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New Material Concepts for the Next Generation of Plasma-Sprayed Thermal Barrier Coatings

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In application as a thermal barrier coating (TBC), partially stabilized zirconia (Zr) approaches some limits of performance. To further enhance the efficiency of gas turbines, higher temperature capability and a longer lifetime of the coating are needed for the next generation of TBCs. This paper presents the development of new materials and concepts for application as TBC. Materials whose compositions have the pyrochlore structure or doped Zr are presented in contrast with new concepts like nanolayers between the top and bond coat, metal-glass composites, and double-layer structures. In the last concept, the new compositions are used in a combination with Zr, as a double, multi, or graded layer coating. In this case, the benefits of Zr will be combined with the promising properties of the new top coating. In the case of metal-glass composites, the paper will be focused on the influences of different plasma spraying processes on the microstructure. The performance of all these different coating systems has been evaluated by burner rig tests. The results will be presented and discussed.

Keywords coating properties, functionally graded materials, nanocrystalline materials, plasma-spraying, thermal barrier coatings, thermal cycling

1. Introduction

Plasma-sprayed ceramic thermal barrier coatings (TBC) are often deposited on components of gas turbines to improve the performance or to extend the life capabilities of these machines.[1] These coatings have to protect the metallic substrate from heat transfer from hot gases, so a low thermal conductivity is necessary for TBCs. The primary industrially used material until now is yttria partially stabilized zirconia (YSZ).

The increasing demands for more efficiency of gas turbines lead to higher operation temperatures and to the need of a longer lifetime for the TBCs. However, YSZ is limited due to phase transition and increased sintering of the porous TBC layer above 1200 °C, which leads to catastrophic delamination of the coating.[2,3]

There are a large number of patents for new materials worldwide to find a successor for YSZ. It is easy to find a composition, which is much better than YSZ in one or two properties. However, to find a candidate that is a better compromise than YSZ in all items of relevant properties was, to our knowledge, not possible up to now.

Some important requirements for a good TBC are low thermal conductivity, large coefficient of thermal expansion, high melting point, good phase stability, low sintering rate, and low Young's modulus.

In this paper, we present an overview of various interesting materials and concepts for new TBC systems. For most of the developments presented here, we have undertaken our own investigations.

Some of our coatings are evaluated with burner rig facilities under realistic thermal operation conditions to get an impression of their performance. For some rather exotic materials, the development of a suitable plasma spraying process is outlined.

2. Experimental

The investigated TBC systems were deposited by plasma spraying using Sulzer Metco (Wohlen, Switzerland) spray equipment. The vacuum plasma spraying (VPS) technique was applied with a F4 gun to deposit a 150 μm NiCoCrAlY bondcoat (Ni 192-8 powder by Praxair Surface Technologies Inc., Indianapolis, IN) on disk-shaped nickel based superalloy IN738 substrates.

The ceramic topcoats with a thickness between 300 and 500 μm were produced by atmospheric plasma spraying (APS) using a Triplex I- or an F4-gun (Fuhrer Metco, Wohlen, Switzerland).

To evaluate the quality of a ceramic material in the application as a TBC, it is important to have a benchmark. Physical properties are often not suitable to predict the real behavior of the ceramic during operation, especially when they are obtained in experiments with bulk materials and not with plasma-sprayed

List of Acronyms

APS	atmospherically plasma-sprayed
CTE	thermal expansion coefficient
MGC	metal-glass composite
MOCVD	metalorganic chemical vapor deposition
PVD	physical vapor deposition
TBC	thermal barrier coating
TGO	thermally oxide grown
VPS	Vacuum Plasma spraying
YSZ	yttria partially stabilized zirconia

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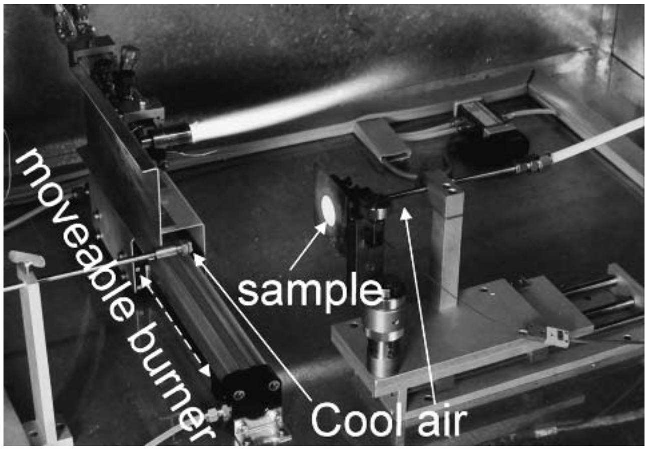


