Proceedings of the International Gas Turbine Congress 2003 Tokyo
November 2-7, 2003

IGTC2003Tokyo TS-129

Recent Developments in the Field of Plasma-Sprayed Thermal Barrier Coatings

R. Vaßen, J.-E. Döring, M. Dietrich, H. Lehmann, D. Stöver

Institut für Werkstoffe und Verfahren der Energietechnik (IWV 1)
Forschungszentrum Jülich GmbH
D-52425 Jülich, Germany
FAX: +49-2461-612455, E-mail: r.vassen@fz-juelich.de

ABSTRACT

Thermal barrier coating (TBC) systems are widely used in gas turbines on thermally highly loaded parts as blades, vanes or combustion chamber to improve the performance of the engines. The standard plasma-sprayed systems consist of a vacuum plasma-sprayed (VPS) MCrAlY (M = Ni or Co) and an atmospherically plasma sprayed (APS) ceramic top layer made of yttria partially stabilised zirconia (YSZ). The performance of such coating systems is strongly related to details of the processing conditions and these relations are currently in industry of large interest. The paper will address the related topics of reproducibility and reliability of the standard TBC systems. Different procedures including on-line diagnostic tools to guarantee high reproducibility of the coatings will be presented.

Although an improved processing can significantly increase the performance of YSZ TBC systems, still a temperature limit exists for long term applications. Due to phase transformations and sintering effects a degradation of the coatings is observed which leads to failure of YSZ based coatings above about 1200°C. However, high surface temperatures are envisaged in gas turbines for a further increase of the efficiency. As a result, the investigation of new ceramics for a TBC application is world – wide a field of intense research.

Recent developments in this field of new thermal barrier coatings for gas turbine applications will be reviewed. A selection of suitable ceramic candidate materials as oxides with pyrochlore, perovskite, spinells, garnets, aluminates and also other structures will be presented.

In addition, the performance of coatings from these materials will be described focusing on our own work on thermal cycling. It turned out in the thermal cycling tests that most of the new TBCs show a relatively poor thermal cycling behavior. The reasons for these early failures were ascribed to the low fracture toughness of the new compositions. A solution to overcome this problem was found with the newly developed double - layer systems, which turned out to be a very promising concept. Results of systems with a two-layer TBC structure consisting of YSZ and pyrochlore materials will be given. At elevated surface temperatures beyond 1300 °C this concept leads to improved thermal cycling life times of at least a factor of 2 compared to the standard YSZ based system.

INTRODUCTION

The development of thermal barrier coatings started in the fifties of the last century with enamels coatings on components for military aero engines (Miller, 1997). With the beginning of the sixtieth century the first flame sprayed coatings were introduced (Bose, 1997) followed by a continuous development in the following decades (Miller, 1997, Bürgel, 1987). After the identification of 7 –8 wt. % yttria stabilised zirconia (YSZ) as a superior material for TBC applications, this material became a standard within the past twenty years (Czech, 2000, Wing, 2000). Although the subject is rather old still a large number of activities is focused on these coatings as is illustrated for example by the large number of overview publications in this field (Arnauld, 1999, Thornton, 1998, Stiger, 1999). Certainly, the large interest is also promoted by the meanwhile wide spread use of TBC systems in both aero and stationary gas turbines (Czech, 2000).

Manuscript Received on March 31, 2003

A typical TBC system consists of a metallic bondcoat layer and an insulative ceramic topcoat, usually YSZ. For mechanically and thermally highly loaded components of aero gas turbines often topcoat produced by electron beam physical vapour deposition (EB-PVD) are used with an underling platinum aluminide bondcoat (Stiger , 1999). As alternative, cost-effective process plasma-spraying is frequently used to deposit the ceramic top coat. In this case typically a vacuum plasma-sprayed MCrAlY (M=Ni,Co) bond coat is used which shows a good oxidation resistance and a high surface roughness (Vassen, 2001). This is essential for a sufficient adhesion of the top coat and hence, the performance of the TBC system. Recently, also high velocity oxygen fuel (HVOF) sprayed bond coats are under investigation as a cost-efficient alternative (Toma, 1999).

