Strategies for the Development of Environmental Barrier Coatings for High Temperature Applications

A. Nöth, J. Maier, J. Vogt, F. Raether

Ceramic coatings provide an excellent protection of components, which are applied in harsh environments. They can withstand high temperatures and corrosive media and form an excellent barrier against reactive molecules and heat. Due to complex requirements, multiphase and multilayer coating systems are developed. A systematic approach for material selection as well as microstructure-, layer- and process design is required to achieve optimum performance of the coatings. This approach is outlined in the present paper. It is demonstrated in the development of an environmental barrier coating system.

Introduction

During the past 50 years, gas turbines were the most important driver for the development of high-performance coatings. Since their efficiency increases with operating temperature, sophisticated metallic materials (e.g. nickel-based super-alloys) and Thermal Barrier Coatings (TBC) were developed since the 1990ies – allowing gas temperatures significantly higher than 1000 °C. In the last decade, operating temperatures could be further increased by substituting metallic parts by Ceramic Matrix Composites (CMC) in the hottest parts of gas turbines [1]. CMC are ceramic materials with a reinforcement component, typically a ceramic fiber, which can be used at high thermal and mechanical loads [2]. Thereupon, the performance of the protective coatings had to be further improved by the development of systems providing a diffusion barrier against hot gas corrosion [3, 4]. These so called Environmental Barrier Coatings (EBC) have to be carefully adapted to the substrate material, which can be a metal, a monolithic ceramic or a CMC. Besides stationary and aircraft gas turbines, a multitude of applications for EBC exist, e.g. in thermal and chemical processing and concentrated solar power technologies [2, 5–7].

Since there is not a single coating material that can fulfill all the requirements, EBC systems are typically layered composites comprising at least a bond coat and a top coat. Current EBC systems for CMC comprise a silicon bond coat, a mullite-based intermediate layer and a rare earth silicate as top coat. For more details on the various EBC systems, the reader is referred to some excellent review papers [8–10]. There are five key requirements the EBC must fulfill to increase the lifetime of high temperature components:

(1) Control of thermal stresses

If the difference in coefficients of thermal expansion (CTE) between the different EBC layers and the substrate is too large, high stress levels arise in the CMC under thermal cycling [11, 12]. This can lead to cracking or delamination of the EBC system. There is an important aspect that is often not considered: the stress states in the EBC are of dynamic nature [13], if temperature gradients occur during fast temperature changes. These temperature gradients are controlled by the heat transfer properties of coatings and substrate and the design of the cooling system.

(2) Phase stability of EBC materials

Phase transformations are in most cases associated with volume and shape changes of the material. This leads to the generation of stresses and can cause cracks, delamination or pore formation [14]. Thus, EBC materials should exhibit no phase transformations up to the application temperature.

(3) Chemical compatibility between EBC layers and substrate

There should be no "negative interactions" between the different EBC layers or the substrate material [9]. Examples for "negative interactions" are chemical reactions that lead to the formation of gases, pores, melts or the appearance of phases prone to corrosion. If this happens, there is a risk of failure of the EBC system. Moreover, the chemical compatibility is also an important factor to achieve good adhesion between the different EBC layers and the substrate.

(4) Environmental durability

The different EBC materials need to show high durability under use conditions. In

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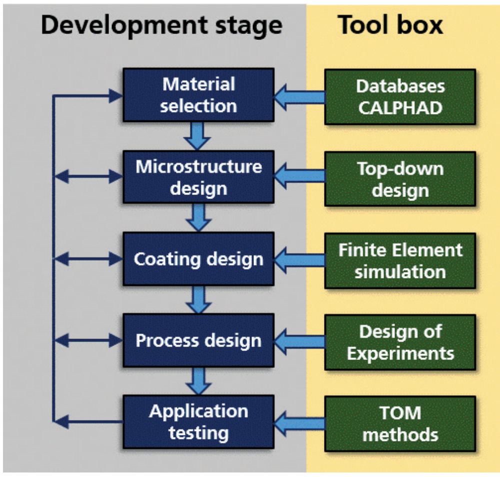

Fig. 1 Stages during EBC development including feedback loops and systematic tools