Fig. 1 Thermal cycling test facility with natural gas burner and hot TBC sample

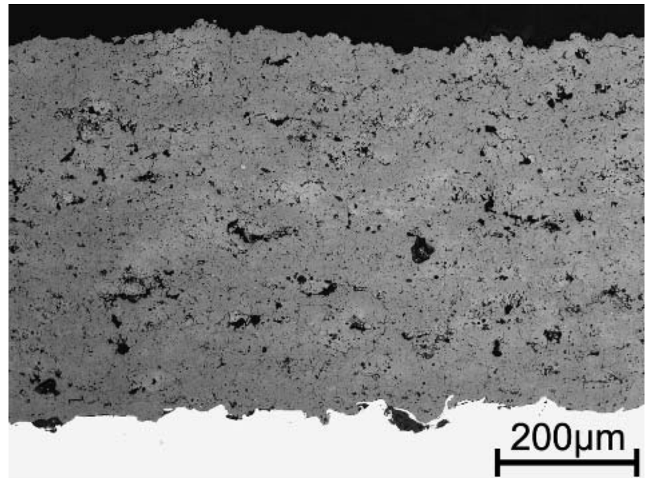


Fig. 2 Optical micrograph of an APS coating of YSZ

coatings. This is especially true because plasma-sprayed coatings of new materials often show distinct differences in microstructure from that of YSZ.

A good benchmark is a thermal cycling test with a burner rig. For our investigation, a burner rig test operating with natural gas was used (Fig. 1). The substrates are cooled by compressed air from the backside. The surface temperature is measured with a pyrometer operating at a wavelength of 8-13 μm and a spot size of 12 mm. For YSZ, the emissivity at this wavelength was determined to be close to 1. Additionally, the substrate temperature is measured by a thermocouple, which is located in the center of the substrate. The surface temperature is varied between about 1240 and 1360 °C; the substrate temperature is adjusted between 930 and 1040 °C. Using the thermal conductivities of the coatings and the substrate, one can estimate that the bond coat temperature is about 30-40 °C higher than the substrate temperature.

In the test facility, a gas burner with a broad flame was used giving a homogeneous temperature distribution. After heating for about 20 s the maximum temperature is reached. After 5 min the burner is automatically removed for 2 min from the surface and the surface is cooled at a rate of more than 100 K/s using compressed air. Cycling is stopped when a visible spallation of the coating occurs.

3. Conventional Thermal Barrier Coating Systems

Plasma-sprayed TBC systems consist in most cases of a MCrAlY (M= Ni, Co) bond coat applied by VPS technique and an atmospherically plasma-sprayed (APS) 7-8 wt.% YSZ topcoat.[4,5,6] In Fig. 2, a micrograph of a polished cross section of an YSZ coating is shown. The performance of these systems mainly depends on the microstructure and hence the processing conditions of the coatings. Compared with new materials, YSZ has an important, material-independent advantage—the material, coating process, and bond coat chemistry have been optimized for operation with zirconia (Zr) for more than 20 years, and a real successor has to outperform these qualities.

4. Chemically Modified Zirconia

The first approach to overcome the limited phase stability of YSZ is to change the stabilizing oxide. Some examples are CaO and MgO, Sc_2O_3, CeO_2,[7-10] which were used instead of yttria to stabilize Zr, but the first two compounds, in particular, led to a performance lower than that of the standard YSZ.

Another very interesting stabilizer for Zr is Ta_2O_5 and Nb_2O_5.[11-13] Both oxides together with Y_2O_3 stabilize the tetragonal phase, cubic phase, or a mixture of these phases of Zr. The coating process for Zr containing these stabilizers with APS need no complicated or unusual process parameters. A micrograph of an APS coating with Tantalumoxide is shown in Fig. 3. Thermal cycling tests with a burner rig show promising results for this material.[13]

Another approch is to substitute the Zr by the chemically quite similar hafnia. Results of investigations on a Y_2O_3 doped hafnia are given by Miller and Zhu[14,15]; their perfomance was promising, but a real improvement compared with the best YSZ material could not be found.

Other oxides like TiO_2 or SiO_2 increase the sinterability of plasma-sprayed coatings.[16]

5. New Materials

New materials include those in which the basic material is no longer Zr. It is the change of the composition to another structure type, for example, garnets, perovskites, and spinels. All these compositions form high-temperature stable oxides.[17-19]

For an application as a TBC, thermal conductivity is a key property, and hence knowledge on mechanisms of heat transfer is important for a focused optimization of materials. In electric isolating solids, the thermal resistivity is due to changes of lattice vibrations, which are usually described as the scattering of phonons. One way to lower the thermal conductivity is to disturb this lattice vibration with additional scattering centers. When the crystal structure changes to a lower symmetry or incorporates more crystallographic different atoms inside the unit cell, the number of scattering centers increases, so the thermal conductivity decreases; or more simply stated, if the crystal structure

