GERMANY

Applications of Ceramic Thermal Spray Coatings

Ceramic thermal spray coatings play a prominent role in a large number of applications. For instance, thanks to their particular functionality, they can allow the use of a component in the first place or considerably extend its lifetime. In many cases, coatings can lead also to considerable cost savings, since an expensive material can be substituted by a cost-effective combination of a high quality coating and a low cost substrate. In this paper, several possible applications are discussed, although this list is certainly not complete.

However, the different applications clearly show the varied possibilities for the implementation of this technology and is intended to widen the horizon for other future fields of application.

Thermal spraying is a coating technology used in many applications for the production of thick layers of ceramic or metallic materials. In this process, powder starting materials in the size range of several tens of micrometres are accelerated and heated in a hot and high-speed gas jet. When the particles impact the substrate, they flatten out, forming a lamellar structure. As a result of the fast cooling after deposition and the brittle condition of the starting material, ceramic coatings are often permeated by microcracks and pores. These microstructural properties are often advantageous for high-temperature applications, e.g. as thermal barrier coatings in gas turbines, as they effectively reduce the stresses caused by thermal shock loading. On the other hand, with targeted adjustment of the process conditions and/or the selection of suitable spraying processes, gastight coatings can be produced. Examples of porous as well as dense ceramic coatings are presented in the following.

One important application of thermal-sprayed ceramic coatings is the production of thermal barrier coatings for aircraft or stationary gas turbines. Fig. 1 a shows the fracture surface of an atmospheric-plasma-sprayed (APS) thermal barrier coating made of yttria-stabilized zirconium oxide (YSZ) with cracks inside and between the sprayed lamellae. This strain-tolerant microstructure can be further improved with the implementation of columnar structures in the coatings (Fig. 1 b). The gaps between the columns can open during heating of a component, which leads to a thermal shock-resistant coating. Such coatings can be produced by means of suspension plasma spraying (SPS), in which, instead of particles, suspensions are introduced into the jet of hot gas or plasma. As the resulting droplets are much smaller than the typically used particles, they can now follow the gas stream of the jet and only impact the roughness peaks on the surface on which the columns are growing. We were able to show that such coating systems can only be fully utilised if the underlying bond-coat is subjected to pre-oxidation prior to deposition of the coating [1]. Such coatings then exhibit thermal cyclic resistance that is more than double that of conventional APS coatings.

Keywords
thermal spraying, ceramic coatings, APS, HVOF, thick coatings

Even SiC/SiC composites as advanced structural materials for high-temperature applications need protective coatings for use in gas turbines. Here, water vapour corrosion plays a critical role as it leads to the evaporation of the silica coating typically formed on SiC and consequently to corrosion of the entire component. This degradation can be reduced substantially by various coatings, e.g. made of $Yb_2Si_2O_7$. In contrast to thermal barrier coatings, here dense coatings are necessary to suppress access of the water vapour. These environmental barrier coatings (EBCs) are predominantly applied by means of atmospheric plasma spraying.

The main problems with this are the microcracks and therefore not gastight and amorphous microstructure of the APS coatings. Crystallization at high temperatures leads to shrinkage and crack formation.