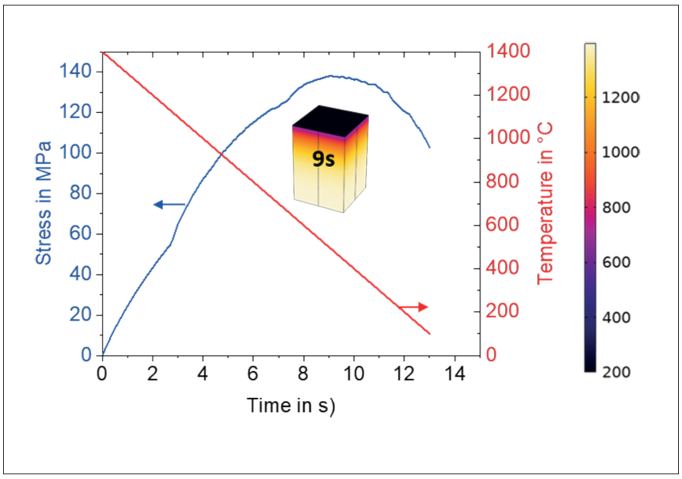

Fig. 2 Tensile stresses in the top coat of a 40 mm thick section of a SiC ceramic coated with a mullite bond coat (thickness: 0,24 mm) and a Y_2O_3–SiO_2–Al_2O_3 top coat (thickness: 0,1 mm) during fast cooling (100 K/s). Maximum stresses occur after 9 s, the temperature distribution is shown as an insert

most cases, high durability means a high resistance to corrosion and in some cases also abrasion and erosion. The specific requirements depend a lot on the use case. In aero-engines for example, the harsh conditions are primarily due to the combination of high temperature, high gas velocity, steam environment and the ingestion of dust particles during flight triggering the occurrence of debris and highly corrosive melts [8, 9, 13, 15, 16].

(5) Thermal protection

In many cases, EBC layers also provide a thermal barrier between environment and substrate, meaning they are simultaneously EBC and TBC systems. The latter requires a low through plane thermal conductivity. However, there is a trade-off between small temperature gradients during thermal cycling, required for stress control (compare item 1), on the one hand and small thermal conductivity, required for thermal protection of the substrate, on the other hand. If low emissivity coatings are used as a top layer in an EBC/TBC system, both the temperature gradient and the heat flow are reduced and the conflict is mitigated.

In this paper, the authors describe strategies and tools used at Fraunhofer-Center HTL to develop EBC systems efficiently. The paper starts with theoretical considerations to identify potential EBC materials that fulfill the above-mentioned requirements followed by an experimental material screening. Then a slurry-based coating technology and the development of a specific EBC system for SiC-based ceramics are described. Moreover, the possibilities offered by innovative characterization methods for the testing of EBC systems are illustrated.

Strategies and tools for EBC development

As outlined in the previous section, EBC systems often consist of several layers, and the individual layers contain several solid phases and pores or cracks. A careful material design is required to reduce the experimental effort in coating development. The principal steps are shown in Fig. 1. First, a selection of appropriate materials is required to ensure thermodynamic stability and mutual compatibility. Thermodynamic databases and CALPHAD methods provide valuable information on the respective phase diagrams and possible reactions [17]. However, data is often missing for rare ceramic phases. Methods are developed to fill this gap by training Artificial Intelligence (AI) algorithms by correlating other easily available material data with existing thermodynamic data [18].

Other important properties of the selected phases are the coefficient of thermal expansion, the elastic moduli (especially the in-plane Young's modulus) and the through-plane thermal conductivity. These data can often be extracted from material databases [19]. Otherwise, they have to be measured at operating temperatures [20]. Material indices are used to define selection criteria if conflicting attributes occur [21].

The material properties of individual layers are calculated from the properties and the arrangement of the contributing phases by microstructure-property simulations. Using appropriate structure generators and Finite Element (FE) methods, a high precision is already obtained by these methods [22]. Moreover, methods for a top-down design of microstructures for preset properties have recently been developed [23]. So, the overall material properties of individual layers are predicted without the need of their synthesis in the lab.

