the bond coat is in the form of a protective oxide scale, alumina, that grows at the bond coat/top coat interface. The bond coat microstructure has two phases β and γ as shown in Fig. 4a. The β phase, NiAl, has an ordered body centered cubic (BCC) crystal structure and acts as an Al reservoir promoting the growth of alumina. γ phase is the matrix. It can be noted that the content of aluminum in the β phase is much higher than in the γ phase (see Fig. 4b).

2.1.3 Thermally grown oxide

Thermally grown oxide (TGO) is a reaction product that is formed at the bond coat/top coat interface when the TBCs are exposed to high temperature. The TGO is protective, offering resistance against both oxidation and corrosion. The required properties of such an oxide layer are that it should be dense, slow growing, have good adherence to the bond coat and be chemically compatible with the top coat material. Three types of oxides, alpha-alumina ($\alpha\text{-Al}_2\text{O}_3$), chromia (Cr_2O_3), and silica (SiO_2), are considered to meet these criteria [46]. In practice, most high temperature MCrAlX coatings rely on the formation of α -alumina as the protective oxide due to the limitations of the other two oxides. Chromia can form volatile oxides at high temperatures and in the case of silica, to form a silica scale, the amount of Si added to the coating needs to be relatively high.

Furthermore, silica diffuses fast into most alloys, and its interaction with the substrates may result in the formation of low-melting phases and/or brittle silicides [46].

Fig. 4 a) $\beta+\gamma$ microstructure in a NiCrAlY coating and **b)** Al content in the β and γ phase.

The alumina scale is dynamic in the sense that the layer grows by reacting with oxygen when the bond coat is exposed to high temperatures. In the initial stages of oxidation, the formation of transient oxides such as $\gamma\text{-Al}_2\text{O}_3$, $\delta\text{-Al}_2\text{O}_3$, and $\theta\text{-Al}_2\text{O}_3$ are observed containing a high concentration of cation vacancies. These transient oxides have a higher growth rate (in orders of magnitude) compared to $\alpha\text{-Al}_2\text{O}_3$ [47]. $\alpha\text{-Al}_2\text{O}_3$, on the other hand, due to the large band gap and high lattice energy, has an extremely low concentration of defects due to which it exhibits low diffusivity for cations and anions [48]. As a result, $\alpha\text{-Al}_2\text{O}_3$ has a low oxide growth rate making it the desirable oxide scale.

The increase of the alumina scale thickness (h_t) with time typically follows

$$h_t = Kt^n \quad (2.1)$$

where t is the time in hours, K is the oxide growth rate constant, and n is an exponent ($n \sim 0.25-0.5$).

The temperature dependence of the oxide growth rate constant follows an Arrhenius type relation [49]

$$K = K_0 e^{\frac{-Q}{RT}} \quad (2.2)$$

where K_o is a general growth constant, Q is the activation energy ($\frac{J}{mol}$), R is the gas constant ($\frac{J}{mol\ K}$), and T is the temperature (K).

During high temperature exposure TBCs are considered functional as long as the growing oxide scale is alumina. When a continuous alumina scale can no longer be formed or maintained, other non-protective oxides such as NiO, CoO, Cr₂O₃ and spinel (Co, Ni)(Cr, Al)₂O₄ are formed [50–53]. The growth rate of these oxides is higher compared to the growth rate of alumina [52] and will eventually result in the failure of the coating. A cross-section of a failed TBC with both the alumina and spinel is shown in Fig. 5.

Fig. 5 Cross-section of a TBC system showing the protective alumina (dark brown in the image) and spinels (in grey).

2.1.4 Substrate

Substrates, or base materials, are the actual turbine components on which the thermal barrier coatings are deposited. The function of the substrate is to provide the required mechanical, fatigue and creep properties for the application at high temperatures. Currently, Ni-based superalloys with more than 10-11 alloying elements are used as the base materials [9]. The strength for these alloys can either come from solution strengthening, as in the case of Hastelloy X, or through precipitation hardening, for instance, Inconel 792, by the formation of ordered FCC γ' . The type of alloying elements dictates the type of hardening mechanism. In general, precipitation hardened superalloys are commonly used in more demanding environments (where more severe thermal and mechanical loads exist) such as for a turbine blade material while solution strengthened alloys are used as combustion chamber materials.

2.2 TBC deposition techniques

The deposition technique for TBC is usually determined by the kind of component being coated such as atmospheric plasma spraying (APS) for combustion chamber, or electron beam physical vapor deposition (EB-PVD) for turbine blades. The main difference between these deposition techniques are the microstructures that can be obtained. APS coatings, in general, tend to have a horizontal splat-on-splat structure with the intersplat boundaries or delaminations roughly parallel to the top coat/bond coat interface. EB-PVD coatings possess a vertical columnar structure that has high strain tolerance. These strain tolerant coatings are capable of surviving for a longer time during cyclic oxidation [54,55]. The limitations of EB-PVD, such as high equipment cost and lack of widespread availability, partly led to the development of an alternative spraying

technique known as suspension plasma spray (SPS), using a liquid feedstock, capable of producing the columnar structure. Both APS and SPS processes are discussed below.

2.2.1 Atmospheric Plasma Spray

Atmospheric plasma spray (APS) makes use of a powder feedstock for deposition. The plasma is generated using a high-frequency direct current. The generated plasma is accelerated out of the nozzle, and the powder particles that are to be deposited are injected directly into the plasma. The particles are, thereafter, accelerated in the plasma flame where they can be molten or semi-molten and impact on the substrate. Due to the impact force, the molten droplets flatten and solidify to form the so-called “splats”. With the successive deposition of the particles, these splats build up and result in the formation of the coating.

Fig. 6 a) Top view of an APS YSZ coating [56], b) cross-section of an APS YSZ coating, and c) cross-section of an APS MCrAlY bond coat.

A typical microstructure of YSZ top coat and MCrAlY bond coat obtained by APS is shown in Fig. 6a-b and Fig. 6c. As can be seen from Fig. 6a, splat cracks are formed when the molten droplets solidify over the already solidified splats. Fig. 6b shows the inter-splat delaminations or boundaries and pores in the cross-section of the coating. A conventional YSZ coating deposited by APS contains about 10-15 % porosity. The function of these pores and inter-splat delaminations is to reduce the thermal conductivity of the material. Note that these delaminations are roughly horizontal and,

therefore, perpendicular to the direction of heat flow. Fig. 6c shows similar features in a bond coat.

The limitation with the APS process is the difficulty to make use of fine powder feedstock. Finely structured coatings (in nano-scales) have been shown to be beneficial for properties such as thermal diffusivity, high CTE and also exhibit better thermal shock resistance compared to conventional YSZ coatings [57,58]. Fine powder feedstocks do not have good flowability, causing blocking, and cannot achieve enough momentum to penetrate the high-velocity plasma stream. The carrier gas velocity needs to be increased to make the fine powders penetrable into the plasma flame. This, in turn, creates a disturbance in the plasma stream resulting in low coating deposition rates [59]. An alternative approach to this is to make use of a liquid feedstock [60].

2.2.2 Suspension Plasma Spray

The suspension plasma spray (SPS) process makes use of a liquid feedstock where sub-micron sized particles are dispersed into a solvent (either water or ethanol) to form a suspension. This suspension is later injected into the plasma flame where it is atomized into fine suspension droplets. The solvent from the droplets evaporates quickly, and the fine powder particles then get deposited with an impact on the substrate generating a fine structured coating [61].

Fig. 7 Cross-section of an SPS YSZ coating with a columnar structure.