Plasma spraying is a complex process which depends on a large number of process variables (Fauchais, 2001). This complexity makes a control of the process and hence, of the microstructure of the coating, difficult. However, the potential of the TBC systems can only be fully used, if the scatter of the performance data is small. Otherwise, early failure of the coatings might occur and the operation temperatures have to be limited so that the integrity of the components without coating will be guaranteed till the next service interval.

Different measures can be taken to control the process in detail. A critical parameter for the performance of the TBC systems is the growth rate of the thermally grown oxide (TGO) formed on the bond coat during high temperature operation. Stresses introduced by this additional layer often lead to failure of the whole system (Vaßen, 2001). As the growth rate of the TGO depends on the chemical composition especially the amount of reactive elements in the bond coat (Clemens, 1997), an oxidation during vacuum plasma spraying should be avoided. Measures to control the oxygen partial pressure will be shown.

To achieve a high reproducibility of the performance of the ceramic top coat also the atmospheric plasma spraying process has to be controlled. Two different approaches will be presented, one based on particle diagnostic systems and one on monthly intervals reference coatings which are characterised by Hg - porosimetry

In addition to the reliability issue the search for alternatives of YSZ is a further important research topic (Jones, 1996, Vaßen, 1998, Vassen, 1999, Schäfer, 1999, Padture, 1997). The maximum surface temperatures of standard YSZ coatings is limited to about 1200°C for long-term operation. At higher application temperatures, which are envisaged for a further improvement of the efficiency of the gas turbines, the YSZ undergoes at least two detrimental changes. The porosity of the coating is reduced due to sintering effects. This leads to a reduction of the strain tolerance in combination with an increase of the Young´s modulus (Funke, 1998). Higher stresses will originate in the coating, which lead to a reduced life under thermal cyclic loading. The second failure mechanism is a phase change of the non-transformable t´-phase, which is present in the as-sprayed YSZ coating (Miller, 1981).

An ideal new thermal barrier coating material should combine a reduced thermal conductivity and an enhanced temperature capability compared to YSZ while the other critical properties (thermal expansion coefficient, corrosion resistance, etc.) should be comparable to the properties of YSZ.

Among the interesting candidates for thermal barrier coatings, those materials with pyrochlore structures and high melting points show promising properties. One of these candidates is $La_2Zr_2O_7$. Previous investigations show the excellent physical properties of this material, i.e. thermal conductivity below the values of YSZ and high thermal stability (Vassen, 1999). However, the thermal expansion coefficient is lower ($9 * 10^{-6}$/K) than the value of YSZ ($10 - 11 * 10^{-6}$/K), which leads to higher thermal stresses in the TBC system as the substrate and the bondcoat have higher thermal expansion coefficients (about $15 \cdot 10^{-6}$/K). In addition, no toughening effects are expected in the material as observed in YSZ (Harmsworth, 1992). As a result, the thermal cycling properties are expected to be not as good as those of YSZ coatings. This problem might occur for most of the new TBC materials, as the need for thermal stability seems to contradict the ability of transformation toughening. A way to overcome this shortcoming was found in the use of layered or graded topcoats (s. Fig.1). The failure of TBC systems often occur within the TBC close to the interface of the bondcoat – topcoat interface. At this location YSZ is used as a TBC material with a relatively high thermal expansion coefficient and high toughness. The YSZ layer is then coated by the new TBC material (e.g. $La_2Zr_2O_7$) which is able to withstand the typically higher temperatures at this location. In the present paper TBC systems with such double layers are compared to conventional YSZ coatings.

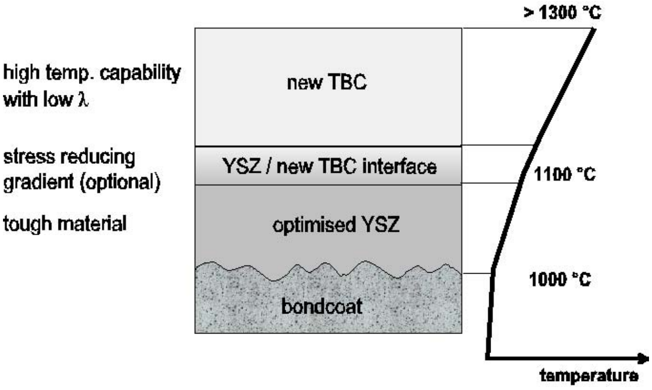


Fig. 1 A schematic drawing illustrating the principle of a double layer TBC systems.