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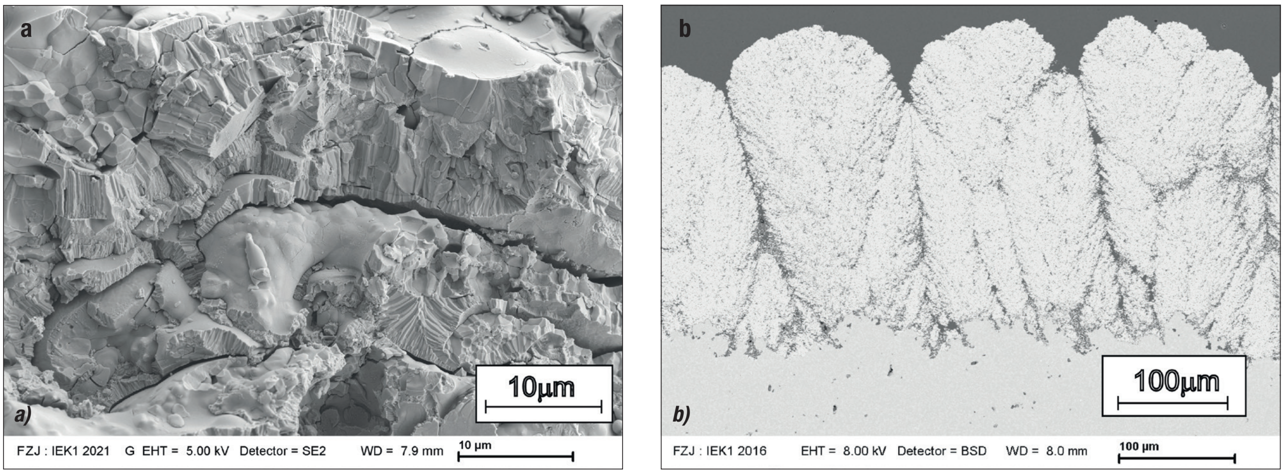

Fig. 1 a–b
a) Fracture surface of an APS coating, b) Cross-section of a columnar YSZ coating produced by means of SPS

With the utilization of very low-pressure plasma spraying (VLPPS), thanks to the direct production of dense and crystalline coatings, these problems can be avoided [2]. This process can also be used to deposit ceramic membranes on porous metallic substrates. On account of the relatively coarse particles used, even large pores in the substrate can be covered, which is very difficult with other methods. In addition, no subsequent densification by means of a temperature treatment step is needed. With this process, on the one hand, oxygen-conducting membranes with a thickness of around 30 µm could be produced from a LaSrCoFe oxide (Fig. 2). Other membrane materials, e.g. proton-conducting La_6WO_{12}, can also be deposited as thin coatings in this way [3].

In solid oxide fuel cells (SOFCs), too, environmental barrier coatings are often deposited by means of thermal spraying. Here interconnector materials are often coated, generally forming a chromium oxide coating. This evaporates during operation and contaminates the cathode of the fuel cell. Here, dense chromium evaporation barriers can reduce the Cr evaporation. The use of MnCoFe oxide spinel as a coating material has proven effective. This material (or the cobalt contained in it) is partially reduced during spraying and deposited as a simple oxide with salt structure. During operation in air above 500 °C, the coating reabsorbs the oxygen and the increase in volume causes the cracks and pores to close. (Fig. 3) [4]. This mechanism is a type of self-healing, as a result of which the defects formed during coating are eliminated and a gastight coating is formed.

In the production and processing of technical fibres and yarns, godets are key components in the textile machines. Godets are high-speed rotating cylinders supported by a bearing on one side that are driven by an electric motor. Several godets are operated in pairs, the yarn being guided over the godet shell and wound once or more times over the godet shell. Godets can fulfil different functions in a textile machine, like, for example, transport and stretching of the yarns. Godets equipped with a heating system are used for drying and heat treatment of technical yarns in the temperature range up to 400 °C.

During yarn processing, godets are exposed to different types of loads. The fast rotation and pressing or friction of the yarns on the surface cause considerable mechanical loads. Heated godets are also subject to thermal stresses. Another potential cause of damage is corrosion caused by chemicals used for treatment of the yarns.

On account of the necessary material properties, like strength, magnetic properties and formability as well as the production costs, godet shells are made of steels, which would not survive these loads without additional surface protection. For many years, hard chromium plating was regarded as the standard method for protection of godet shells. On account of the environmental impact and the limited performance range of hard chromium plating, thermal-sprayed coatings have become established as the state of the art. Ceramic coatings have proven especially suitable for this application as they exhibit high wear-, corrosion- and temperature-resistance as well as being environment friendly.