The primary interest in such a spraying technique comes from its ability to generate both a vertical columnar microstructure and as well as a horizontal compact microstructure. Thermal conductivity values of SPS TBC coatings are shown to be lower than EB-PVD coatings in spite of having a columnar structure [62]. Furthermore, with control of the column compaction, SPS deposited coatings can achieve thermal conductivity values lower than that of APS deposited TBCs [62]. A microstructure, with vertical columns, generated by SPS is shown in Fig. 7. Note that only the top coat is

deposited by SPS. Further details about the SPS process and its limitations can be found in the Refs [63,64].

2.3 Advanced Ceramics and Environmental Barrier Coatings

Despite the widespread usage of YSZ as a top coat material it still faces the limitation of high temperature phase stability. Alternative materials to YSZ, such as pyrochlores, have shown promising results but lack the ferroelastic toughening mechanism that is observed in YSZ [65].

As an alternative to Ni-based superalloys and TBCs, a new class of materials, with inherent high temperature capabilities, are being developed. Ceramic matrix composites (CMCs) and environmental barrier coatings (EBCs) are being looked into as the next step in the evolution of superalloys and thermal barrier coatings. CMCs may, for example, comprise of a SiC-based matrix reinforced by SiC fibers with a moderately weak fiber/matrix interface [65].

Although CMC based components are capable of running at much higher temperatures (~ 1400 °C) compared to superalloys, they are still susceptible to active oxidation and recession in the presence of water vapor (reaction of water vapor with the protective silica scale on CMC results in the form of gaseous products which eventually causes a recession of CMCs). Due to the very high operating temperatures of CMCs, they also suffer from calcia-magnesia-alumino-silicate, collectively referred to as CMAS, degradation. For protecting the CMCs, a new class of coatings, environmental barrier coatings are used. These coatings are invariably multi-layered, similar to a TBC, with the first layer being the bond coat (currently, Si is widely considered as the bond coat material). The second layer is a dense, low-CTE EBC, where rare-earth silicates with various additions are considered. A third layer is also usually included to mitigate the CTE-mismatch strain. The fourth layer, having the function of a top coat, provides thermal insulation and resistance to CMAS degradation [65].

3 TBC Failure Mechanisms

The durability of thermal barrier coatings is crucial for gas turbines. Failure of TBCs can either induce critical damage or reduce the life of turbine components depending on the service temperature of the gas turbine. When TBCs are used for life extension, their failure will not cause catastrophic damage but shortens the life of the turbine component. If TBCs are incorporated into the design criteria of turbine components, their failure can cause critical damage to the turbine components.

TBC failure can occur in a multitude of ways depending on the TBC system and the service conditions. More than one failure mechanism can be active adding further complexity in making the performance study of TBCs difficult. The word “failure” in the context of thermal barrier coatings means that the coating is no longer able to satisfy its functional requirements. In general, when the top coat spalls off, then the TBC is no longer useful and considered to be failed. Spallation of the top coat can be due to thermal fatigue, corrosion or erosion.

3.1 Thermal Fatigue

Thermal fatigue refers to the damage caused by cyclic thermal stresses due to temperature changes. For a land-based gas turbine, this occurs due to the start and stop of the gas turbine. With a keen interest in operating the turbines at higher temperatures and as well as with an increase in the frequency of starting and stopping the gas turbines, thermal fatigue becomes very important. TBC degradation during thermal fatigue can occur due to a combination of different factors described below.

3.1.1 Mismatch in the coefficient of thermal expansion

Due to the difference in the coefficient of thermal expansion (CTE) between the coating, TGO, and the substrate thermal stresses occur in the TBC. The CTE of the top coat is about $10.7 \times 10^{-6} \text{ 1/K}$ [66], for TGO it is $8 \times 10^{-6} \text{ 1/K}$ [66] while for the substrate it is $16.6 \times 10^{-6} \text{ 1/K}$ [67]. Due to the thermal mismatch stresses, cracks can initiate and propagate at or near the TGO/top coat interface.

To study the failure due to CTE mismatch between the top coat and the substrate, thermal shock tests, also known as burner rig tests [68], are conducted. During such tests the heating and the cooling rates are much higher than the conventional thermal cycling tests and the dwell time at high temperature is very short. As a result, the TGO

growth is minimal, and hence the contribution to the failure during thermal shock tests mainly comes from the thermal stresses due to CTE mismatch between the coating and the substrate [69]. Conventional thermal cycling tests, also known as furnace cycling tests, are also widely used to study the thermal fatigue performance of TBCs. Here, the dwell times are much higher (usually range from 30 minutes to 1 hour) and the degradation is due to the CTE mismatch, sintering of the top coat, bond coat oxidation and inter-diffusion. A more detailed explanation of thermal cycling tests conducted in the present research is given in Chapter 5.

3.1.2 Sintering of top coat

Sintering refers to a process where the densification of material occurs by the closing of the pores and micro-cracks. APS TBCs have micro-cracks, fine pores and irregularly shaped pores from the deposition process that lower both the thermal conductivity and the elastic modulus. At high temperature, sintering of micro-cracks and fine pores occur [70] resulting in increased thermal conductivity and elastic modulus. Increased thermal conductivity is not desirable as the thermal gradient across the coating is reduced, and the coatings tend to lose their functionality.

Elastic modulus (stiffness) of the coating is dependent on both the micro-cracks and the porosity of the coating. The stiffness of the coating has a direct influence on the life of TBCs where coatings with a lower elastic modulus survive longer compared to coatings with a higher elastic modulus. Reported values of elastic modulus in the literature range from 10-60 GPa [30,66,71–79]. The reason for such a huge variation could be due to the use of different spraying parameters, powder size and also the measurement techniques. For instance, bending tests yield global stiffness (lower values) while the indentation tests give local stiffness (higher values) [78].

The increase of elastic modulus, due to sintering, has been observed to be rapid in the beginning and with increased exposure time the rate of increase of the elastic modulus slows down to eventually plateauing out [76,78,80,81]. This trend can be described by a linear function of the Larson-Miller parameter [82] taking the form

$$LMP = T \cdot (\log t + C_k) \quad (3.1)$$

$$E = m \cdot LMP + c \quad (3.2)$$

where LMP is the Larson-Miller parameter, T is the temperature (K), t is the time (hours), and C_k is a constant. C_k often takes a value of 20. E is the elastic modulus as a linear function of LMP , m and c are the slope and the intercept, respectively.

Another approach to describe the elastic modulus change due to sintering was presented by Zhu and Miller [83] and is given as

$$\frac{E_c - E_c^o}{E_c^{inf} - E_c^o} = C_E \left\{ 1 - e^{\left[\frac{-t}{\tau} \right]} \right\} \quad (3.3)$$

where E_c is the coating modulus at any given time t , E_c^o and E_c^{inf} are the coating modulus at the initial time and an infinitely long time, respectively; τ is the relaxation time, and C_E is a constant related to temperature and stress in the coating system.

3.1.3 Bond coat oxidation and inter-diffusion

Oxidation of the bond coat during high temperature exposure is also considered to be an important cause of TBC failure. During the high temperature dwell time in a TCF cycle, the bond coat is oxidized, and a thermally grown oxide layer grows at the bond coat/top coat interface. With prolonged exposure the thickness of the oxide layer increases. The stresses in the oxide layer are due to 1) growth stress as a result of conversion of a high-density metal into a low-density oxide, and 2) CTE mismatch between the coating layers and the TGO. The total residual stresses in the TGO is then the sum of the TGO growth stresses and the stresses due to CTE mismatch. The magnitude of the growth stresses for alumina at room temperature is approximately -1 GPa, and they constitute roughly 30% of the total residual stresses in the TGO [11]. Once the oxide layer reaches a critical value (generally considered in the range of 6-10 μm), the oxide layer spalls off together with the top coat, and this marks the end of the coating life.