EXPERIMENTAL

For the investigations VPS and APS industrial scale thermal spray facilities of Sulzer Metco, CH, have been used. Bond coat material were in most cases a NiCoCrAlY – powder (Ni 192-8) produced by Praxair Surface Technologies Inc., Indianapolis, IN. A F4 torch was used during VPS, the oxygen partials pressure in the chamber was measured with an oxygen sensor by Panametrics, USA. Typical thickness values of the bond coat are 150 µm

For the APS process mainly a three cathode gun (TRIPLEX I) was taken. The YSZ topcoat powder was a 7.8 wt.% yttria stabilized zirconia powder (Metco 204 NS) delivered by Sulzer Metco GmbH, Hattersheim, Germany. During topcoat deposition the argon and helium plasma gas flow rates were 20 and 13 standard liter per minute (slpm), the plasma current was 300 A, and the carrier gas flow 1.5 slpm. The feeding rate was 5 %, which corresponds to about 9 g/min. The spray gun was mounted on a 6 axis robot moving with a speed of 500 mm/s. The topcoat thickness was about 300 µm.

In a few cases also bond coats and complete YSZ systems delivered by Sulzer Metco have been used.

The pore size distributions of the topcoats were measured at free - standing coatings with mercury porosimetry using two units Pascal 140 and 440 produced by CE Instruments, Italy. Coatings were removed from the substrates by using hydrochloric acid.

The particle properties were monitored by the DPV2000 system (Tecnar Automation, Canada). The temperature was obtained by two-colour pyrometry, the velocity was measured by a time-of-flight method and the diameter was estimated from the emission of the particle.

New TBC materials as $LaYbO_3$ and $La_2Zr_2O_7$ have been produced via solid state reactions and subsequent spray drying to obtain flow-able powders with a suitable particle size distribution for plasma spraying.

For the evaluation of the performance of new TBC materials thermal cycling experiments have been used. Disc shaped nickel base superalloy IN738 substrates with a diameter of 30 mm were coated with a 150 mm bond coat and different ceramic topcoats.

Thermal cycling was performed in two gas burner test facilities operating with natural gas and oxygen. The substrates were cooled by compressed air from the back. The surface temperature was measured with a pyrometer operating at a wavelength of 8-11.5 µm and a spot size of 12 mm. For YSZ the emissivity for this wavelength was determined to be close to 1, which was taken as emissivity. Additionally, the substrate temperature was measured by a thermocouple mounted in a drilling. After 5 minutes the burner is automatically removed for 2 minutes from the surface and the surface is cooled from the front at a rate of more than 100 K/s using compressed air. Cycling was stopped when a clearly visible spallation of the coating occurred.

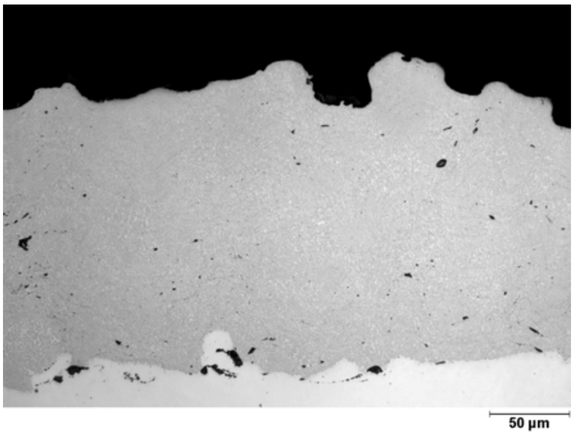
RESULTS AND DISCUSSION

Reliability

One possible way to guarantee a high degree of reliability of the coating process is the establishment of control routines in which the status of the coating facilities is evaluated. We follow this strategy by spraying and characterizing in monthly intervals coatings of well known bond coat (VPS) and topcoat (APS) materials using always the same process parameters. For both type of coatings polished sections will be investigated by optical microscopy. Typical examples are shown in Fig. 2. In Fig. 2a the low amount of porosity and the homogeneous microstructure (homogeneous distribution of γ and β phase within the coating) of the bond coat is obvious. This microstructure is important to avoid local deterioration of the properties which would result in a reduced performance of the whole TBC system. Fig. 2b reveals the porous, micro-cracked topcoat microstructure which is essential for the strain tolerance of the coatings.