Thermal-sprayed coatings for godets are usually produced by means of APS and high-velocity oxygen fuel spraying (HVOF). HVOF generally leads to denser coatings but also higher production costs. Common ceramic coatings are Al_2O_3, TiO_2, Cr_2O_3 and combinations of these (Fig. 4). With different ratios of the components, various properties like hardness, toughness, coefficient of friction and surface finish can be obtained. However, on account of the nature of the process, ceramic coatings exhibit residual porosity. This porosity reduces the residual stresses in the coatings and increases thermal shock resistance. Open porosity can, however, enable the infiltration of corrosive media, which can then reach the substrate and lead to corrosion and detachment of the coatings. Two strategies are used to improve corrosion protection with the coatings. On the one hand, corrosion-resistant metallic coatings, usually on nickel basis, are applied as a primer. These metallic coatings can also be applied by means of APS or HVOF. Second, the ceramic coatings are sealed (Fig. 5). Here, liquid resins are applied to the surface of the ceramic coatings with different methods, like, for example, spraying, brushing with a paintbrush or vacuum-assisted infiltration. Thanks to their suitable properties and the capillary effect, the resins infiltrate the open pores. After hardening, induced chemically,

thermally and/or with UV light, a solid material is formed in the pores of the ceramic coatings.
Another aspect of the production of thermal sprayed coatings for godet shells is mechanical machining. On account of the high rotational speed and transverse load caused by the one-sided bearing, the dimensions of a godet shells have very narrow tolerances.
Despite a relatively high accuracy of the spraying process, variations in the coating thickness are possible, which have to be corrected afterwards. In addition, depending on the yarn and process step or function of the godet, different surfaces are required. As the "as-sprayed" surface of the coatings is usually unsuitable for the application, the surface condition is modified by machining processes such as brushing, grinding and polishing. Then, the godet shells must be balanced. This is effected with selective boreholes on the end face of the shell or with Rauschert's proprietary ring balancing method [5].
A big advantage of coated godet shells is the option of repair. To this end, old, worn coatings are removed and the surface of the shell is ground. In the event of severe damage to the substrate that makes the removal of more material necessary, thick metal coatings can be applied by means of APS or electric arc spraying, so as to restore the original starting dimensions. After another grinding process, the shells are ready for application of a new coating.

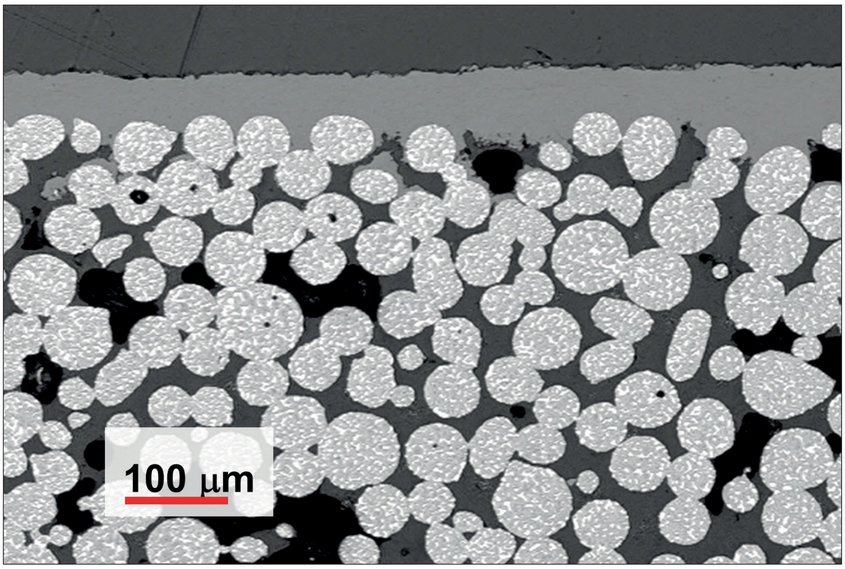

Fig. 2
Cross-section of an LSCF oxygen-conducting coating on a porous NiCoCrAlY substrate