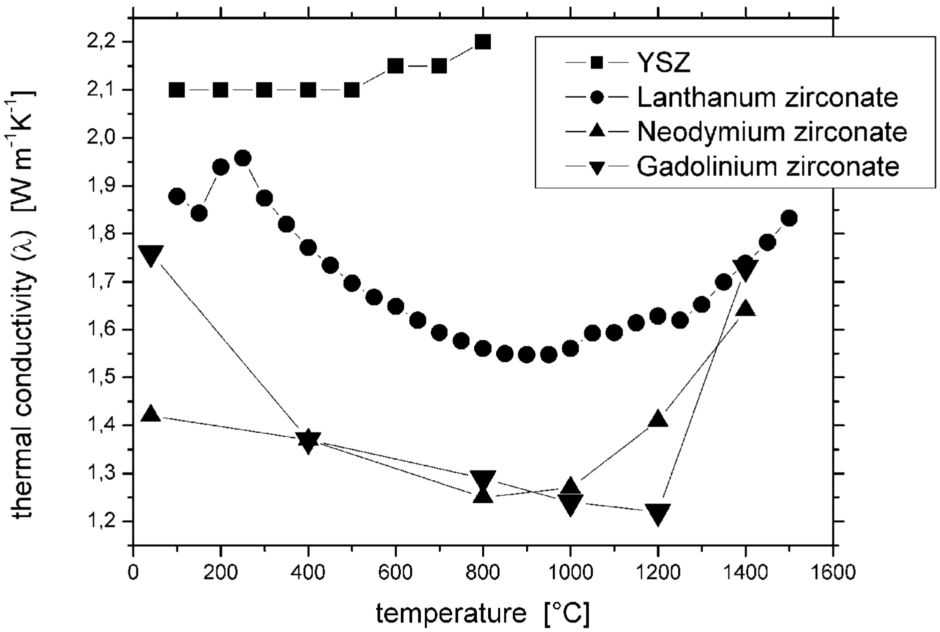


Fig. 3 Optical micrograph of an APS coating of tantalum and yttrium stabilized zirconia

becomes more complicated the thermal conductivity will decrease.[20-23]

Therefore, it is not astonishing that some compositions in with structure types like pyrochlores or hexaaluminates (magnetoplumbite) have excellent thermal properties for application as a TBC.

Certainly this list of structure types and materials cannot be complete due to the fact that not all of the work is published.

The perovskite material $BaZrO_3$ examined by our own investigations revealed poor properties compared with YSZ. $SrZrO_3$ shows a phase transition at a temperature of 600 °C. Therefore, both compounds are inadequate for a TBC application.[17,24]

Some very promising compounds crystallize in the pyrochlore structure,[23,25] for example $La_2Zr_2O_7$, $Nd_2Zr_2O_7$, and $Gd_2Zr_2O_7$. These three compounds have a melting point above 2000 °C; they are stable up to the melting point (no critical phase transition) and their thermal conductivities are significantly lower than the one of YSZ (Fig. 4).

It is uncertain if the increasing values of the thermal conductivity at temperatures above 1000 °C in Fig. 4 are realistic. This increase is probably an artificial effect caused by the method for thermal diffusivity measurement, which is the laser flash experiment. Only a few groups quantify thermal diffusivities of ceramic materials in the temperature region above 1000 °C due to the transparency for thermal radiation of the substances, which makes it necessary to coat the surface of the sample specimens with an opaque layer. This layer (in our case graphite) tends to disintegrate at elevated temperatures, which can lead to improper values of the thermal diffusivity. The values of thermal conductivity at high temperature given in Fig. 4 could therefore be too high.

In $La_2Zr_2O_7$, the thermal expansion coefficient (CTE) is smaller than that of YSZ (Fig. 5), which might be partially compensated by a lower Youngs modulus. The CTE of $Nd_2Zr_2O_7$ and $Eu_2Zr_2O_7$, which also crystallize in the pyrochlore structure, is significantly higher than that of $La_2Zr_2O_7$ and is in the same range as standard YSZ (Fig. 5). However, europium zirconate has the disadvantage of a partial transition of the oxidation state, with unknown consequences.[23]

Lanthanum magnesium hexaaluminates ($LaMgAl_{11}O_{19}$) crystallizes in the magnetoplumbite structure.[26] The good phase stability up to the melting point (T_{mp} > 2000 °C), and the thermal conductivity, which is a little bit better than YSZ (1.2-2.6 $Wm^{-1}K^{-1}$), as well as the structural neighborhood of $LaMgAl_{11}O_{19}$ and the TGO (mainly Al_2O_3), raise high expectations.

Nevertheless, the CTE is notably smaller than that of YSZ (8.8-10.6 K^{-1}). The microstructure of plasma-sprayed coatings looks very different compared with standard coatings (Fig. 6) and all coatings have a large amount of amorphous phase after coating (about 50% and more).[27] It was not known how this material behaved under operation conditions until now.