In addition to the microstructural analysis, the oxygen level of the bond coat and the pore size distribution of the topcoat are determined during the monthly inspections. As pointed out before these two parameters are assumed to be critical for the TBC system performance. In order to control these parameters during the spraying process an oxygen sensor was introduced in the VPS chamber. The correlation of the oxygen partial pressure in the VPS chamber and the oxygen content is shown in Fig. 3. The oxygen content of the starting powder was about 400 ppm. The results indicate a rather linear dependence between the oxygen level in the coating and the oxygen partial pressure in the vacuum chamber. The scatter in the data indicates that the existence of additional factors which influence the oxygen level in the coating. These factors include deviations between the mean chamber pressure and the actual oxygen pressure close to the particles, variations in the initial oxygen level in the powders and others. Nevertheless the oxygen partial pressure in the chamber seems to be the major influencing factor and the control by the implementation of an oxygen sensor essential for the production of reliable coatings. In our institution a limit of the oxygen partial pressure in the chamber for the deposition of bond coats was defined which is fixed to 4500 ppm. It should ensure that the oxygen levels in the coatings are below about 650 ppm. This corresponds to an acceptable oxygen up-take during spraying of about 60%.

a)



b)

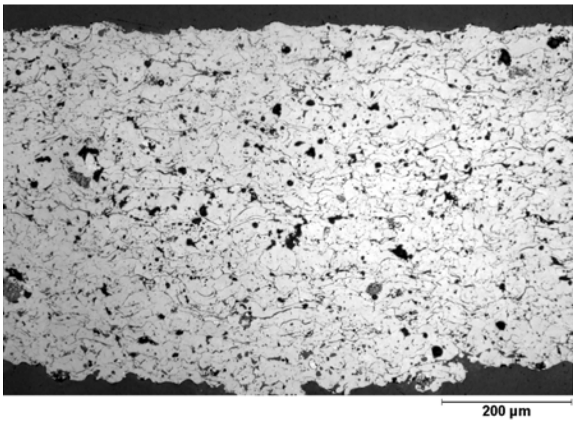


Fig. 2 Standard coatings used to control the performance of the VPS (a) NiCoCrAlY – bondcoat) and the APS (b) YSZ – topcoat) process.

For the manufacture of reliable topcoats the control of the APS process by particle diagnostic tools was considered. These tools are powerful in determining the correlation between process parameters and particle properties. An example is given in Fig. 4. The expected increase of particle temperature with increased current and reduced stand-off distance is clearly visible.

During the monthly spraying of topcoat standards also the mean temperature and velocity of the particles was measured at the maximum flow rate. The results are plotted in Fig. 5. While the velocity range is rather narrow between 136 and 152 m/s, the velocity increased considerably from the first investigation in November to the last in March from 2860 to 3100°C. In the pore size distributions given in Fig. 6 a slight decrease in the porosity levels from about 13.9 % to 12.6% is found. Although the

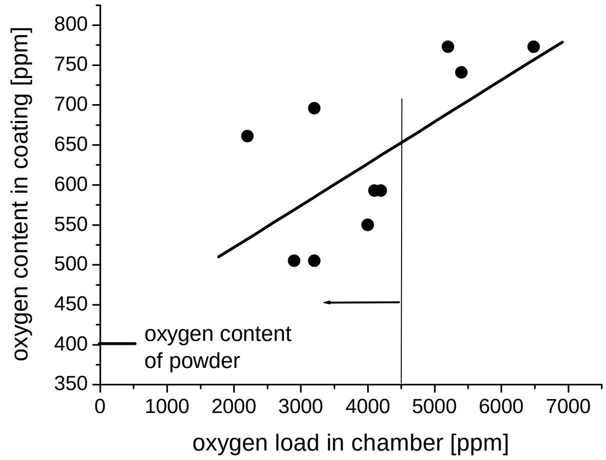


Fig. 3 Correlation between the oxygen partial pressure in the VPS chamber and the oxygen content in MCrAlY coatings. In addition, the oxygen content of the powders as well as the limit for bond coat

deposition is given.

differences in the pore size distributions are close to the scatter typically observed in Hg porosimetry measurements (<+/-0.5%) there seems to be a correlation between higher particle temperature and lower porosity levels, which was also found in earlier investigations. For the particle velocity no such clear correlation can be found.