The expensive godet shells can be refaced several times over, which improves the cost efficiency, resource efficiency and sustainability of the godet shells.
Roller bearings are also important machine components, e.g. in electric drives, which profit from thermal-sprayed coatings. The coating of the outer ring with a resilient current-insulating coating is useful to avoid the passage of current to other components and electropitting. As a result, the lifetime of the bearing and the adjoining components is extended. On the basis of the technical requirements, ceramic coatings are suitable for this application. These are usually produced by means of APS. A suitable coating material is Al_2O_3, which is mixed in many cases with small amounts of TiO_2, to improve the mechanical properties of the coatings.
The coating thickness is defined by necessary level of current insulation, which in many cases can reach voltages over 3000 V. So that insulation is guaranteed even in the case of high humidity, the coatings are additionally sealed with suitable resin systems. That is extremely important for certain applications, like, for example,

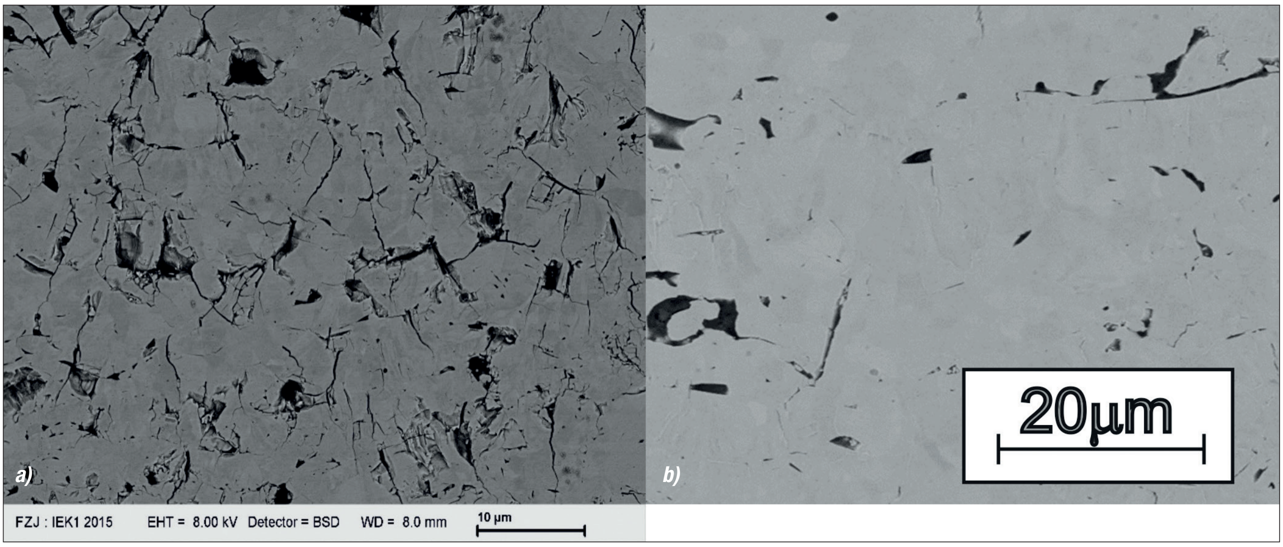

Fig. 3 a–b
a) Cross-section of a self-healing MnCoFe-oxide coating in the as-sprayed state b) and after heat treatment (500 °C, 4 h)