6. New Concept: Double and Graded Layer

Besides the very promising thermophysical properties for compositions in pyrochlore structure (for application as a TBC), a relatively poor thermal cycling behavior of plasma sprayed $La_2Zr_2O_7$ coatings was found. One successful way to overcome this problem is the use of layered or graded coatings with an YSZ adjacent to the top of the bond coat. The final top coat, exposed to the highest temperature during operation, consists of $La_2Zr_2O_7$.

In Fig. 2 and 7, single layers of YSZ and $La_2Zr_2O_7$ are presented. A double layer is shown in Fig. 8 and a graded layer in Fig. 9.[28,29]

In the graded coatings, first one or two cycles are sprayed with only YSZ powder, giving an YSZ layer of about 40 or 60 μm on the bond coat. Afterwards, 4 cycles with a continuous

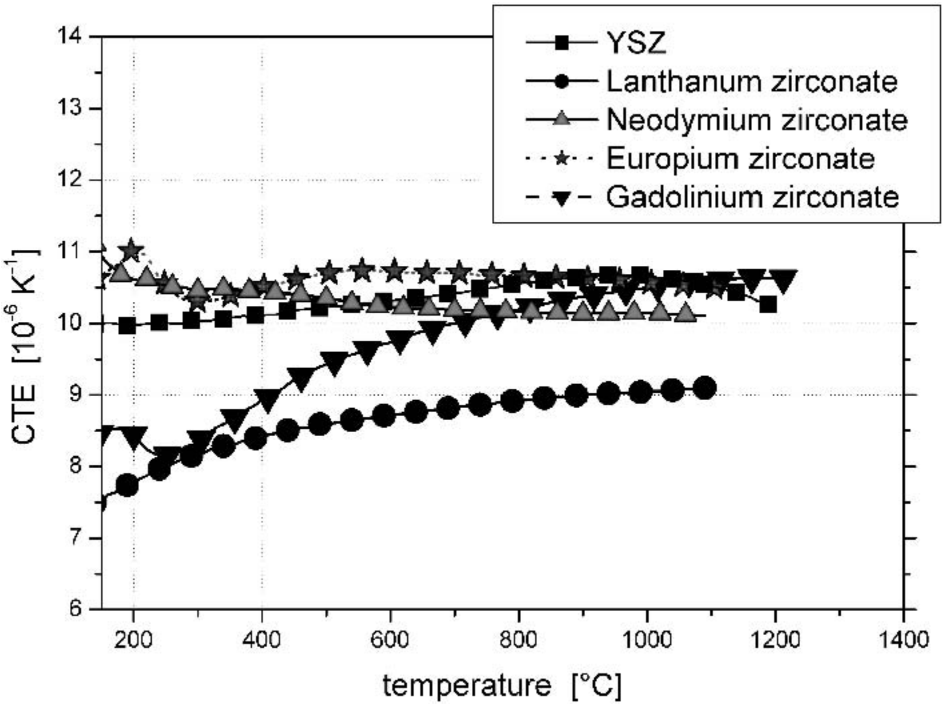


Fig. 4 Thermal conductivities of some pyrochlore compositions (measured with bulk material)

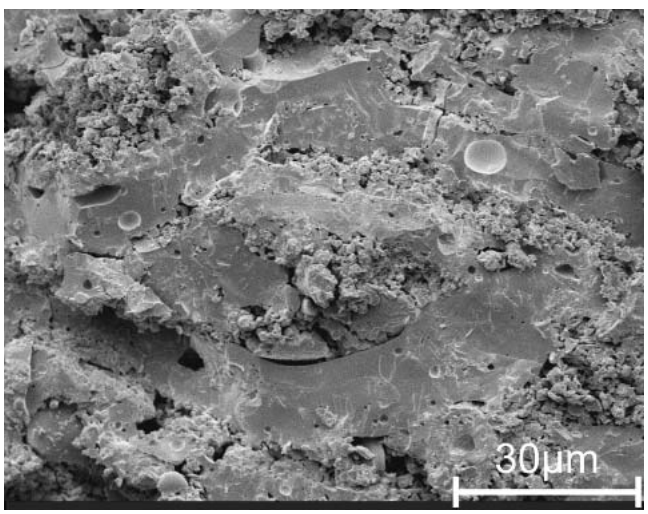


Fig. 5 Thermal expansion coefficient of some pyrochlore compositions (measured on bulk material; only for YSZ an APS coating was used)