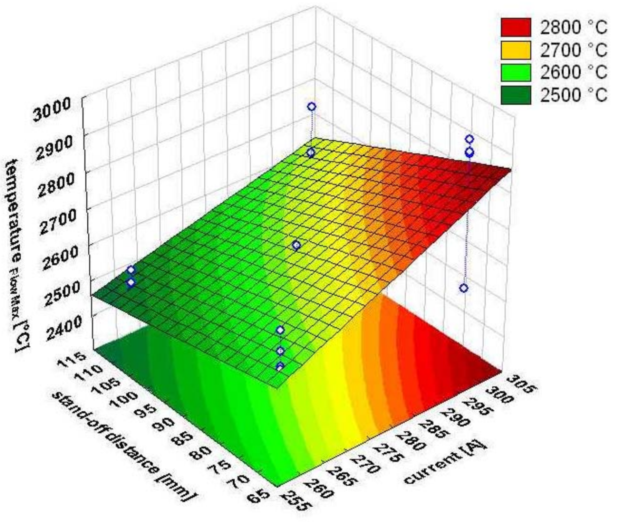


Fig. 4 The influence of plasma current and stand-off distance on the temperature of the particles at the maximum flow rate for a Triplex I torch.

Of special interest is also the power of the plasma gun, which is an easy determinable process parameter and sometimes used to control the process (see Fig.4). November and March coatings have similar power levels, however, they exhibit different porosity levels. Obviously, it seems to be impossible to control the microstructure of the coatings by a simple adjustment of the power level.

Additional experiments over longer periods of time will be performed to prove the given statements furthermore.

In addition, it should be kept in mind, that the particle properties are not determining solely the microstructure of the coating and hence, its performance. Also process parameters as substrate temperature, robot velocity or feeding rate play an important role.

Therefore future efforts are targeting on the development of monitoring tools for microstructural analysis during the spray process.

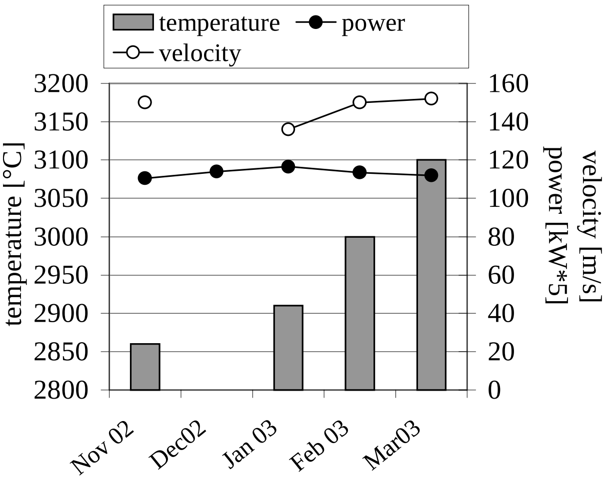


Fig. 5 Results of mean temperature and velocity measurements for subsequent months. Additionally, the power of the plasma gun is given.

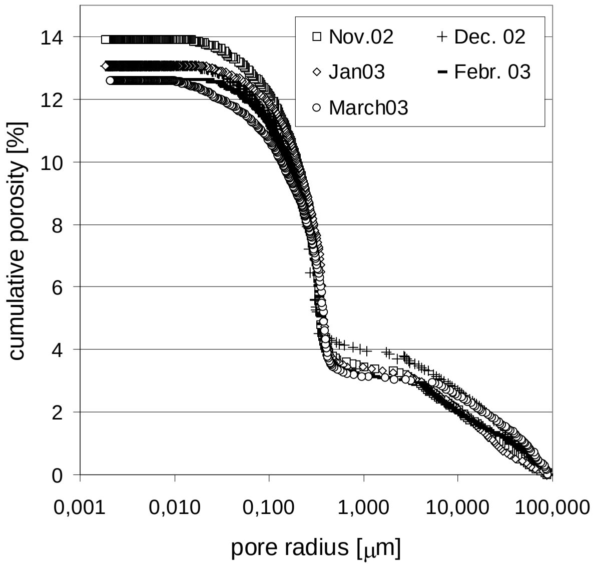


Fig. 6 Pore size distributions of YSZ coatings measured by Hg porosimetry sprayed in subsequent months with equal process parameters.