It is also possible for the TBC to fail at lower TGO thickness, known as “chemical failure”. This occurs when the aluminum content in the bond coat is too low to support the continuous formation of α -alumina. α -alumina, then, is no longer the preferred oxide and other alloying elements in the bond coat such as Ni, Cr, Co start to oxidize forming spinels. The formation of spinel occurs either from the alloy or the decomposition of the alumina scale as given in reactions (a) and (b), taken from Ref. [84]. It should be noted that the formation of spinels marks the start of accelerated oxidation.

The alumina scale is thus replaced or, partially replaced, by a layer of chromia, NiO, CoO and (Ni, Co)(Cr, Al)₂O₄ [50–53,85]. Furthermore, without the protective oxide scale (α -Al₂O₃) the oxygen can diffuse deep into the bond coat resulting in internal oxidation [53]. On the other hand, it has been reported that the internal oxidation of bond coat, in APS TBCs, can result in the formation of “island-like” oxides which help in reducing the stresses at the coating interface [86]. An additional benefit of internal oxidation, as reported by Patterson et al. [87], is that the effective CTE of the bond coat is reduced (due to the presence of internal oxides) and thus the CTE mismatch between the YSZ and the bond coat is reduced, and thereby reducing the thermal stresses.

Another factor that contributes to the depletion of aluminum in the bond coat (apart from oxidation at the bond coat/top coat interface) is inter-diffusion. At high temperatures, due to the difference in the activities of Al in the bond coat and the substrate, Al diffuses from the coating into the substrate, a phenomenon known as inter-diffusion. Al activity in the coating is always higher than in the substrate as shown in Fig. 8 (the activity calculations were made in Thermo-Calc) and this difference will result in Al diffusing into the substrate. Inter-diffusion may be minimized by selecting the

substrate-coating system in such a way that the difference in their activities is minimal. It is important to note that faster Al-diffusion into the substrate will result in the depletion of Al inside the bond coat, and consequently result in the early formation of non-protective oxides. It has been shown that the thermal cycling fatigue life can be different for the same TBC top coat/bond coat system but on different substrates [88].

Apart from the Al-diffusion, diffusion of other elements between the coating and the substrate is also undesirable as the elements that give the functional properties for both the coating and the substrate tend to diffuse out. Outward diffusion of refractory elements from the substrate into the coating can change the TGO growth rate and reduce the oxidation resistance of the coating [89].

Fig. 8 Activity of Al in different commercial substrates (left) and MCrAlY coating systems (right).

3.2 Corrosion

Corrosion is one of the commonly occurring problems in gas turbines [90]. The source for the corrosive species can either come from the intake air, from the usage of low-grade fuel or ingestion of foreign particles which in their molten state can infiltrate the coating. Corrosion almost always occurs when the species are in their molten state. Corrosive species in their solid state are usually benign. Corrosion can destabilize the coating, cause accelerated oxidation or cause mechanical damage to the coating. Corrosion is further classified as type I and type II corrosion. Type I refers to corrosion that occurs above the melting point of the salt (800-950 °C). Type II refers to corrosion that occurs at lower temperatures (600-800 °C) [91]. Type II corrosion may also occur if the deposited salts form a eutectic mixture with the melting point of the eutectic being significantly lower than the individual constituents that form the mixture [11]. In the present work, depending on the location of the dominant damage, corrosion is differentiated into top coat and bond coat corrosion.

3.2.1 Top coat corrosion

Top coat corrosion can be caused due to the presence of vanadium pentoxide. Vanadium is present in the fuel and upon reaction with oxygen forms vanadium pentoxide (V_2O_5).

Additionally, NaCl from the intake air reacts with sulfur (from the fuel) and oxygen to form sodium sulfate (Na_2SO_4). Corrosive attack of either V_2O_5 or a mixture of Na_2SO_4 and V_2O_5 can be very severe. Pure Na_2SO_4 does not directly react with YSZ (the conventional top coat material), but its infiltration into pores and cracks may cause thermo-mechanical damage [92].

The reaction of vanadium pentoxide (V_2O_5) and sodium sulfate (Na_2SO_4) results in the formation of a low-melting eutectic, sodium metavanadate (NaVO_3). There has been considerable research done on the corrosion behavior of thermal barrier coatings in the presence of the above-mentioned salts [32,56,93–99]. The tests reported in the literature have been conducted from 700–1050 °C using different salt concentrations, with a majority of the tests focused on YSZ coatings. Limited research on the corrosion mechanism of other top coat materials such as gadolinium zirconate [94,95,100], ceria-stabilized zirconia [101–103], titania-stabilized zirconia [103], scandia and yttria co-stabilized zirconia [104] and zirconia-alumina [99] have been reported as well.

Fig. 9 SEM images of a) YVO_4 top view, b) cross-section of YVO_4 inside the micro-cracks, and c) EDS maps taken on (b).

The general corrosion mechanism at temperatures of 900 °C (and above) for YSZ thermal barrier coatings is that the V_2O_5 or NaVO_3 attack the zirconia stabilizer, yttria, and form yttrium orthovanadate (YVO_4). YVO_4 has a rod-like structure (see Fig. 9a). The molten salts infiltrate the coating through both the micro-cracks and pores and leach yttria from YSZ. SEM image of a coating cross-section showing the formation of YVO_4 , along with the EDS maps is given in Fig. 9b-c. Leaching of yttria will destabilize YSZ and result in the undesirable tetragonal to monoclinic phase transformation of zirconia and thus damaging the coating. Furthermore, there is also stress associated with YVO_4 formation which may contribute to the overall corrosion damage [105].

For suspension plasma spray (SPS) coatings, the columnar boundaries (the gaps between the vertical columns) act as active pathways for the molten salts. If the top coat material is reactive, like YSZ, the molten salts can be confined to the upper parts of the coating. If the top coat material instead has a low reactivity, as in the case of gadolinium zirconate, the boundaries between the columns can allow for extensive salt infiltration and the corrosion product, GdVO_4 , is formed between the columns. An example of such a scenario is shown in Fig. 10a where the low reactive gadolinium zirconate (abbreviated as GZ) allows for the infiltration of corrosive salts. An EDS map confirming the presence of vanadium between the columns is shown in Fig. 10b. The presence of such corrosion products can reduce the strain tolerance of SPS coatings and cause cracking in the coating.

Fig. 10 a) Molten salt infiltration in an SPS coating through the columnar gaps, and b) EDS map showing the presence of corrosion product (vanadium) in the columnar boundary [94].

At temperatures above $\sim 1200^\circ\text{C}$, the ceramic top coat can also be susceptible to damage by silicates from the atmosphere like dust, sand, volcanic ash and runway debris (for aero-engines). These silicates referred to as CMAS, when molten, penetrate deep into the top coat causing them to fail prematurely [106,107]. These deposits solidify as the temperature drops and the difference in the CTE between the CMAS and the coating results in the TBC degradation. The corrosion damage can be considered to be more mechanical in this case. SPS coatings are more susceptible to these molten silicates. An example of an SPS coating allowing the infiltration of molten silicates through both the columns and columnar boundaries (indicated by black arrows) is shown in Fig. 11. The infiltrated silicates are from 'Laki volcanic ash', Iceland, and the tests were conducted on a free-standing coating at 1250°C . A more detailed description of CMAS degradation, in general, can be found in Refs [108–110].

Fig. II An SEM image showing the infiltration of molten silicates in a free-standing gadolinium zirconate coating manufactured by SPS. Black arrows indicate molten silicate infiltration through the columnar boundaries. Courtesy of Satyapal Mahade.

3.2.2 Bond coat corrosion

Corrosion of the bond coat commonly occurs in the presence of sulfates and chlorides of sodium/potassium or sulfur gas. Sodium/potassium sulfates are formed due to the reaction between sodium/potassium chloride (salt constituents in the intake air [II]) and oxygen and sulfur (from the fuel).