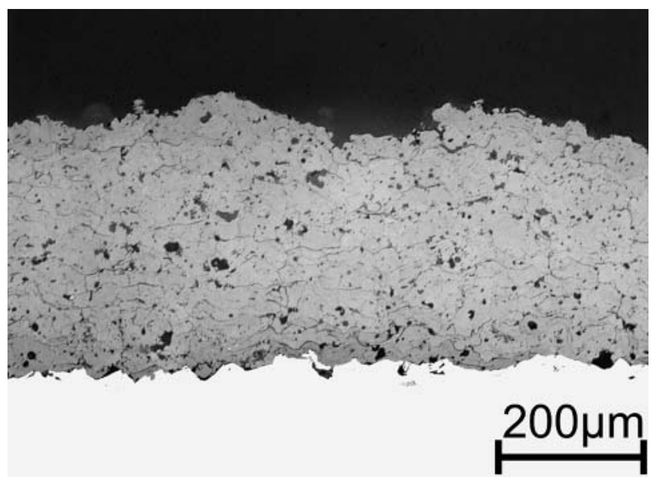


Fig. 6 SEM picture of $LaMgAl_{11}O_{19}$ (fracture edge); the coating exhibits two different regions: small platelets and a "molten mass."

variation of YSZ/$La_2Zr_2O_7$ powder is sprayed. The thickness of the graded area is varied between about 90 and 150 µm. Finally, a $La_2Zr_2O_7$ topcoat is applied giving a total coating thickness of 280-350 µm.

In the case of the two-layered system, the YSZ layer is directly deposited on the bond coat and has a thickness of 100-160 µm. The total thickness is between 320 and 360 µm.

The cycling numbers in Table 1 present the poor quality of a single layer of $La_2Zr_2O_7$ and the limits of YSZ. At the high temperature on the surface, the graded, and especially the double layer coatings, can manifest their longer lifetime under realistic operation conditions.

The first tests with double layers for other materials—for example, $Nd_2Zr_2O_7$/YSZ—showed good results.

7. New Concept: Metal-Glass Composites

A new concept for thermal barrier coating systems based on a mixture of metal and glass is called metal-glass composite (MGC).

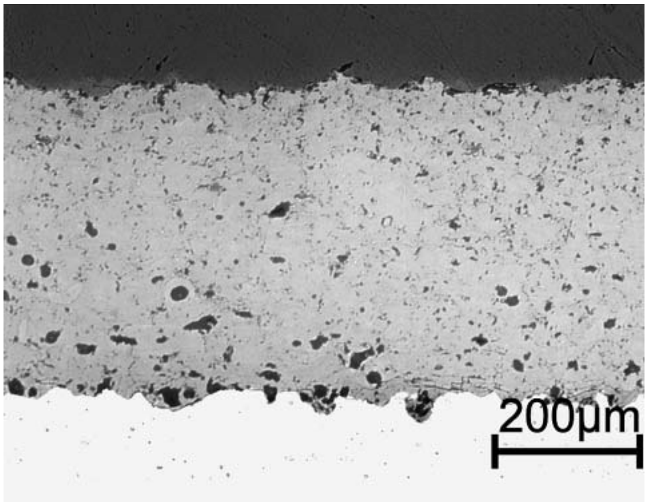


Fig. 7 Optical micrograph of an APS coating of $La_2Zr_2O_7$

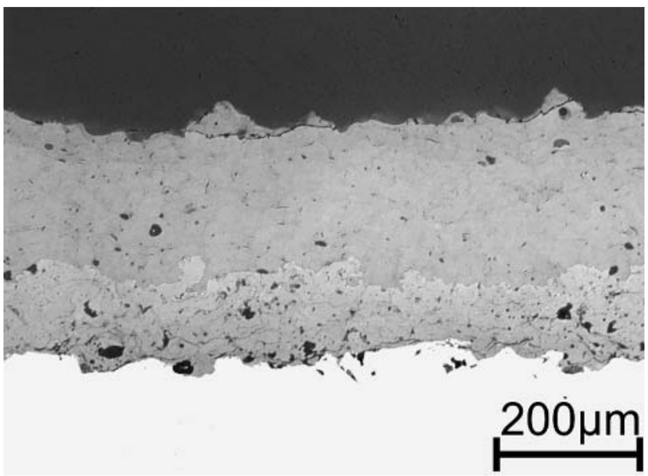


Fig. 8 Optical micrograph of an APS coating of $La_2Zr_2O_7$/ YSZ, 2-layers (bottom YSZ, top $La_2Zr_2O_7$)

For the preparation of MGC, industrially available bond coat powder and ordinary white container glass were chosen (composition, Table 2). To use plasma spraying for the deposition of MGC, the powders had to be adapted. The glass powder with a grain size smaller than 1 μm was premixed and mechanically alloyed with commercial bond coat powder. Taking into account the metallic component of the composites, only VPS is a possible spraying technique for these powders. In the MGC system the thermal expansion coefficient depends on the metal-glass ratio and vary between 9.5 and 12.3 10^{-6} K^{-1}. Thus it is possible to adapt the CTE to individual operation conditions, e.g., for TBCs thicker than 1.5 mm.

Additionally, the glassy phase in the MGC allows creep in the coating at temperatures above 600-700 °C. The creep reduces tensile stress in the coating during heating and leads to compressive stress during cooling, which is better supported by brittle materials.