New thermal barrier coatings

As discussed in the introduction different materials mainly oxide ceramics have been investigated with respect to an application as TBC material. A number of different oxides is listed in Table 1. Certainly the given properties can only be a rough estimation as different materials belonging to the same group of oxides can show distinct differences in their properties. This can be used to design ideal materials by substituting certain elements in the composition. This will be discussed later. From our own results and the information found in literature it will be tried to give some rough summarizing information on the different materials:

Perovskites seem to have often a rather low thermal and chemical stability, although the physical properties are rather encouraging.

Several of the pyrochlores show good physical properties and sufficient stability. However, low toughness values make it necessary to use double layer systems, i.e. first a layer of YSZ and then one of the new ceramic,.

Spinels have no optimal physical properties, but application might be possible, maybe also in a double layer system.

Garnets and mullite doesn´t show adequate physical properties.

Oxides with the magnetoplumbite structure reveal very interesting, encouraging properties. A major problem is the typically high amount of amorphous phase in the sprayed coatings.

Ceria seems to have too high sintering rates for a high temperature application.

All these materials can be further optimized by doping them with certain elements. An example is the doping of $La_2Zr_2O_7$ with rare earth elements. Substitution of La by 30 % Gd reduces the thermal conductivity of the bulk material at 800°C from 1.6 W/m/K to about 0.9 W/m/K (Lehmann, 2002).Similar effects have also been found for perovskite type materials (Bast, 2002).

Besides adequate physical properties also the performance of the whole TBC system under realistic operation conditions is essential for an application of new materials as TBCs. Unfortunately hardly any results are published on these issues so far. We can therefore report only on our own results.

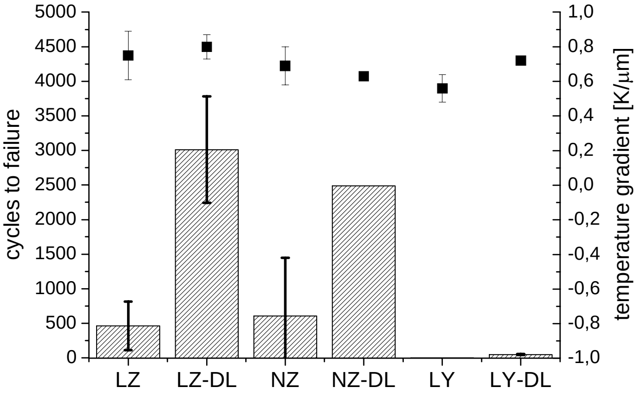


Fig. 7 Cycles to failure of different new TBC systems (LZ = $La_2Zr_2O_7$, NZ = $Nd_2Zr_2O_7$, LY = $LaYbO_3$, DL = double layer) at a surface temperature between 1200 and 1260°C and a bond coat temperature between 970 and 1030 °C (1070°C for $LaYbO_3$). In addition, the mean temperature gradient across the TBC is given.

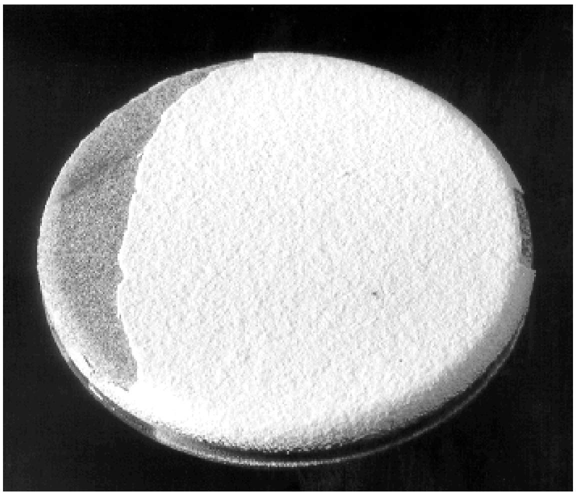


Fig. 8 $La_2Zr_2O_7$ single layer TBC after 960 cycles with a mean bond coat and surface temperatures of 1010°C and 1241°C, respectively.