The bond coat's resistance to corrosion comes from the addition of Al and Cr [II]. Corrosion attack first starts with initiation followed by propagation. During the initiation stage, the elements in the alloy are oxidized, and electrons are transferred from the metallic atoms to reducible species in the deposit [III]. The initial reducible species (oxygen) comes from sodium sulfate and the gas environment. As a result, the reaction product barrier, for instance, alumina, that is formed beneath the deposit often exhibits features similar to those for the gas-alloy reaction in the absence of deposit [III]. However, there are differences because sulfur is also present in this case. Sulfur enters the alloy from the deposit and due to this the composition of the deposit (sodium sulfate) adjacent to the alloy changes [III]. The molten deposit can now become more basic or more acidic compared to its initial condition, and this will affect the reaction product barrier. This barrier can be compromised leading to a situation where the liquid deposit has access to the alloy, and then the degradation proceeds to the propagation stage [III].

The propagation mode in hot corrosion depends on how the molten salt deposits damage the protective oxide scale. Two possible propagation modes are basic and acidic fluxing. Basic fluxing occurs when the oxide ions in the molten salt react with the protective oxide to form soluble species, and acidic fluxing involves the dissolution of the oxide by donating its oxide ions to the melt [III]. It has to be noted that for a sustained corrosion attack, a negative solubility gradient is required [II]. Another

propagation mode, sulfidation, includes the transfer of sulfur from Na₂SO₄ melt into the alloy and the subsequent oxidation of sulfur degrades the coating [112].

The corrosion mechanism can be different for different corrosive species as will be discussed below. Common test conditions reported in the literature include 1) a mixture of sodium sulfate (Na₂SO₄) and sodium chloride (NaCl) [113–116], 2) a mixture of sodium sulfate and potassium sulfate [117], and 3) salts in the presence of sulfur [117]. Corrosion tests in the presence of water vapor have also been reported [118]. Tests with these type of salts are primarily aimed at inducing corrosion in the bond coat, and the chosen test conditions are generally representative of the bond coat temperature during the service.

Although the majority of the published literature is on the salt mixtures, the discussion below is focused by isolating the influence of only one type of salt.

Corrosion in the presence of Na₂SO₄

Corrosion in the presence of Na₂SO₄ will be due to basic fluxing. At the onset of corrosion, the following reactions (c)-(d) occur.

Reaction (c) occurs in the molten salts, and it rapidly increases the concentration of oxygen ions. For bond coats with Al or Cr, the metal ions react with O²⁻ at the interface of the molten salt and coating forming, Al₂O₃ or Cr₂O₃ (reaction e) [119]. When the oxygen ions are in sufficient quantity, the basic dissolution in the fusant occurs (reaction f). This has been reported previously by other researchers [119,120].

Dissolution of the oxide scales will eventually consume Al (part of the aluminum can be lost due to inter-diffusion, see section 3.1.3) and alumina is reformed through the diffusion of aluminum to the interface. Once the continuous formation of alumina is no longer possible, the molten salts can penetrate the coating and degrade it [120,121].

Corrosion in the presence of NaCl

Sodium chloride's influence on corrosion can be understood by the reactions (g)-(k). The chloride ions react with oxygen and form oxide ions and in the process release chlorine (reaction g). The anti-corrosion element, for instance, Al, in the coating then reacts with chlorine to form aluminum chloride (see reaction h) [119].

The formed metal chlorides can react with SO₃ if present due to Na₂SO₄, (formed from reaction d),

Due to the low melting point of $Al.Al_yS_z$, the newly formed eutectics either evaporate or shrink during cooling, forming molten holes releasing chlorine in the process. Chlorine migrates into the coating and reacts with Al in the bond coat forming metal chlorides (reaction h) and waiting for further corrosion according to reaction (i). As the Al depletes over time, the concentration of Cr increases and the following reaction occurs (j) when the Cr concentration reaches a sufficiently high value.

Fig. 12 Backscatter SEM image of a suspension plasma spray thermal barrier coating in the presence of $Na_2SO_4 + NaCl$ at 900 °C. The black arrows indicate the internal oxidation close to the bond coat/top coat interface and the white arrows in the inset show the voids due to the volatilization of the metallic oxides due to the reaction with chlorine [122].

It has also been reported in the literature [114,123,124] that the MCl_x can volatilize into the interface of the salts/oxide scale. As a consequence of this, voids are formed inside the bond coat as illustrated in Fig. 12.

The main difference between reaction (i) and (k) is the fact that (i) occurs in or near the voids while (k) occurs at the interface of molten salts/oxide scale [119]. Cl_2 acts as a catalyst by repeating the reactions (i) or (k) or both and accelerate the corrosion damage [119]. It is considered that the corrosion damage is accelerated in the presence of sodium chloride compared to pure sodium sulfate [116,120,124].

Corrosion in the presence of a mixed-gas atmosphere containing SO_2

Data on the corrosion behavior of thermal barrier coatings in the presence of a mixed-gas atmosphere containing SO_2 are scarce. In the present research, this topic has been

studied. Atmospheric plasma spray TBCs were exposed to a mixed-gas atmosphere with the initial composition of $1\text{SO}_2\text{-}0.1\text{CO-}20\text{CO}_2\text{-N}_2$ (bal.) in vol. % at 780°C . The test conditions were based on the actual engine conditions of some Siemens gas turbines. Four different coating architectures were studied which included: 1) only bond coat, 2) bond coat + top coat, 3) bond coat (on all sides of the sample) + top coat, and 4) bond coat (on all sides of the sample) + pre-oxidized + top coat.

Fig. 13 Optical micrographs of TBC samples exposed to mixed-gas type corrosion for different coating architectures [125]. The black arrows represent nickel sulfide while the white arrows represent chromium oxides. Copyright by ASME, "Influence of top coat and bond coat pre-oxidation on the corrosion resistance of thermal barrier coatings in the presence of SO_2 ," by Krishna Praveen Jonnalagadda, Kang Yuan, Xin-Hai Li, Xiaojuan Ji, Yueguang Yu and Ru Lin Peng, Paper No. GT2018-76412.

Test results showed that the corrosion damage was severe at the coating edges with the formation of nickel sulfide where there was no bond coat protection. At the center of the coating, relatively mild corrosion was observed which consisted of chromium oxides/sulfides. It was also noted that having a top coat could restrict the growth of corrosion products close to the edges [125]. Having bond coat deposited on all the faces reduced the extent of corrosion, and also pre-oxidized samples showed better corrosion resistance than the non-pre-oxidized samples [125]. A summary of the test results is shown in Fig. 13.

3.2.3 Effect of bond coat corrosion on the TCF performance

The literature on the performance of corroded samples during thermal cycling is extremely limited while it is important to understand how the corrosive species inside the TBC influences the TCF performance. It has been established in the above sections that the presence of a corrosive salt or gas can result in the formation of non-protective oxides at the interface. Even though the corrosive attack may be minor, the influence of these oxides can be highly detrimental to the thermal cycling fatigue life of the TBCs.

Suspension plasma spray TBCs were exposed to two different kinds of corrosive conditions in the present work, $\text{Na}_2\text{SO}_4 + \text{NaCl}$ and mixed-gas type corrosion, to understand the influence of bond coat corrosion on the TCF performance. Both the test conditions and the results are discussed below.

Fig. 14 TCF life given as cycles to failure before and after corrosion.

Multi-layered suspension plasma spray TBCs (a single-layered YSZ, a double-layered GZ/YSZ, and a triple-layered dense GZ/GZ/YSZ) were exposed to a salt mixture of 75 wt. % $\text{Na}_2\text{SO}_4 + 25$ wt. % NaCl at 900 °C for 16h. The salt concentration was

6 mg/cm². After the exposure time of 16h, the samples were cooled down to room temperature inside the furnace. After cooling, the samples were visually inspected for damage and later exposed to the same salt mixture again before putting the samples inside the furnace. The process was repeated for nine corrosion cycles after which these samples were subjected to thermal cyclic fatigue tests between 100-1100 °C with a hold time of 1h at 1100 °C. The TCF life was then compared to the standard (non-exposed) samples, and the results are given in Fig. 14. After the corrosion tests, the difference in the TCF lives between different coatings became minimal.