An optical micrograph (Fig. 10) of the cross section of an as-sprayed MGC-TBC shows the typical lamellae structure of

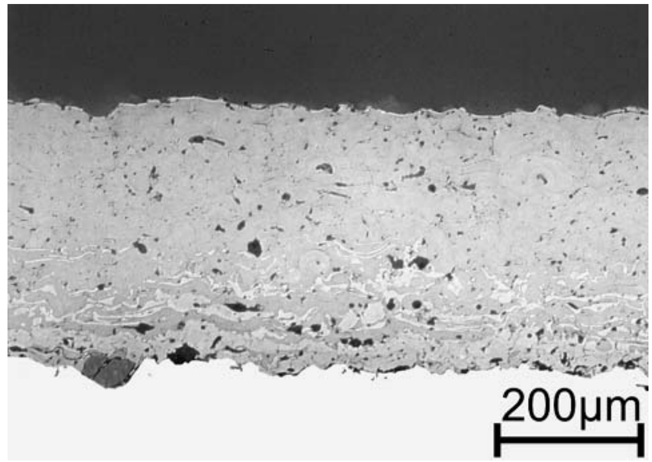


Fig. 9 Optical micrograph of an APS coating of $La_2Zr_2O_7$ / YSZ, graded (bottom YSZ, top $La_2Zr_2O_7$)

Table 1 Thermal Cycling Test of Single, Graded, and Double Layers With an YSZ and $La_2Zr_2O_7$. Cycle-Number Up to the First Appearance of Failure

Composition	Coating Type	T Surface, °C (a)	No. Cycles
YSZ	single	1320-1350	220-1000
$La_2Zr_2O_7$	single	1200-1260	135-977
YSZ/$La_2Zr_2O_7$	graded	1240-1260	2079-2792
YSZ/$La_2Zr_2O_7$	double	1240	4046
YSZ/$La_2Zr_2O_7$	double	1320-1350	1000-2346
YSZ/$Nd_2Zr_2O_7$	double	1320	1748

(a) Mean temperature at the surface of the thermal barrier coating.

Table 2 Composition Data of MGC-Powder

	NiCoCrAlY Powder	Silicate Glass Powder
Grain size, μm	25-40	<10
Content in the MGC, wt.%	63	37
Composition, mol%	29.7% Ni	71% SiO_2
	31% Co	14% Na_2O
	30% Cr	+K_2O
	8% Al	10% CaO
	0.7% Si	2% MgO
	0.6% Y	3% Al_2O_3

plasma-sprayed coatings, where the light component is metal, the gray one is glass, and black represents pores. The uppermost layer does not show any microcracks; neither were inclusions or oxides found at the interface. The porosity is a closed porosity of about 5%.

Another advantage of the gas tight composite coatings is their ability to protect the bond coat from severe oxidation. Correspondingly, long life times have been found for these TBCs in oxidation tests.[30,31]

Coatings with pre-mixed and conditioned powder show much better results during thermal cycling. For surface temperature of 1250 °C, more than 1500 cycles are obtained, while the samples failed after about 500 cycles under the 1350 °C conditions.

