Slurry-Based Environmental Barrier Coatings for Silicon Carbide and its Composites – a Straightforward Approach

When silicon carbide is exposed to combustion gas, rapid material recession occurs. Therefore, an Environmental Barrier Coating (EBC) needs to be deposited on silicon carbide and its composites in order to insert these high-performance lightweight materials in gas turbines replacing the currently used heavy superalloys. State-of-the-art coating techniques for EBCs like plasma spraying or chemical and physical vapour deposition result in an unfavourable microstructures or high costs. Therefore, a simple double-layer EBC system based on mullite and rare earth silicates has been developed, which can be applied via simple and cost-efficient wet-chemical coating techniques. The top coat based on rare earth silicates is densified via a novel approach using a crystallizing glass system. Some promising results of this slurry-based approach are presented.

Introduction

For long-distance travelling, currently and in the foreseeable future there is no alternative to air transportation. As a matter of fact, the revenue passenger kilometres are growing at a rate of 5,5 %/a and are expected about to double with the next 15 years [1].

At the same time, air transportation is also a source for emission of large amounts of climate-damaging gases. This prompted the European Union to declare the FLIGHTPASS 2050, targeting a reduction of the emissions of CO_2 and NO_x by 75 % and 90 %, respectively [2]. Achieving these objectives requires radical changes in the design and propulsion of future aircrafts. A considerable reduction of climate-damaging gases can be achieved by increasing the gas inlet temperature in order to raise the efficiency of gas turbines [3, 4]. Currently used metallic materials have an upper limit of the use temperature of about 1100 °C, above which intolerable creep is observed.

Currently, the most promising alternative to metallic materials are SiC-fibre-reinforced SiC ceramic matrix composites (SiCf/SiC–CMC), which allow an increase in operation temperature of the gas turbines of about 100–200 °C combined with a reduction of 2/3 of the weight [5, 6]. Nevertheless, using SiCf/SiC in combustion environment at temperatures above 1100 °C leads to a rapid recession due to water vapour corrosion [7, 8]. Thus, SiCf/SiC–CMCs need to be protected by an Environmental Barrier Coating (EBC).

There are several key requirements the EBC has to fulfil to make use of the potential of SiCf/SiC-CMCs in gas turbine applications. These are match of the Coefficient of Thermal Expansion (CTE) with the substrate material, environmental durability, adherence, chemical compatibility and phase stability [9, 10].

Since not all of these requirements are fulfilled by a single coating material, multilayer coatings comprising at least two layers (bond coat and top coat) have been developed. Current EBC systems under development comprise a silicon bond coat, a mullite-based intermediate layer and a rare earth silicate as top coat [10, 11].

These EBCs are typically deposited by Atmospheric Plasma Spraying (APS) [9, 12–14] or to a minor extent by chemical

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[15, 16] or physical vapour deposition [17, 18]. These methods are expensive and time consuming. APS is a line-of-sight process which is problematic for coating complex shaped parts [10]. Additionally, APS coatings often have cracks, open pores or need substrate surface treatment for adhesion [9, 10]. The deposited coatings often show volume changes due to shrinkage, crystallization or phase transitions during the first thermal cycling, which changes the stress state in the coatings and, in the worst case, can likely lead to cracks and spallation of the coatings [19, 20].

In this paper, the development of a slurry-based EBC system is presented that can be deposited by cost-efficient wet-chemical coating techniques like dipping, painting or spraying. Sintered SiC coupons (SSiC) were used as a cheap model substrate. The authors developed a two layer EBC system consisting of a mullite bond coat and a top coat based on the material system Y_2O_3–Al_2O_3–SiO_2, in the following referred to as YAS. The top coat was applied as a crystallizing glass, allowing to achieve a crystalline and dense top coat at temperatures below 1400 °C. The EBC system successfully passed Furnace Cycle Testing (FCT) and hot-gas corrosion testing, which shows the potential of this cost-efficient approach.