As to further understand the influence of corrosion on the TCF life, corrosion tests on SPS YSZ TBCs were conducted at 780 °C for a period of 168h where the samples were exposed to a mixed-gas type atmosphere containing SO₂. Heating and cooling of the samples was done inside the furnace in the presence of the test gas. TBC samples after corrosion were subjected to TCF tests between 100-1100 °C with a 1h hold time at 1100 °C and compared with the TCF lives of the standard samples. Due to corrosion, about 61% drop in the TCF life was observed [126].

3.2.4 Approaches to prevent/reduce corrosion

Approaches to prevent or reduce the corrosion damage depends upon the type of salt and the operation temperature of TBCs. In general, fuel cleanliness is considered to influence the initiation and the propagation of corrosion attack [90]. The content of alkali metal, vanadium, and sulfur should be carefully controlled [127].

Additives such as MgO are added to the fuel to reduce top coat corrosion caused by vanadium. The effect of magnesia is to react preferentially with the vanadium pentoxide and form high melting vanadates [90]. It should be noted that some of the MgO is also converted to sulfate and, therefore, excess MgO is required to be added to the fuel. The typical ratio (by weight) to combat degradation due to vanadium is Mg/V~3 [11]. Other approaches include changing the material of the top coat (deposited by APS) from YSZ to, for instance, gadolinium zirconate, which was shown to exhibit better corrosion resistance in the presence of vanadium [95]. However, it has to be noted that the corrosion resistance can also be dependent on the microstructural features such as having a columnar structure (SPS) versus a horizontal splat on splat structure (APS). It has been observed, in the present research, that when SPS TBCs were exposed to salts containing vanadium, gadolinium zirconate, in fact, showed severe corrosion damage compared to SPS YSZ [94]. Furthermore, a composite of gadolinium zirconate and YSZ (in 1:1 weight ratio) has shown a better resistance compared to pure gadolinium zirconate [45].

For combating MCrAlY type bond coat corrosion, it is important to limit the level of Na in the air. A limiting level of 0.008 ppm (by weight) is suggested for the content of Na in the air, below which the hot corrosion will not exist [90]. Other approaches (on plasma-sprayed coatings) that were tried included the addition of oxides such as YSZ dispersed in a bond coat as YSZ is essentially inert in the presence of Na₂SO₄ + NaCl. However, it has been shown that such graded coatings with dispersed oxides are

detrimental to the corrosion resistance of bond coat. The increased degradation was attributed to the increase in the boundaries between the bond coat and the dispersed oxide which will act as active pathways for the molten salt infiltration [114]. Using a gradient coating enriched in Al has shown to improve the corrosion resistance of a NiCoCrAlY coating [121]. Additionally, pre-oxidizing the bond coat before exposure to the molten salts can improve the corrosion resistance [124].

For combating the corrosion in the presence of mixed-gases containing SO₂, it was observed that depositing the bond coat on all sides of the substrate and also pre-oxidizing the bond coat before the corrosion tests can help in reducing the corrosion damage [125].

3.3 Erosion and FOD

Erosion of the top coat occurs due to the impact of abrasive particles on the coating surface. Small particles usually cause erosion whereas large particles cause FOD (foreign object damage). These can accelerate the damage and reduce the life of TBCs.

4 Modeling

With increasing variations in the service conditions of gas turbines and increasing research on new coating materials as a substitute for YSZ, having a model that can predict the final failure is important. Relying only on the experimental data for understanding the failure mechanisms is both expensive and time intensive. Furthermore, models (for instance by using finite element methods) can provide important insights on a microscopic scale which is not possible to obtain through any other means. Finally, a successful model can help in reducing conservatism during the part design, and the capabilities of the TBC can be exploited to the fullest.

Since the failure of a TBC system can due to the simultaneous presence of different mechanisms described in chapter. 3, incorporating all of them into one universal model is not possible. Instead, the approach should be to focus on failure mechanisms that have more probability to co-occur. For instance, during a thermal cycling condition, the following co-occur 1) thermal mismatch, 2) TGO growth, and 3) sintering of the top coat. Models that address these failure mechanisms, either explicitly or implicitly, can be considered to be effective and have physical significance. From the point of usability, it is important that the TBC life models are easy to implement and have good accuracy.

Defects, in the form of crack-like delaminations, exist inside the ceramic top coat due to the nature of thermal spray deposition technique such as atmospheric plasma spraying [128,129]. Additionally, it is considered that the coating is in a stress-free state at high temperature. Stresses, then, are due to cooling of the coating to lower temperatures. These stresses, in turn, result in crack propagation. Stresses in the TBC can be influenced by several factors such as pores in the top coat, micro-cracks, bond coat/top coat interface roughness, TGO growth, internal oxidation of the bond coat, etc. At lower TGO thicknesses, the cracks propagate predominantly inside the top coat and, with increasing TGO thickness, the crack path changes to be closer to the top coat/TGO interface [130]. Internal oxidation of the bond coat can also change the TC/TGO interface undulation as well as the stresses [86,131]. A comprehensive study of interfacial stresses in TBC has been reported and reviewed by several researchers [86,131–145].

4.1 Status of TBC life models

There are many life models proposed so far based on the understanding of crack propagation mechanisms. A summary of those models is given in this section along with their limitations.

4.1.1 Stress-inversion theory

The stress-inversion theory is based on the stress state at the rough interface between the bond coat and the top coat. According to the theory, in the initial state of a TBC without the TGO layer, tensile stresses exist at the interface peaks while compressive stresses exist at the interface valleys. During thermal cycling, due to the TGO growth, stress-inversion occurs resulting in tensile stresses at the valley and compressive stresses at the peaks [146]. A crack starting from the TGO peak, will, therefore, propagate to the bordering valley as the TGO grows. This occurs at multiple locations in the coating and will eventually lead to coating spallation. It has been observed that a shorter time to stress-inversion is associated with a shorter TBC life [144]. Gupta et al. have shown that the stress-inversion theory model can be used to qualitatively rank coating lives during thermal cycling fatigue tests [138]. Other studies using stress-inversion to estimate the life of TBCs have also been reported [147,148].

The limitations of such a theory is that the theory only considers the interfacial roughness as the primary parameter for stress-inversion. Cracking inside the top coat may alter the stress state at the interface which is not accounted for by the stress-inversion theory [138]. Also, this theory does not account for the crack propagation path or in other words, does not give information about the failure location (for instance, if the failure is entirely inside the top coat or TGO or a mixed-type failure). The other limitation with this theory is that the formation of non-protective oxides (NiO, chromia, spinel) are not considered. These oxides are detrimental to the life of a TBC.

In the present work, an FE model on a realistic interface was used to study the stress-inversion effect on the crack propagation. It was observed that the stress-inversion did occur with an increase in the TGO thickness. However, the effective stress intensity factor did not change significantly, and it was concluded that the cracking in the valley region is unlikely to contribute to the TBC failure (via crack growth toward the valley). This effect is shown in Fig. 15 [149]. This further supports the argument that the stress-inversion, by itself, cannot be a reliable criterion to estimate the life of TBCs.

Fig. 15 The influence of TGO growth and additional roughness on a crack growing from the off-peak position toward the valley. Tensile maximum principal stresses (in $\text{N}/\mu\text{m}^2$) for TGO thicknesses of a) 2 μm , b) 4 μm , and c) 8 μm . The corresponding stress intensity factors are given in d) K_I , e) K_{II} , and f) K_{eff} . Note that the compressive stress is grayed out in all the images [149]. Copyright by ASME, “A Study on Crack Configurations in Thermal Barrier Coatings,” by Robert Eriksson and Krishna Praveen Jonnalagadda, Paper No. GT2017-63610.