Next, the coating system and the substrate are simulated in a FE model. Thermal loads are applied, according to the operating requirements, and the resulting stresses are calculated. If these stresses are unacceptable, other microstructures and compositions are considered, until a promising system has been identified. Fig. 2 shows as an example the calculated thermal stresses in the bi-layer EBC described in the next section.

Last but not least, processing of the coating system has to be designed. At this stage, cost issues are also considered.

The state-of-the-art deposition technology for EBC coatings is Atmospheric Plasma Spraying (APS). With APS, the feedstock material is injected through a plasma at high velocity, where it is (partially) molten to form droplets of micrometer size. The droplets are sprayed on the substrate, where they solidify on the surface. With APS, a large variety of different material types can be deposited with a high deposition rate. However, coatings are often porous or cracked, can contain residual amorphous material and control of the microstructure of the coatings is limited. APS is a line-of-sight method with large overspray and difficulties to coat complex-shaped parts. Moreover, the equipment and its operation are rather expensive. As an alternative to APS, we developed a slurry-based deposition technique for EBC. The slurries can be applied to the substrates by spraying, brushing or dipping, which also enables the coating of complexed-shaped parts (Fig. 3). At this stage, the coatings can be machined by simple tools, if necessary. After deposition, the coatings are sintered in a furnace to densify and to form a strong bonding to the substrate.

The slurries can be designed to achieve a high-packing density of the coatings without cracks. Thicknesses of up to 200 μm are possible in a single coating step. The slurry deposition technology also offers a large flexibility in the design and control of the microstructure of the coatings. This includes grain size and shape as well as the pore structure, if needed. Multiphase-composite coatings can be designed to tune the properties of the coatings. Moreover, the technology is rather simple, it is easy to implement, cost-efficient in operation and needs only low investments. During process development, Design of Experiments (DOE) is very helpful to reduce the experimental effort. In the next section, the development process is illustrated by means of an EBC system for high temperature use of SiC ceramics.

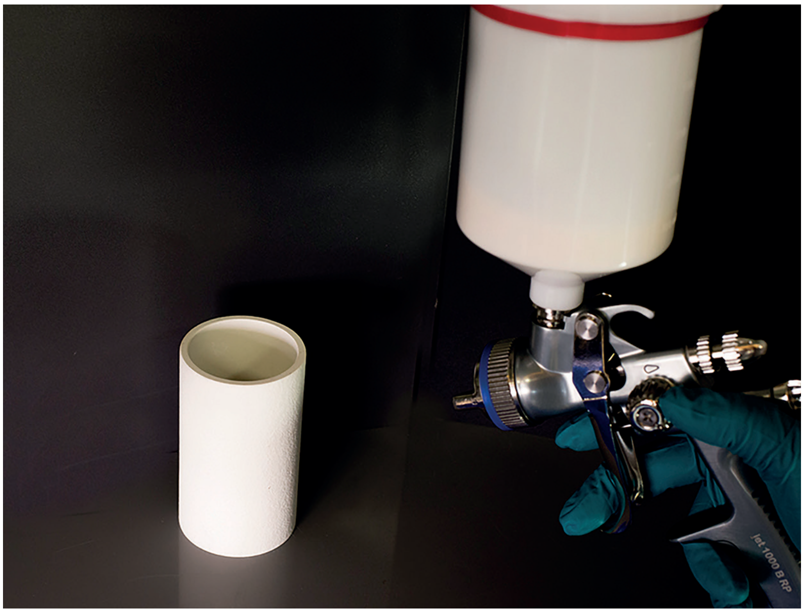
Fig. 3 **Example of the slurry-based deposition technique based on spraying**

Development of a bi-layer EBC for SiC ceramics

Based on the preview steps, a quick screening of promising materials was done. Bulk samples of these materials were prepared in form of cylinders with a diameter of 10 mm. The samples were then exposed for some 100 h to the flue gas atmosphere of a gas-fired furnace at temperatures of 1400 °C. Thereafter, the samples have been assessed in terms of dimensional stability, void formation, change of mass and appearance and their interaction with the substrate material. Based on this material screening, the authors selected $3Al_2O_3{\cdot}2SiO_2$ (mullite) and $Y_2Si_2O_7$ (yttrium disilicate) for further development (see below).