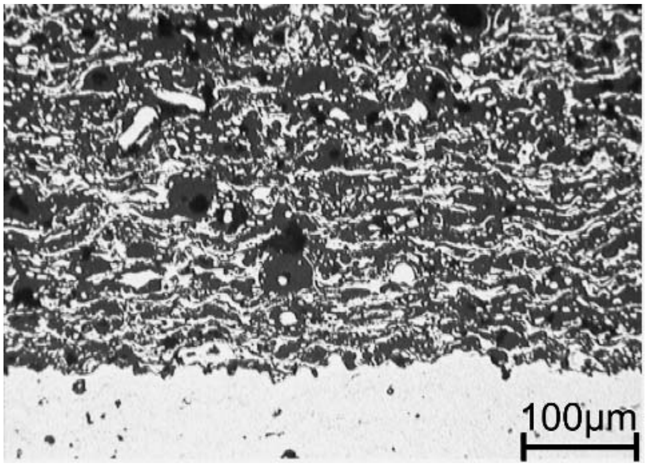


Fig. 10 Micrograph of a cross section of a VPS sprayed MGC-TBC

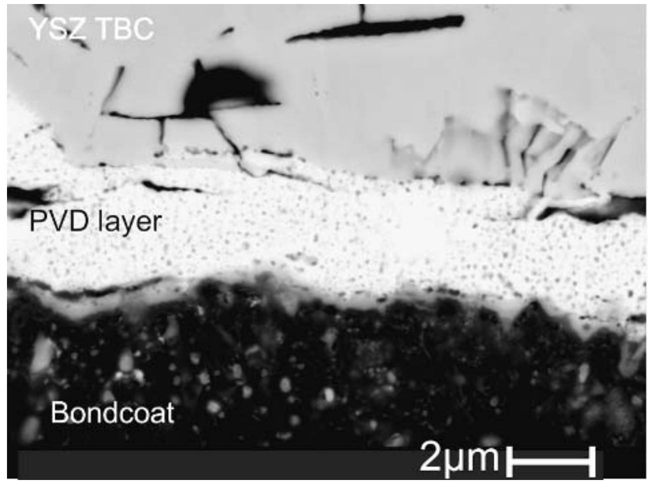
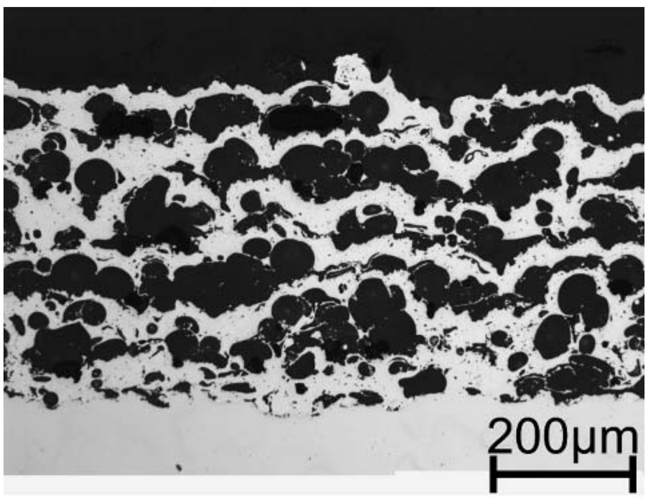
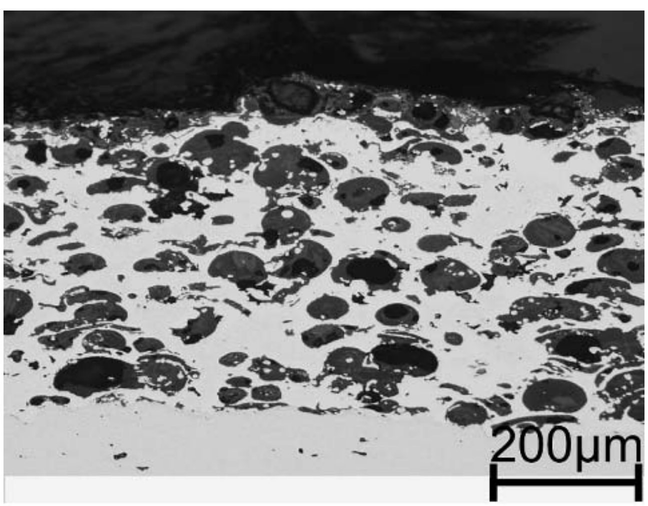


Fig. 12 SEM-picture of a PVD coating of La2Zr2O7, thickness 1.5 μm, on the top a TBC of YSZ



(a)



(b)

Fig. 11 Micrographs of a co-sprayed MGC-TBC: **(a)** with opposite injectors, and **(b)** injectors enclosing an angle of 10°

Figure 11(a) shows a MGC-TBC that was sprayed with two injectors located at opposite sides. This method leads to coatings with alternately layers of glass and metal. The reason is that the trajectories of metal and glass particles diverge after crossing in the plasma flame, so they do not meet the sample at the same place. When the plasma burner is moved over the sample surface, one of the particle types meets the surface before the other, which is then deposited on top of the first one, leading in this way to the observed layered structure. It is not possible to adjust the flow of the carrier gas, which transports the powder through the injectors, to allow the impact area of both particle types to be the same. For these conditions, the carrier gas flow would fall below the minimum flow, required for a continuous powder transport.

With the other injector setup enclosing a small angle between the particle jets, a more homogeneous distribution of the metal and glass splats could be obtained (Fig. 11b). Nevertheless, the microstructure of those coatings stays coarse, probably due to the big particle size of the glass balls with a d_{50} of about 20 μm. Thermal cycling of those coatings in the burner rig test showed very bad performance with failure during the first 5 cycles.

8. New Concept: Nanocrystalline Layer

An important failure mechanism of TBC in high temperature operation is the spall off of the ceramic topcoat. This mechanism is caused by the increase in thickness of a thermally grown oxide layer (TGO) between bondcoat and TBC. TGO is formed due to the oxidation of the bondcoat during operation. The standard TBC is not able to prevent oxidation due to cracks inside the coating.[32] The oxygen diffusion through YSZ is for the formation of a TGO of minor importance.

One option to prevent the catastrophic failure of spallation is to reduce the thermal mismatch between TBC and TGO/bond coat. For example, an additional more ductile interlayer might compensate the mismatch. Now the idea was that a coating with a nanocrystalline structure could create this tolerant interlayer.