4.1.2 Models based on Paris’ law type relation

Paris’ law, used widely to understand fatigue crack propagation, has the general form,

$$\frac{da}{dN} = C \Delta K^m \quad (4.1)$$

where a is the crack length, N is the number of cycles, K is the stress intensity factor, and C , m are the fitting parameters. Thermal cycling of TBCs result in micro-crack propagation, and Paris’ law type relation has been a base for the TBC life model [150–

[152] including the ones in the present work. The Paris' law relation was modified to account for mode-mixity. Bargraser et al. have used a relation similar to Paris' law to study the crack growth behavior for a steady-state growth of in-plane cracks in YSZ [153]. The relationship between the crack growth rate ($\frac{d\bar{a}}{dN}$) and the maximum effective crack length, $\bar{a}$, is expressed as

$$\frac{d\bar{a}}{dN} = B\bar{a}^m \quad (4.2)$$

where B and m are the empirical constants.

4.1.3 Other models

Wei et al. used the concept of critical localized interface height to width ratio and modeled the interfacial stress [154]. Their model considered the stresses due to the top coat sintering, thermal mismatch, and creep due to the TGO growth. Life prediction by the model showed a good agreement between the model and the experiment. However, the model did not consider the micro-crack growth paths. Additionally, the formation of non-protective oxides was not considered. Busso et al. have developed a software tool to predict the failure time of TBCs (for EB-PVD systems) where the failure is more likely to occur when the interface height to width ratio is higher [155].

4.2 The motivation for new TBC life models

In most of the published work on TBC life prediction models, the crack growth path was not considered. It can be possible for different TBC systems to have different crack growth paths which in turn will influence the damage development [128,151]. This is important as the crack growth path will eventually decide the location of the failure. In the present work, a fracture mechanics based life model was developed based on the model previously established by Brodin, Jinnestrand, and Sjöström [151,152,156]. The modeling approach and the limitations are discussed in section 4.2.1.

4.2.1 Micro-crack growth model

In this model, several pre-defined crack growth paths were considered as shown in Fig. 16 [149]. The model makes use of a Paris' law type equation for the crack growth and is given as

$$\frac{da}{dN} = C(K_{eff})^m \quad (4.3)$$

where $\frac{da}{dN}$ is the crack growth rate, C and m are the fitting parameters, and K_{eff} is the effective stress intensity factor taking into consideration mode I (K_I) and mode II (K_{II}) stress intensity factors. K_I and K_{II} were obtained through FE modeling in ABAQUS.

The crack growth rate was obtained by measuring the crack lengths from cross-sectional micrographs as a function of TCF cycles. The measured crack lengths were fit

to a distribution for obtaining the average crack length at different TCF cycles. This average crack length was later normalized using a characteristic length so that the damage is in the range of 0 to 1 (at failure). The crack length, a , is then replaced by a damage value, D , and the damage development per cycle is given by,

$$\frac{dD}{dN} = C(K_{eff})^m \quad (4.4)$$

Fig. 16 a-h showing different crack growth paths that could contribute to TBC failure [149]. Copyright by ASME, "A Study on Crack Configurations in Thermal Barrier Coatings," by Robert Eriksson and Krishna Praveen Jonnalagadda, Paper No. GT2017-63610.

The fitting parameters C and m are assumed to be temperature independent and were obtained by approximating a linear relation between $\frac{dD}{dN}$ and K_{eff} on a log-log scale. These were later used for predicting the TCF life at different temperatures. A more detailed description can be found in Ref [157]. This model accounted for the CTE mismatch, bond coat oxidation, and sintering of top coat.

Limitations of this modeling approach included 1) poor predictive capabilities at very high temperatures, and 2) the effect of hold time (an essential part for land-based gas turbines) could not be properly introduced. Formation of non-protective oxides was also not considered.

Another disadvantage of this model was that the crack length measurements were cumbersome and also depend on the operator doing the measurements. As an alternative to the crack length measurement, spallation data obtained through video monitoring was used to estimate the damage development and obtain the fitting parameters. Nevertheless, the above limitations remained and a new model was desired that is capable of addressing the limitations of the present model.

4.2.2 A simplified crack growth model

A simplified crack growth model based on the energy release rate, assuming a macro-crack growth, was developed in this work [158]. The requirements set for this model were that there should not be any FE implementation and no cumbersome crack length measurements. The model should be capable of including the hold time effect and also consider the influence of non-protective oxides along with alumina.

This model also makes use of the Paris' law type relation but the stress intensity factor was replaced by the energy release rate, G . The crack growth rate is then given by

$$\frac{da}{dN} = A \cdot G^B \quad (4.5)$$

where A and B are the fitting parameters, and G is the energy release rate. Through some assumptions and simplifications, the final relation as given in equation (4.6) can be obtained [158].

$$N_f = a_c \cdot G^{b_c} \quad (4.6)$$

where N_f is the TCF cycles to failure, and a_c , b_c are the fitting parameters, respectively.

5 Experiments and Characterization

This chapter discusses the details about experiments conducted in this research and the technique for sample preparation for subsequent characterization.

5.1 Experimental methods

5.1.1 Thermal cycling tests

Thermal cycling fatigue (TCF) tests are one of the most commonly conducted laboratory scale experiments for TBCs that are being used by both the academia and the industries. The TCF tests can provide a reliable estimate of the thermal fatigue life of TBCs. In this work, during the TCF tests, the samples are placed inside a furnace where they are thermally cycled between 100 and 1100 °C with a dwell time of 1h (in most cases) and 5h. Forced cooling to 100 °C takes place using compressed air in about 10 min.

During the TCF tests, the samples either move to the cooling stage where the compressed air cools them and the furnace remains stationary, or the furnace moves out, and the cooling system comes atop the ceramic plate and the samples are cooled. The latter setup has been used in the present research, and a schematic of the TCF test rig is illustrated in Fig. 17. The conventional way to assess the failure of thermal barrier coatings during TCF is identifying the cycle at which the visible damage in the top coat is ~20%.

Fig. 17 Schematic illustration of a thermal cycling test rig.

There are certain limitations with the TCF testing of thermal barrier coatings. The conditions during TCF are isothermal, i.e., the entire sample is at the same temperature. In contrast, thermal barrier coatings in a gas turbine are primarily designed to provide a thermal gradient. Ranjbar-Far et al. have shown that having a homogenous temperature may accelerate the failure and reduce the lifetime of the coatings [159]. It is also considered that the life of TBCs during thermal cycling, to a certain extent, is related to the TCF test rig.

5.1.2 Estimation of spallation data through video monitoring

Fig. 18 Illustration of the video camera set-up and the appearance of the samples during cooling as observed from the video camera.

Visual inspection of the samples by video monitoring, using a commercial grade video camera, can provide information on damage development during the TCF tests. A video camera is set up in such a way that during the start of each cooling cycle, the TCF furnace sends a signal directly to the camera to trigger an automatic recording for the first 29 seconds of the cooling cycle. Fig. 18 shows the appearance of the samples at the beginning of the cooling cycle and the position of the video camera.

The principle behind the damage detection is that the delaminated regions of the sample under inspection cool down faster compared to the regions that are still intact. Due to the faster cooling relative to the undamaged regions, the color of the coating appears grey where delamination has taken place. For the intact regions of the coating, the color will be bright red. In Fig. 18, from the sample image on the left, region 1 in grey indicates delamination. Region 2 indicates that the coating is still intact and 3 indicates spallation. The sample image to the right shows a perfectly intact coating at the center.

The damage observed from the video camera is then estimated by measuring the delaminated and the spalled regions as “damaged area” in pixels. Dividing this by the total area in pixels gives the accumulated damage development at that particular TCF cycle.