Depending on the specific material system, densification by sintering sometimes needs quite high temperatures. In case of coatings, this is a problem if the sinter temperature exceeds the temperature limit of the sub-

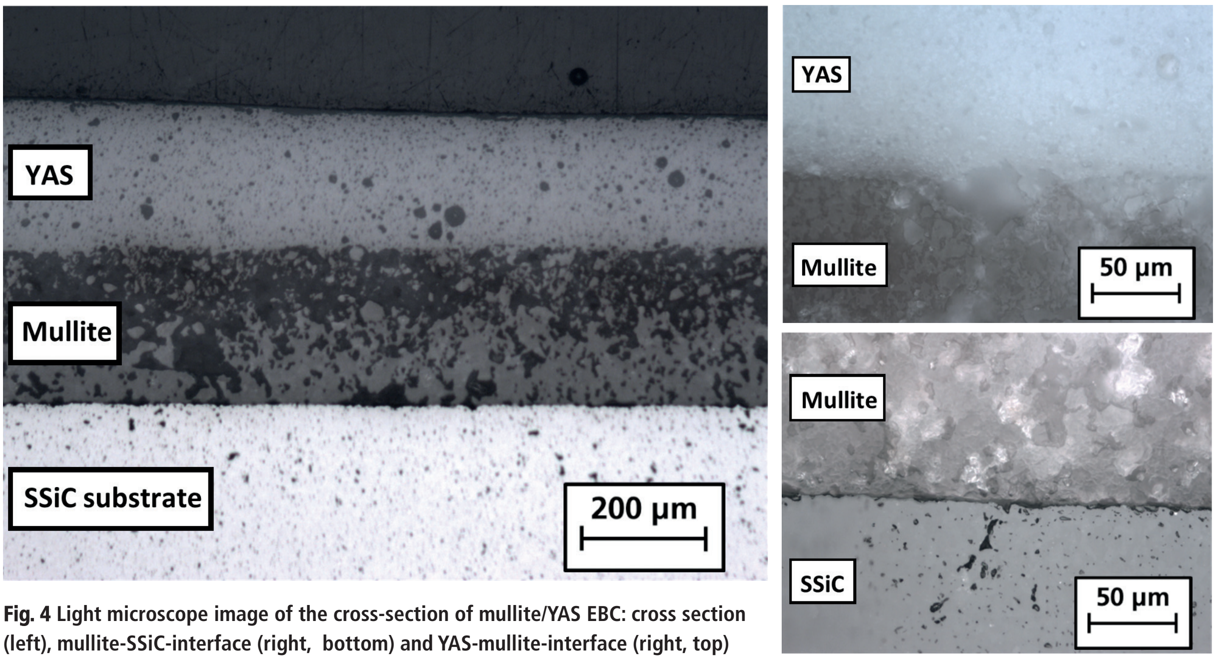

Fig. 4 **Light microscope image of the cross-section of mullite/YAS EBC: cross section (left), mullite-SSiC-interface (right, bottom) and YAS-mullite-interface (right, top)**