Gas burner test facilities have been used to evaluate the performance in our institute. At first, results will be discussed for moderate surface temperatures. In Fig. 7 the cycles to failure for pyrochlore and perovskite based systems are shown. For the investigated systems the cycle number to failure is considerably higher for the double layer systems. In case of the single layer systems large parts of the coatings spalled off very early before a thick TGO has grown. An example of such a failure is shown in Fig. 8. The double layer systems made of pyrochlore materials exhibit at the moderate surface temperatures life times comparable to standard YSZ systems. For the given temperatures the failure is driven in the new double layer and standard YSZ systems by the growth of the TGO and the stresses arising from this growth. The cycles to failure for the given bond coat temperature range (970°C to 1030°C) are for both systems between about 1500 and 5000 cycles.

Also for the $LaYbO_3$ system the double layer approach could significantly enhance the performance. However, it is still worse than for a standard YSZ at the used the bond coat temperature (1070°C) which is about 500 cycles.

It should be noted that the TBC thickness was similar for all coatings between 280 and 460 µm, which is also shown by the rather low variation in the thermal gradient across the coatings (s. Fig. 7). As a result, the improved performance of the double layer system is not caused by different coating thickness.

Whereas for moderate surface temperatures the performance of pyrochlore based double layer systems is comparable to the standard YSZ systems, a distinct difference is observed for higher surface temperatures. In Fig. 9 the number of cycles to failure is plotted as a function of the surface temperature for standard YSZ and double layer systems using $La_2Zr_2O_7$ and in one case $Nd_2Zr_2O_7$ as the second layer. In this plot only high surface temperatures above 1320 °C are considered.

Obviously the double layer systems perform much better than the YSZ systems at high temperatures. While for the YSZ the number

Table 1 Summary of some materials investigated for an application as TBC material.
(λ thermal conductivity, α thermal expansion coefficient, E Young´s modulus, additional information also from Bast, 2002)

Material	**Examples**	**Paper**	**Patent**	**Properties**
Perovskite	$BaZrO_3$, $SrZrO_3$	Vassen, 1999	Beele et al., Siemens, 1999	Medium to high λ, medium to high α, rather low stability
	$REAlO_3$, $LaYbO_3$	Dietrich, 2003	R. Subramanian et al., Siemens, 1999	Improved (claimed) or reduced (published) phase stability, reduced sintering, reduced toughness
Pyrochlores	$A_{1/2}B_2O_{6/7}$	Vassen, 1999	Maloney, United Technolgy Corp. + others, 1996	Improved thermal/chemical stability, reduced α, low λ, low toughness
	$A_{2-x}B_{2+x}O_{7-y}$ $(La/Gd)_2Hf_2O_7$		R. Subramanian, Siemens, 1999, 2000	Improved phase stability, reduced sintering
Spinels	e.g. $MgAl_2O_4$		Beele et al., Siemens, 1999	Low α, high λ, reduced toughness
Garnets	$(Y/Gd/Er/La)_3Al_5O_{12}$	Padture, 1997		Higher λ compared to YSZ
	$(Y/Dy)_3Al_5O_{12}$		R. Subramanian et al., Siemens, 1999	Improved phase stability, reduced sintering
Magnetoplumbite	$(La/Nd)MeAl_{11}O_{19}$ Me e.g Mg	Schäfer, 1999, Gadow, 2002, University Stuttgart	Gadow et al., University Stuttgart, 1998, 2000	Reduced sintering, λ and α comparable to YSZ, E reduced, high amorphous amount after spraying
Ceria	CeO_2	J. Wilden, 1998, University Chemnitz		Diffusion into MCrAlY, high sintering rate
Mullite	$Si_2Al_6O_{13}$	K. Kokini, 1996, Purdue University		Reduced HT-relaxation, for thick TBCs (low T), low α, high λ