5.1.3 Corrosion tests

Three types of corrosion tests were conducted in this work 1) corrosion tests with salt mixture of vanadium pentoxide (V_2O_5) and sodium sulfate (Na_2SO_4), 2) corrosion tests with salt mixture of sodium sulfate (Na_2SO_4) and sodium chloride ($NaCl$), and 3) corrosion tests in the presence of mixed-gas containing SO_2 .

The first two tests with salt mixtures were conducted at Linköping University. The salt mixtures were weighed carefully and manually spread on the top coat surface. These samples were later put inside the furnace already pre-heated to the desired test temperature. After the high temperature exposure, the samples were removed and allowed to cool in the air. In the case of cyclic corrosion tests, the samples were visually inspected and photographed after reaching the minimum temperature. After that the salt mixture was spread again and the process was repeated.

Mixed-gas corrosion tests were conducted at Swerea KIMAB, Stockholm, Sweden. A tube furnace was used which had a provision for circulating the gas. The samples were placed on a horizontal ceramic plate and kept inside the tube furnace. The test gases enter from one end and exit from the other. Heating and cooling of the samples was done with the test gas. Furthermore, to minimize the risk of an oxidizing atmosphere, the furnace was purged with argon gas for 19h before the start of the tests.

5.2 Characterization

5.2.1 Sample preparation

Metallographic sample preparation for thermal barrier coatings is different from the sample preparation for metals. Preparing TBCs for microscopy analysis can be challenging due to the following reasons.

1. Particles from the ceramic layer, known as pull-outs, tend to come out of the coating and may scratch the surface. Apart from resulting in additional scratches to the sample, the main problem with the pull-outs is that they make the ceramic layer appear more porous than it is. As the coating properties are considered to depend significantly on porosity, inaccurate measurement of porosity can result in misinterpretation of the coating properties.
2. The interface between the thermally grown oxide (TGO) and the ceramic coating can be sensitive to damage after thermal cycling. Without proper care during sample polishing, the interface can be easily damaged, and it would be challenging to ascertain if the damage is either process/testing induced or if it is induced due to polishing.

The sample is infiltrated with a low viscosity epoxy resin under vacuum to mitigate the damage in the TBC system during polishing,. Epoxy infiltration, when correctly done, can infiltrate up to depths of 1500 μm (as observed in the present work). Epoxy infiltration into the cracks and pores can reduce the extent of damage during both grinding and polishing. Additionally, any damage introduced during the specimen preparation can be easily identified as there would be no epoxy in those effected areas.

After epoxy infiltration, the samples are cut to reveal the cross-section. Rough grinding is carried out initially to remove any effects of cutting. Rough grinding is done with discs of grit sizes 120, 220 and 500/600. Fine grinding is later carried out with diamond abrasives of sizes 15 μm , 9 μm , 6 μm , 3 μm , 1 μm , and 0.25 μm . Final polishing is done with colloidal silica suspension. The samples were later sputtered with carbon to reduce the charging of ceramic. This is required for the subsequent analysis in the scanning electron microscope.

5.2.2 Porosity measurement

Porosity has a pronounced influence on several coating properties such as thermal conductivity [160], elastic modulus [161], fracture toughness, etc. Accurate measurement of porosity is thus essential to understand the behavior of the coatings. For porosity measurements, an image analysis software, ImageJ [162] was used.

Fig. 19 optical micrograph showing the cross-section of top coat with epoxy filled pores and pull-outs.

To distinguish the actual pores from the pull-outs optical microscopy was used. Regular pores appear “with a tint of green” under an optical microscope after the epoxy infiltration. This is illustrated in Fig. 19. As pull-outs are caused due to polishing, they appear black. For porosity measurement with image analysis, good contrast between the ceramic coating and the epoxy filled pore is essential. Although the optical microscope can be useful in identifying the regions with minimal or no pull-outs, an SEM can provide good contrast between the pores (carbon) and the ceramic material due to the large difference in the atomic number between them. Using a threshold algorithm in ImageJ, the area of regions that appear black (pores) and bright (ceramic) is measured, and the area fraction gives an estimate of the porosity. At least 25-30 SEM images need to be taken to get a reliable estimate of the porosity.

Other methods to measure porosity include water impregnation, mercury porosimetry, and point counting. In water impregnation technique, a free-standing coating is immersed in water under vacuum to allow infiltration of water into the pores. Measuring the weight of the coating before and after immersion can give an estimate of the coating porosity [163]. In mercury porosimetry technique, a free-standing coating in the vacuum is infiltrated with mercury through the application of external pressure. Total porosity can be estimated by the total amount of mercury infiltrated into the coating [164]. In the point-counting method, a test grid is superimposed over the micrograph, and the number of test points falling within the constituent of interest is counted and divided by the total number of grid points yielding a point fraction [165].

6 Summary of appended papers

The objective of the present work, as stated in the chapter. I, is to provide the industry with new coating systems, new deposition processes along with optimizing the existing deposition processes and provide lifing tools. Different combinations of coating materials and deposition processes were tried. The obtained coating systems were evaluated for corrosion resistance under different conditions. Also, tangentially, life models capable of predicting the fatigue life during thermal cycling were developed. This chapter, based on the appended papers, will focus on the two important aspects of this work: corrosion and modeling.

6.1 Corrosion

Corrosion is one of the commonly observed failure mechanisms during the operation of a land-based gas turbine. In this work, corrosion of thermal barrier coatings under different conditions were evaluated using both suspension plasma spray and atmospheric plasma spray TBCs.

From paper I, To evaluate the resistance of SPS TBCs to a salt mixture of $V_2O_5+Na_2SO_4$, corrosion tests were conducted on a single-layered YSZ, double-layered $Gd_2Zr_2O_7/YSZ$ and a triple-layered dense $Gd_2Zr_2O_7/Gd_2Zr_2O_7/YSZ$. Tests were conducted at 900 °C for 8h with a salt concentration of 6 mg/cm². The test results showed that due to the higher reactivity of yttria (in YSZ) with the molten salts, they were immobilized at the upper portions of the coating. Also, the corrosive product YVO_4 was observed inside the pores. For $Gd_2Zr_2O_7$ based coatings, due to the lower reactivity of the corrosive salts with Gd_2O_3 , deeper penetration of the molten salts was observed, and the corrosive product was formed between the columns (in the column boundaries).

Severe corrosion induced damage was observed in gadolinium zirconate based coatings, and the reason was attributed to the combination of both material and microstructure. A low reactivity material allowed for extensive salt infiltration through the columnar gaps (boundaries between columns). As the corrosive products filled the columnar gaps, the strain tolerance of the coatings was reduced. Also, the lower fracture toughness of $Gd_2Zr_2O_7$ allowed for easy crack propagation compared to YSZ. The results highlighted the importance of a suitable combination of material and microstructure for having good resistance against corrosive salts [94].

From paper II, As a continuation to understand the corrosion behavior of the bond coat (with SPS deposited top coat), salt mixture of Na_2SO_4+NaCl was used. Cyclic

corrosion tests were conducted between 25 °C and 900 °C using a salt concentration of 6 mg/cm² for every cycle. To improve the fracture toughness of Gd₂Zr₂O₇, it was blended with YSZ (in 1:1 wt. ratio) to make a composite of Gd₂Zr₂O₇+YSZ. Additionally, a dense GZ layer was deposited on top of the composite of Gd₂Zr₂O₇+YSZ as a sealing layer to see if it reduced the corrosion damage. The bottom layer was YSZ for both the TBCs. Test results showed that severe bond coat degradation had occurred for both the double- and the triple-layered TBCs. However, the extent of damage was relatively higher for the triple-layered TBC compared to the double-layered TBC. The reason for the relatively higher damage was attributed to the following: The top coat material, either the composite of gadolinium zirconate and YSZ or the standard gadolinium zirconate, was inert to the molten salts. Having a sealing layer in this situation meant fewer infiltration channels for the molten salts. As a result, salts overflowed to the sample edges' (where there was no protection) and led to damage development from the edge. This study suggested that an inert sealing layer may not improve the corrosion resistance of the TBC and may, in fact, increase the damage [122].