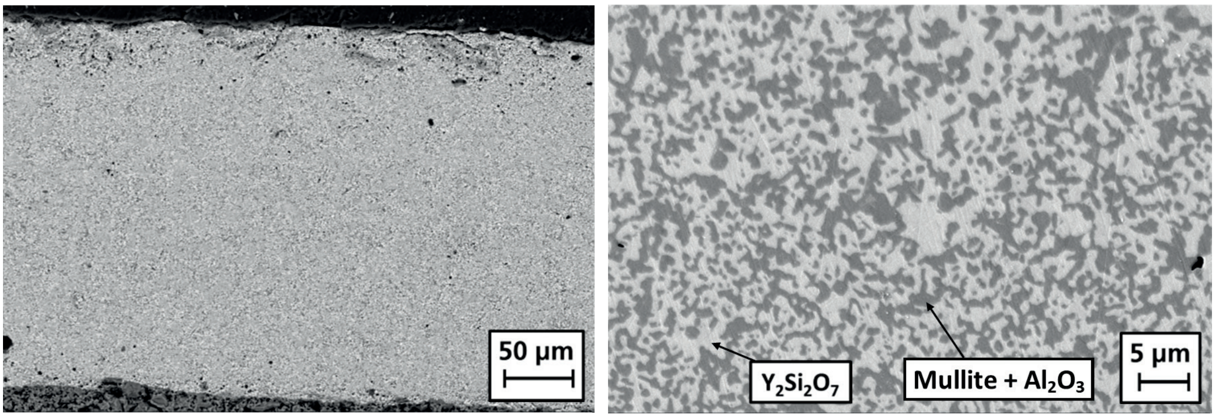

Fig. 5 SEM image of the YAS top coat on a mullite coated SSiC substrate: cross section (left) and top view (right)

strate. On the other hand, low-sintering materials often show insufficient thermal stability for the use as EBC.

Considering these aspects, different strategies are feasible: sintering temperature can be decreased by using smaller particles or sintering additives. Liquid phase sintering or melt infiltration processes can be used as well to decrease sintering temperature. Yet, the authors followed another more promising approach to develop a well densified and thermally stable top coat keeping the processing temperature below a tolerable threshold. This approach is based on a system which is easily densified in the amorphous state by a viscous sintering mechanism and then crystallized to form stable crystalline phases.

As material system, Y_2O_3–SiO_2–Al_2O_3 (YAS) was identified fulfilling the requirements for the top coat of the EBC system as described above. Based on the identified compositions, a glass frit from mixed powders was prepared. After milling of the glass frit, a slurry was formulated for the coating process. The applied coatings were heat treated using a cycle with two steps. First, at 1050 °C the coatings were densified to more than 95 % by viscous sintering. After densification at 1050 °C, the temperature was increased to a maximum of 1390 °C to crystallize the coating (step 2). Crystallization resulted in the formation of a phase mixture of $Y_2Si_2O_7$, Al_2O_3 and $3Al_2O_3{\cdot}2SiO_2$ as verified by X-ray diffraction. Due to its favorable properties, the authors selected mullite as an interesting candidate for the bond coat of the present EBC system.

Drawbacks of mullite as discussed in the literature [9, 24, 25] were considered and systematically mitigated by material and processing design, e.g., post-crystallization effects of mullite were avoided by using well-crystallized mullite powders and sintering the coating after slurry deposition. Fig. 4 shows a cross-section of the mullite/YAS–EBC on an SSiC substrate. The coatings were crack-free and good adhesion was observed between the substrate and between the different layers.

Fig. 5 shows SEM images of the YAS top coat applied on SSiC substrate with mullite bond coat. The YAS top coat exhibited good densification without larger pores or voids. Small pores could be detected. These pores were mainly closed. The YAS layer consisted of a phase mixture of $Y_2Si_2O_7$, Al_2O_3 and $3Al_2O_3{\cdot}2SiO_2$, which were finely dispersed.

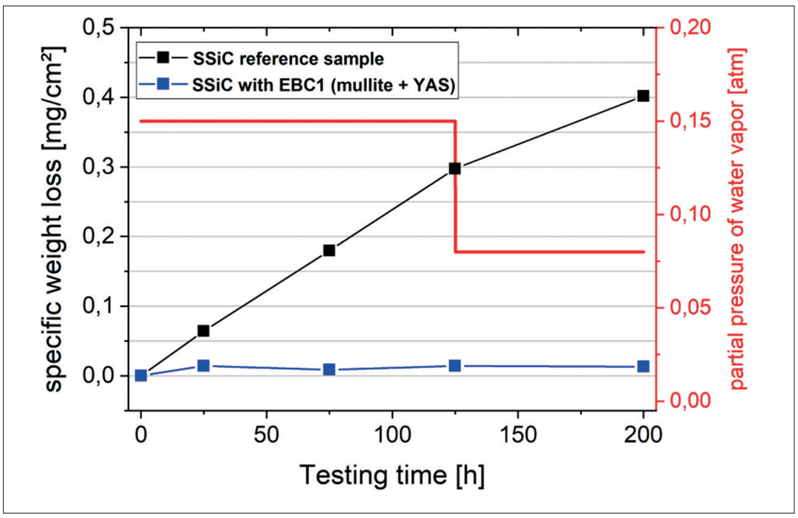

Fig. 6 Specific weight change of a mullite/YAS coated SSiC sample in comparison to an uncoated SSiC reference sample in a hot gas corrosion test. The samples were tested at 1200 °C with a gas velocity of 100 m/s