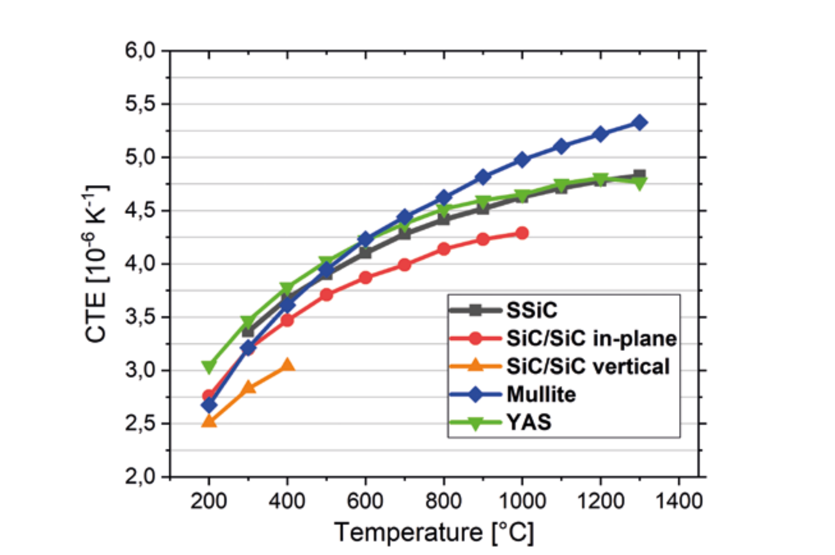

Fig. 1
CTE values of the coating materials mullite and YAS in comparison to the substrate materials SSiC and SiCf/SiC

Experimental

The EBC coating system is applied in a two-step process. At first, a water-based mullite slurry is prepared containing the respective powder raw material, dispersant, rheological additives, defoamer and a binder. The slurry is brushed, sprayed or coated onto the substrate material followed by drying. After that, the green layer is sintered to yield a well adhering bond coat with a distinct residual porosity.

Following the bond coat, a similar slurry containing a YAS glass powder is produced, and coated on top of the first coating like described above. As the porous bond coat quickly soakes in the water of the slurry, the application of the green top coat resembles a slip-casting process, resulting in well adherent green layers with a high packing density of the glass particles.

After drying, the top coat is being densified and crystallized in a specific furnace cycle. After debinding of the green layer, the glass is first being annealed at its softening point, which leads to an intense densification due to viscous flow resulting in a gas-tight top layer with closed porosity. Subsequently, the densified layer is annealed at a second temperature level yielding a dense and crystalline ceramic top coat.

Characterisation and application-relevant tests

The results of CTE measurements on bulk samples of the substrate materials SSiC and SiCf/SiC, the mullite bond coat and YAS top coat material are shown in Fig. 1. It can be seen that the CTEs of the two coating materials coincide reasonably well with the substrate materials, which is an important requirement for a high thermomechanical durability of the coating system.

In order to test the adhesion and the thermomechanical durability of the coating system, thermal cyclic loading tests were conducted. Two dense rectangular SSiC samples with a size of 25 mm × 25 mm × 2 mm and 24 mm × 14 mm × 2 mm were coated with the mullite-YAS EBC on their entire surface as described above. The samples were then cycled 500 times between room temperature and 1135 °C, simulating the thermal cycling in the hot-path of a gas turbine. The two respective samples before and after the thermal cyclic loading are shown in Fig. 2. No major changes in appearance could be detected, except a slight staining due to deposits from the furnace. The weight changes of the two thermally cycled samples were 0,03 % and 0,04 %, respectively. Fig. 3 shows a SEM analysis of one of these samples after the cyclic loading test. No delamination or crack opening can be seen at the interface between the mullite bond coat and the SSiC substrate, which demonstrates the good adhesion and thermomechanical stability of the bond coat. Likewise, no delamination or crack

Fig. 2
Mullite-YAS-EBC on SSiC samples before (l.) and after (r.) 500 cycles from room temperature to 1135 °C and back. The samples are placed on top of black lines, which are used to track shape deviations

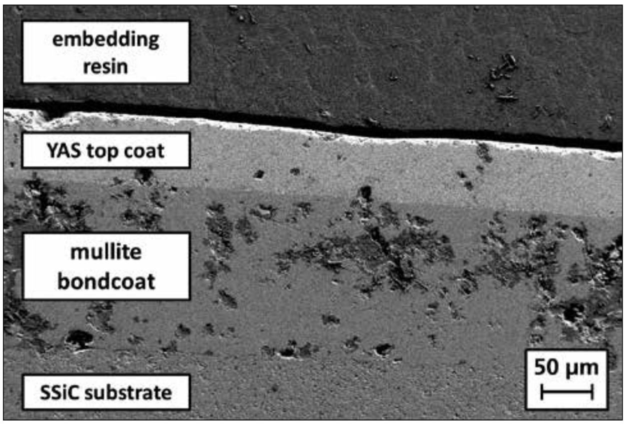

Fig. 3
SEM image of mullite-YAS-EBC coating on a SSiC substrate after 500 cycles of thermal loading from room temperature to 1135 °C and back (SE detector, EHT 3 kV, magnification 343×, WD 8 mm)