From paper III, As a continuation to understand the corrosion performance of SPS coatings, SPS YSZ TBCs were exposed to a mixed-gas containing atmosphere (ISO₂-0.1CO-20CO₂-N₂(bal.) in vol. %) at 780 °C for a period of 168h. Due to the reaction of the gases with the substrate (in this case Hastelloy X), nickel sulfide was formed which later grew from the side and infiltrated the top coat through the columnar gaps. Additionally, due to the reaction of the gas with the bond coat, chromium oxides, chromium sulfides, and alumina were formed at the bond coat/top coat interface and also inside the top coat (chromium oxides). These corrosion exposed samples were later subjected to thermal cyclic tests between 100-1100 °C with a 1h hold time at 1100 °C. These samples were compared with the standard (non-exposed) TBC samples. TCF test comparison showed that the corrosion exposed samples suffered a significant loss in the TCF life (~61%). The reason for the decrease in the TCF life for corrosion exposed samples was attributed to three factors 1) presence of chromium oxides inside the top coat's columnar gaps can reduce the strain tolerance, 2) CTE mismatch between the chromium oxide and the YSZ top coat which can lead to additional stresses and accelerate the failure, and 3) a fast-growing alumina [126].

From paper IV, To study the influence of corrosive salt mixtures of V₂O₅+Na₂SO₄ on APS TBCs, a thin (relatively dense) TBC and a thick (porous) TBC were subjected to corrosion tests at 750 °C and 900 °C for 8h. Salt concentrations of 4, 10 and 20 mg/cm² were used. Corrosion test results showed that a thick and porous coating exhibited lower corrosion resistance at all temperatures and salt concentrations. For a thin TBC coating, it was found that a combination of high salt concentration (20 mg/cm²) and low temperature (750 °C) resulted in the highest corrosion damage. The reason for such an observation was that at 750 °C the salts reacted directly with zirconia forming Zr₂V₂O₇, a meta-stable phase, which subsequently decomposed into monoclinic zirconia. At 900 °C, this meta-stable phase was absent and the salts only reacted with the zirconia stabilizer, yttria [56].

6.2 Modeling

Two TBC life models were developed in this work. The first one was a fracture mechanics based model making use of a Paris' law type relation and micro-crack length measurements. This model was developed to account for different crack growth paths that can be observed in a TBC system during thermal cycling. A second model was later developed to address the limitations of the first model.

From paper V, Different crack growth paths that could be possible during the TCF tests were modeled in ABAQUS and the stress intensity factors were calculated. It was observed that as long as a crack propagated inside the top coat, the stress intensity factor remained low. Once the crack started to propagate along the TGO/top coat interface, the stress intensity factor increased. Experimental investigation of the TBCs through TCF tests showed that the failure occurred partly in the top coat and partly in the TGO. This meant that the crack propagation path completely inside the top coat could be excluded. Of the remaining crack growth paths, cracks that start along the TGO/top coat interface and later kink out into the top coat showed a damage development curve that was rapid in the beginning and slowed toward the end of the coatings' life. For a crack starting inside the top coat and later growing along the TGO/top coat interface, the observed damage development curve was the opposite. Through extensive microstructural investigations and crack length measurements, the crack growth path that was closest to the experimental observations was selected [128].

From paper VI, As a next step, the model was used for understanding the difference in the TCF lives between two different samples. A high purity nano TBC and a standard TBC were both subjected to standard thermal cycling conditions. It was observed that the standard TBCs exhibited a significantly higher TCF life compared to the high purity nano TBC. The failure type was similar in both the TBC systems (a mixed-type failure). Both the TBC systems were modeled to explain the difference in the TCF life. It was observed that the high purity nano TBCs had higher stress intensity factors compared to the standard TBCs. This was due to the lower porosity in high purity nano TBC (higher elastic modulus) compared to the standard TBCs. Although the difference in the stress intensity factors was small it was believed to have prolonged the TCF life of standard TBCs by a few hundred cycles [166].

From paper VII, As a final step, the model was used for predicting the TCF life at different temperatures for the standard TBC system. Change in elastic modulus due to sintering of the top coat at different temperatures was assumed to be a linear function of the Larson-miller parameter. Bond coat oxidation and CTE mismatch between different layers were also considered. At first, the fitting parameters to the Paris' law type equation were obtained using the micro-crack length measurements at 1100 °C. These parameters, assumed to be only material dependent and independent of temperature, were used for predicting the TCF life at temperatures of 1050 °C and 1150 °C. The predictive capabilities were reasonably good at 1050 °C and 1100 °C while the model showed a poor prediction at 1150 °C.

In the same work, as an alternative to the crack length measurements, spallation data obtained through video monitoring was used to obtain the fitting parameters. The advantage of this approach was that the cumbersome crack length measurements could be avoided and the estimation of spallation data is a simple and straightforward approach. Also, multiple samples can be continuously monitored at the same time. The fitting parameters obtained through video camera monitoring were reasonably similar to the ones obtained from micro-crack length measurements. A limitation of video monitoring approach was that it is only valid for one crack growth type, i.e. for cracks growing initially in the top coat and later along the TGO/top coat interface.

The predictive capabilities of the model through the video monitoring approach appeared to be similar to the approach by micro-crack length measurements. Nevertheless, the limitations of the model persisted, i.e., the poor prediction at 1150 °C [157]. Other limitations of this modeling approach were that the hold time effect could not be properly introduced and also the influence of non-protective oxides (chromia, nickel oxide, and spinels) were not included. Further improvements to this micro-crack length model were not possible, and hence a new model was desired to be developed that could address the limitations of the current model and at the same time simplify the implementation procedure on real coated components.

From paper VIII, A new model based on the energy release rate, assuming a macro-crack growth, was developed. The main advantage of this model is its ease of implementation, and it also addressed the limitations of the previous model. The model assumes that the entire strain energy of the top coat and the TGO contributes to the TBC failure. A direct relation (starting from the familiar Paris' law type equation) between the number of cycles to failure and the energy release rate was established. A simple linear correlation between the maximum crack length (observed through cross-sectional micrographs) and the fraction of spallation was shown. Since the fraction of spallation at failure is generally user defined and held constant, the requirement for crack length measurements was removed.

Two TCF life data points at different temperatures were used to obtain the fitting parameters for this model, and a failure curve was obtained. Model predictions at different temperatures and hold times were done and compared with the experimental data. Very good predictive capabilities of the model at different temperatures and hold times were observed.

The hold time effect on the TCF cycles to failure is an important part for a land-based gas turbine. To study this further, TCF lives published in the literature were plotted on a log-log scale of cycles to failure versus hold time. It was observed that there exists a power law relation between the cycles to failure and the hold time. This became a linear relation on a log-log scale. The slopes of all such curves (plotted from literature) were observed to be similar. This led to the conclusion that any model that could have a linear relation on a log-log scale and have slope similar to the ones from the literature can be considered to capture the hold time influence effectively. The model was then used to predict the cycles to failure for several random hold times, and it was observed that the model could capture the hold time influence well for up to 50 h [158].

7 Future work

This thesis is partly focused on developing fatigue life models capable of predicting the final failure. Next step should be to implement this model on an actual turbine component like the combustion chamber. Further work could be to expand the model to include other TBC systems such as EB-PVD and SPS.

For corrosion, further work could be to understand the influence of column compaction in an SPS coating on the corrosion resistance so that more durable coatings can be designed.

8 Bibliography

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Part B

Appended papers

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