Testing of EBC systems

The mullite/YAS EBC system described in the previous section was selected for application-relevant tests for its use in aero-engines. For that, it was applied on an SSiC substrate. The thermal cycling stability was studied in a Furnace Cycle Test (FCT) at MTU Aero Engines. The sample was cycled 500 times between room temperature and 1135 °C. The EBC system successfully passed these tests. No cracks or spallation of the coating was detected. A mass change of only +0,03 % was observed.

Moreover, the stability of the EBC system in hot gas environment was studied in a test rig at Fraunhofer IKTS. A temperature of 1200 °C with a partial pressure of water vapor of 0,15 respectively 0,08 atm were selected as test conditions. After an exposure of 200 h, the sample protected by the EBC showed a mass gain of only 0,006 mass-%

compared to 0,36 mass-% in case of an uncoated SSiC reference sample (Fig. 6).
With X-ray diffraction studies, it was confirmed that no change in phase composition of the YAS top coat occured. The coated samples adhered well on the substrates without spallation or visible cracks. Therefore, it was concluded that the EBC system also passed the hot gas test successfully.
Other thermomechanical properties of EBC systems can be measured with a special thermooptical measuring furnace recently developed at Fraunhofer-Center HTL: TOM_wave (Fig. 7). TOM_wave combines a furnace with a 600 W CO_2 laser. The furnace is used to heat the sample to a base temperature (T_{max} is 1750 °C) in a controlled atmosphere, while the CO_2 laser is used for additional short-term heating of the sample.
With this principle, samples can be thermally cycled between two threshold temperatures while detecting the response of the sample in-situ with various sensors. Microphones are used to detect cracking or spallation of the samples in-situ [26]. Heat transfer properties are measured using the same device as well as fast and sensitive pyrometers for temperature measurement. By a modified laser flash technique and an inverse fitting method, through-plane thermal conductivity and hemispherical emissivity are obtained [27].
Another useful device for EBC development is under construction at Fraunhofer-Center HTL: TOM_chem. Materials can be characterized up to 1450 °C in variable, controlled atmospheres while injecting particles or vapors into the gas stream. In TOM_chem, material behavior is studied in-situ by measuring the weight change and monitoring the exhaust gas composition [28]. This provides the unique possibility to setup specific and application-relevant test conditions in a flexible way. One example includes the simulation of the corrosive environment in aero-engines due to melt formation of ingested sand, volcanic ash and other debris.

Fig. 7 Thermooptical Measuring Device TOM_wave for the high temperature characterization of thermomechanical properties

Conclusions and outlook

Fraunhofer-Center HTL uses its expertise in material and process design for developing cost-effective, yet high-performance coatings. A close interaction of experimental and computational tools has been utilized, which was named Integrated Computational Ceramic Engineering (ICCE) [29] – according to the Integrated Computational Materials Engineering, which is well known in the development of metals [30]. Within a large project called DiMaWert, an efficient development chain for ceramic materials is currently established. It is based on a mixture of experimental and digital tools, where the increasing performance of AI methods is considered [31]. A decrease of more than 50 % of development cost and time can be achieved using these tools.
With EBC systems, the bi-layer coating presented in the previous section has demonstrated the capacity of a well-aimed development process for ceramic coatings. The developed EBC system successfully passed tests under application-relevant conditions for its use in aero-engines.
Due to the objective to decarbonize economy, future combustion processes will most likely be fueled by hydrogen instead of hydrocarbons as used today. In many applications, this increases the material requirements, e.g., temperature capability and corrosion resistance.
An example are future aircraft turbines, where current state-of-the-art EBC systems with Si bond need to be replaced by Si-free coatings [32]. To address this issue, Fraunhofer-Center HTL developed a Si-free, composite bond coat in the material system ZrO_2–TiO_2 [33]. Good adhesion was demonstrated on SiC and SiC/SiC-CMC materials, and further developments on compatible top coats for various applications, amongst others special low-e coatings, are under way.

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