Fig. 4
Mullite-YAS-coated SSiC samples before (top) and after (bottom) hot-gas corrosion test at 1200 °C for 200 h. The size of the sample was about 36 mm × 9 mm × 3 mm

opening could be observed on the interface of the mullite bond coat and the YAS top coat. After the successful furnace cycle test, the performance of the mullite-YAS-EBC was studied in a hot-gas corrosion test. A rectangular SSiC sample with a size of 35 mm × 8 mm × 2 mm was coated with the mullite-YAS EBC. For the hot-gas corrosion test, the chamber temperature was set to 1200 °C, the gas velocity was set to 100 m/s, and the partial pressure of water vapour was adjusted to 0,15 atm for the first 125 h, and then to 0,08 atm for another 75 h.

Fig. 4 shows photographs of the sample before and after the hot-gas corrosion test. No major changes in the appearance of the samples could be observed. The results on the specific weight change during the corrosion test are shown in Fig. 5. While the uncoated sample showed a specific weight loss of about 0,40 mg/cm² (0,36 %) due to corrosion, the sample with mullite-YAS EBC showed a specific weight loss of only 0,013 mg/cm² (0,006 %) indicating the chemical stability and functionality of the mullite-YAS-EBC system.

The X-ray diffraction patterns before and after the corrosion test are shown in Fig. 6. The top coat consists of $Y_2Si_2O_7$ and minor amounts of mullite. Al_2O_3 could be detected in trace amounts. After the hot-gas corrosion test, no major changes in the phase composition could be observed by X-ray diffraction analysis indicating the thermodynamic stability of the coating in a hot-gas environment at 1200 °C. Fig. 7 shows SEM images of the YAS top coat before and after 200 h of hot-gas corrosion test. The YAS top coat shows a fine-grained microstructure with closed porosity before and after the test.

No major changes in the microstructure could be detected. Together with the results shown in Fig. 4–6, the authors conclude that the mullite-YAS EBC deposited by a slurry-coating process is a viable EBC system for SiC and its composites under the tested conditions.

Conclusions

A viable mullite-YAS EBC was deposited on SSiC substrates using a slurry-based coating process. The authors developed a

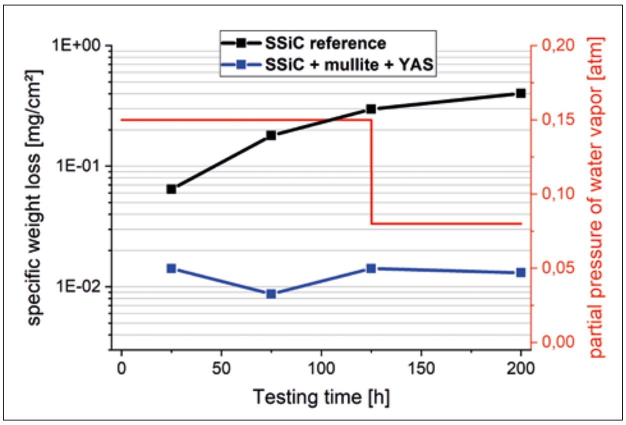

Fig. 5
Specific weight change of a mullite-YAS coated SSiC sample (blue) in a hot gas corrosion test at 1200 °C and a gas velocity of 100 m/s vs. an uncoated SSiC reference sample (black). The red line shows the partial pressure of water vapour