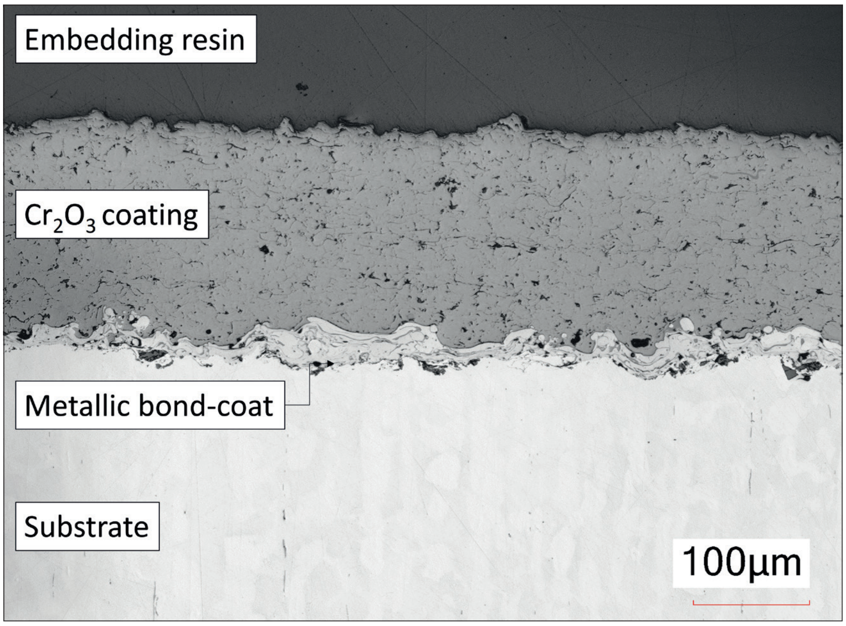

Fig. 4
Microstructure of a Cr_2O_3 coating produced by means of APS with metallic bond-coat for godets

Fig. 5
Godet shell with thermal sprayed ceramic coating and sealing

wind turbines, on account of the application conditions.
Another application of thermal-sprayed coatings is to separate components in diffusion bonding processes to prevent any undesired bonding. Diffusion bonding is a process for joining solid bodies without extraneous materials.
The joining partners with a suitable surface finish are brought into close contact by means of pressing. With the effect of temperature in a suitable environment (inert gas or vacuum), they are joined together without any gap. This process is, however, not selective and so all contact surfaces are joined together. If, however, bonding is not desired in some places, separation layers based on thermal-sprayed coatings are introduced between the parts.
Thanks to the separation layers, several joining groups can be stacked on top of each other without them being bonded together, permitting a more economical operation of the furnaces. Moreover, weighting elements, which are sometimes used for pressing of the components, can be coated to ensure that there is no bonding between the components and the weighting elements.
The separating layers and weighting elements are metallic parts made of a suitable alloy, depending on the processing conditions. Zirconia layers are used as coatings.
Key feature of zirconia is the high thermal expansion coefficient, which allows the use of the coatings on metals at high temperatures without spalling. In addition, the material is sufficiently inert so that there is no bonding to the joining partners. The coating is produced by means of APS. As after-treatment, only the surface is machined so that the separation layers do not leave any impressions on the joining partners.