A second idea to minimize the oxidation process is to bring in a gas-tight coating between the TBC and the bond coat. For this

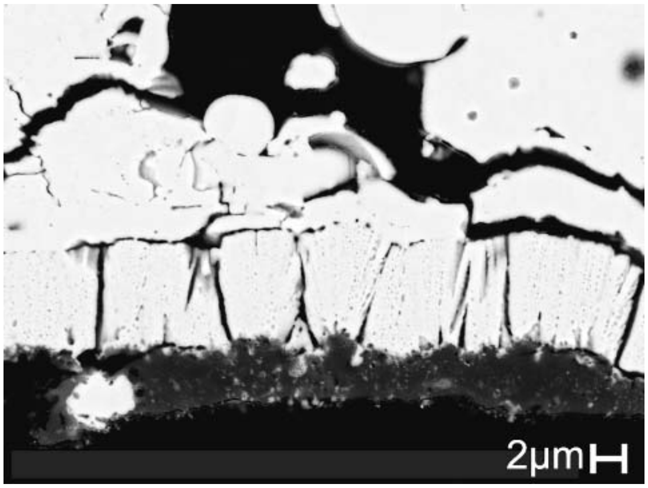


Fig. 13 SEM-picture of a PVD coating of YSZ, thickness 5.4 μm, on the top a TBC of YSZ

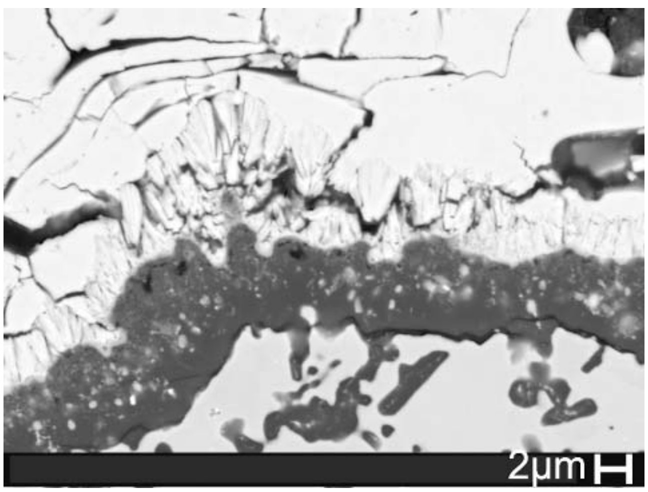


Fig. 14 SEM-picture of a MOCVD coating of YSZ, thickness 4.8 μm, on the top a TBC of YSZ

Table 3 Thermal Cycling Test of PVD and MOCVD Layers With an YSZ Topcoat; Cycle-Number Up to The First Failure

Coating	Figure	Thickness, μm	Cycles to Failure at 1250 °C (a)	Cycles to Failure at 1350 °C (a)
YSZ standard	…	300	3600	few hundred
YSZ/MOCVD	14	4,8	687	…
YSZ/PVD	13	5,4	580	513
YSZ/PVD	…	3,2	1324	432
LZ/PVD	12	1,5	1597	589

(a) Mean temperature at the surface of the thermal barrier coating

coating, it is important to have a thermal expansion coefficient comparable to those of the TBC and the bond coat, and the ductility of the coating should be high enough to stay gas tight during thermal cycling.

Nanocrystalline coating with these properties can be produced by physical vapor deposition (PVD) or by metal organic chemical vapor deposition (MOCVD). It is possible to get a layer with a few micron thicknesses, which is still dense. The complex coating process is described in detail by Teixera et al. and by Yang, Eastman, Soyez et al.[33-36]

In Fig. 12-14, PVD and MOCVD coatings of YSZ or $La_2Zr_2O_7$ are shown after a heat treatment in a burner rig. All these samples were coated with YSZ (Metco 204 NS, 300 μm thickness) before testing with the burner rig. The test results are presented in Table 3.

After the thermal cycling treatment, the coatings of YSZ have a lot of cracks through the PVD or MOCVD layer. Only $La_2Zr_2O_7$ has almost no cracks after the heat treatment (Fig. 12-14). This crack-free layer is nearly gas tight, which can be concluded from the very small increase of the TGO layer between bondcoat and the lanthanum zirconate nanolayer.

These first investigations on nanolayers between the bondcoat and the TBC topcoat show results that are not better than these of a single standard YSZ TBC at the moment. However, it is encouraging that these experiments—especially with lanthanum zirconate coatings—can reach the good properties of YSZ. Thus this concept might lead to improved TBCs after optimization of processes and materials.

9. Conclusion

This overview outlines a variety of promising candidate materials for a TBC application. Some of the materials and concepts showed at least partially improved properties compared with standard YSZ systems. In particular, the double-layer concepts prove to give superior performance compared with standard YSZ coatings at elevated temperatures.

The future will show if these materials will meet the expectations in a real gas turbine environment.

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