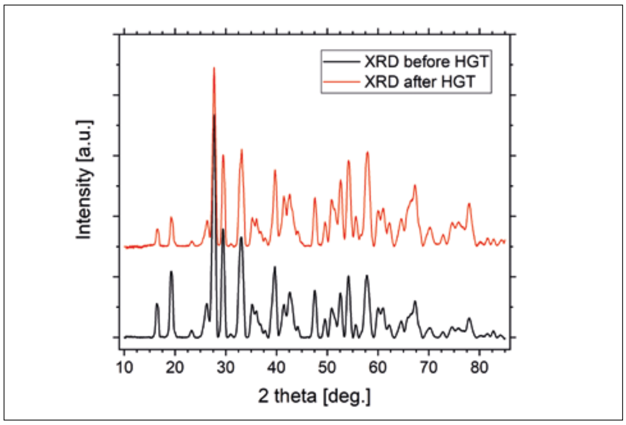

Fig. 6
X-ray diffraction pattern of the mullite-YAS coated SSiC sample before and after the Hot-Gas Corrosion Test (HGT) at 1200 °C for 200 h

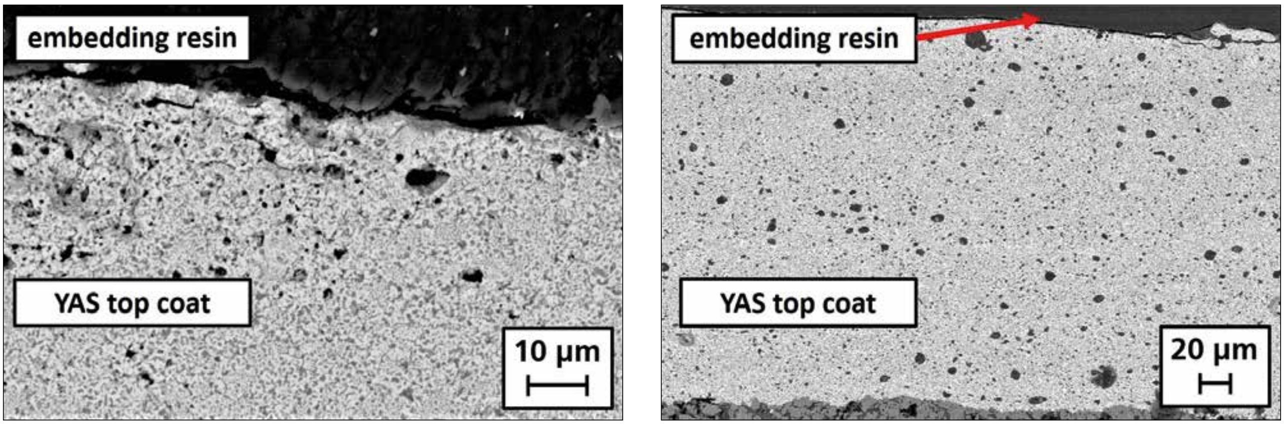

Fig. 7
SEM images of the YAS top coat before (l.) and after (r.) the hot-gas corrosion test at 1200 °C for 200 h (BSE detector, EHT 15 kV and 10 kV, magnification 1000× and 275×, WD 8,2 mm and 8,4 mm, respectively)

novel approach to densify and crystallize a $Y_2Si_2O_7$-based top coat using a crystallizing glass in the material system Y_2O_3–SiO_2–Al_2O_3. This approach represents a cost-efficient alternative to currently used coating techniques like APS, CVD or PVD.
One can observe good adhesion of the EBC system to the SSiC substrate. Due to good matching of the CTE of the coating materials with respect to the substrate, the thermal cycling resistance of the EBC is excellent, as proven in a furnace cycling test with 500 cycles between room temperature and 1135 °C.
The functionality of the EBC coating was tested in a hot-gas corrosion test at 1200 °C for 200 h. As promising results, no major changes in the macroscopic ap-

pearance, phase content or microstructure could be observed after the test. The specific weight loss of the sample with EBC coating was decreased by almost two orders of magnitude with respect to an uncoated reference sample.
Future work is dedicated to transfer of the results to apply the EBC on SiCf/SiC substrates and testing of the EBC system under higher application temperatures.