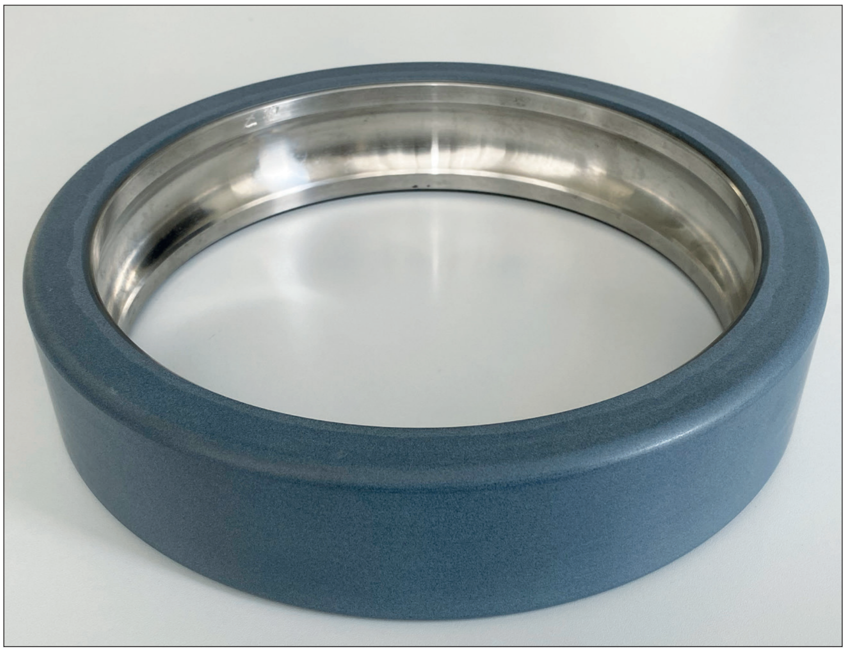

Fig. 6
Roller bearing ring with thermal-sprayed ceramic coating and sealing

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References

[1] Joeris, J.; et al.: Preparation of highly durable columnar suspension plasma spray (SPS) coatings by pre-oxidation of the CoNiCrAlY bondcoat. COATINGS **13** (2023) [9]

[2] Vassen, R.; et al.: Environmental barrier coatings made by different thermal spray technologies. COATINGS **9** (2019) [12]

[3] Ivanova, M.E.; et al.: Lanthanum tungstate membranes for H2 extraction and CO2 utilization: fabrication strategies based on sequential tape casting and plasma-spray physical vapor deposition. Separation and Purification Technology **219** (2019) 100–112

[4] Grünwald, N.; et al.: Microstructure and phase evolution of atmospheric plasma sprayed Mn-Co-Fe oxide protection layers for solid oxide fuel cells. J. of the Europ. Ceram. Soc. **39** (2019) [2] 449–460

[5] DE102022127288A1 – Verfahren zum Auswuchten eines Rotationskörpers und Wuchtmaschine

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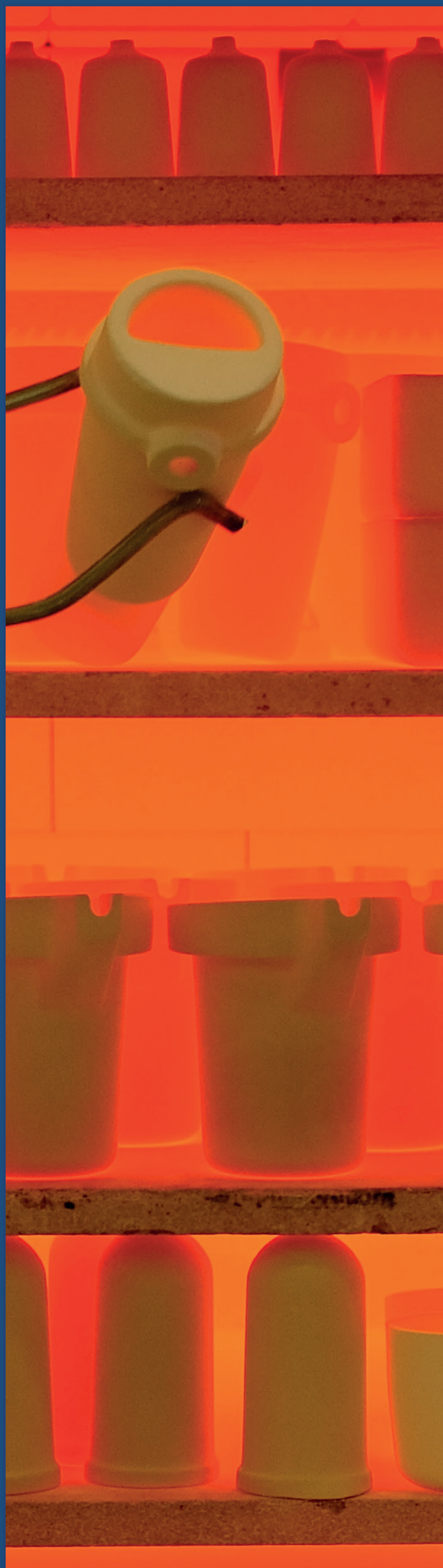

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