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References

[1] International Air Transport Association, Annual Review 2018, 2018 www.iata.org/publications/Pages/annual-review.aspx (accessed 10 February 2019)
[2] European Commission, Flightpath 2050: Europe’s vision for aviation; maintaining global leadership and serving society’s needs. Report of the High-Level Group on Aviation Research, Luxembourg
[3] Clarke, D.R.; Oechsner, M.; Padture, N.P.: Thermal-barrier coatings for more efficient gas-turbine engines. MRS Bull. **37** (10) (2012) 891–898. https://doi.org/10.1557/mrs.2012.232
[4] Perepezko, J.H.: Materials science. The hotter the engine, the better. Science **326** (5956) (2009) 1068–1069. https://doi.org/10.1126/science.1179327
[5] Gardiner, G.: Aeroengine composites, Part 1: The CMC invasion. Composites World **31** (2015)
[6] Zok, F.W.: Ceramic-matrix composites enable revolutionary gains in turbine engine efficiency. Amer. Ceram. Soc. Bull. **95** (2016) 22–28
[7] Eaton, H.E.; Linsey, G.D.: Accelerated oxidation of SiC CMC’s by water vapor and protection via environmental barrier coating approach. J. Europ. Ceram. Soc. **22** (2002) [14–15] 2741–2747. https://doi.org/10.1016/S0955-2219(02)00141-3
[8] Jacobson, N.S.: Corrosion of silicon-based ceramics in combustion environments. J. Amer. Ceram. Soc. **76** (1993) [1] 3–28. https://doi org/10.1111/j.1151-2916.1993.tb03684.x
[9] Hardwicke, C.U.; Lau, Y.-C.: Advances in thermal spray coatings for gas turbines and energy generation: A review. J. Therm. Spray. Tech. **22** (2013) [5] 564–576. https://doi.org/10.1007/s11666-013-9904-0
[10] Lee, K.N.: Environmental barrier coatings for SiCf/SiC. Ceramic Matrix Composites: Materials, Modeling and Technology (2014) 430–451
[11] Xu, Y.; et al.: Rare earth silicate environmental barrier coatings: Present status and prospective. Ceramics Int. **43** (2017) [8] 5847–5855. https://doi.org/10.1016/j.ceramint.2017.01.153.
[12] Lee, K.N.; Fox, D.S.; Bansal, N.P.: Rare earth silicate environmental barrier coatings for SiC/SiC composites and Si_3N_4 ceramics. J. Europ. Ceram. Soc. **25** (2005) [10] 1705–1715. https://doi.org/10.1016/j.jeurceramsoc.2004.12.013
[13] Richards, B.T.; Wadley, H.N.G.: Plasma spray deposition of tri-layer environmental barrier coatings. J. Europ. Ceram. Soc. **34** (2014) [12] 3069–3083 https://doi.org/10.1016/j.jeurceramsoc.2014.04.027
[14] Richards, B.T.; Zhao, H.; Wadley, H.N.G.: Structure, composition, and defect control during plasma spray deposition of ytterbium silicate coatings. J. Mater. Sci. **50** (2015) [24] 7939–7957. https://doi.org/10.1007/s10853-015-9358-5
[15] Basu, S.N.; et al.: Functionally graded chemical vapor deposited mullite environmental barrier coatings for Si-based ceramics. J. Europ. Ceram. Soc. **28** (2008) [2] 437–445. https://doi.org/10.1016/j.jeurceramsoc.2007.03.007
[16] Xu, J.; t al.: Stability of interfaces in hybrid EBC/TBC coatings for Si-based ceramics in corrosive environments. Int. J. of Refractory Metals and Hard Materials **49** (2015) 339–349. https://doi.org/10.1016/j.ijrmhm.2014.08.013
[17] Yokoi, T.; et al.: Preparation of a dense ytterbium disilicate layer via dual electron beam physical vapor deposition at high temperature. Mater. Letters **193** (2017) 176–178. https://doi.org/10.1016/j.matlet.2017.01.085
[18] Zhang, X.; et al.: CMAS corrosion and thermal cycle of Al-modified PS-PVD environmental barrier coating. Ceramics Int. **44** (2018) [13] 15959–15964. https://doi.org/10.1016/j.ceramint.2018. 06.019
[19] Lee, K.N.; Eldridge, J.I.; Robinson, R.C.: Residual stresses and their effects on the durability of environmental barrier coatings for SiC ceramics. J. Amer. Ceram. Soc. **88** (2005) [12] 3483–3488 https://doi.org/ 10.1111/j.1551-2916.2005.00640.x
[20] Richards, B.T.; et al.: Fracture mechanisms of ytterbium monosilicate environmental barrier coatings during cyclic thermal exposure. Acta Materialia **103** (2016) 448–460. https://doi.org/10.1016/j.actamat.2015.10.019