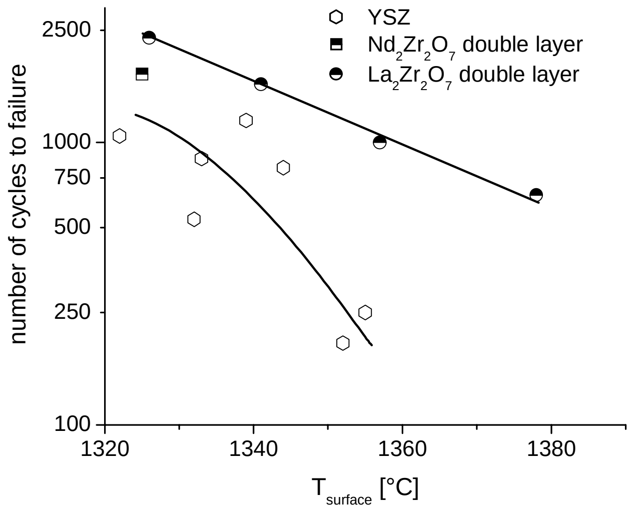


Fig. 9 Number of cycles to failure for standard YSZ systems (also those of Sulzer Metco) and double layer systems consisting of a YSZ and a $La_2Zr_2O_7$ (in one case a $Nd_2Zr_2O_7$) - layer.

of cycles to failure drop down drastically at 1350 °C to values below 250 cycles it is still above 1000 cycles for the new system and remains high at even higher temperatures. The microstructural analysis of both systems reveal distinct differences in the failure mode. In the YSZ systems the ceramic top coat spalls off within the ceramic starting from the surface. In contrast, the double layer systems shows a spallation close to the interface bond coat – topcoat. This fact indicates that TGO growth is mainly responsible for the failure, hence, even longer life times can be expected with improved bond coats. Further details on the performance of double layer systems are also found in Vassen, 2002.

It should be stated that new double layer systems with new ceramics on top can be produced with similar reproducibility or reliability as conventional YSZ based TBCs. As prerequisites commercial powders with well defined properties have to be available and the used thermal spray facilities should have at least two separate powder feeding systems.

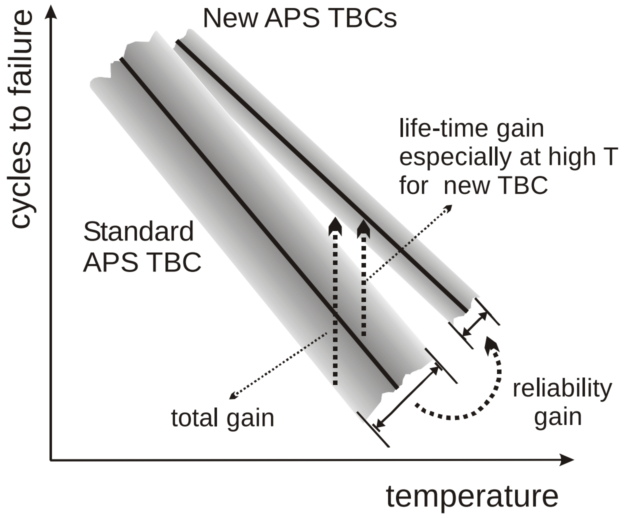


Fig. 10 Schematic drawing of the correlation between performance gain by improved reliability and improved temperature capability of TBCs.

In Fig. 10 the influence of the two described strategies for an improvement of the performance of TBCs is presented in a schematic form. The reliability target mainly reduces the scatter of the life time data. By this approach a significant temperature gain can be realized. The development of new TBC improves the temperature capability and hence, the life time especially at high temperatures.

As shown in the present paper both strategies offer a large potential for the further improvement of TBC systems.

SUMMARY

Two important directions of developement in the field of plasma-sprayed thermal barrier coatings have been described in the present paper.

The first development adresses the processing of plasma-sprayed coatings and targets on an improvement of the reliability of the coatings. Several measures to ensure reliable TBC systems have been described, for example particle diagnostic tools, oxygen sensors, and monthly sprayed reference coatings.

For the second development, the one of new TBC materials, an overview of the activities described in literature was given. In addition, our own results on perovskite and pyrochlore based systems have been described. The developed double layer systems show in the gas burner test facilities at elevated temperatures above 1300 °C a much better performance than standard YSZ system.

Both strategies offer a large potential for the further improvement of TBC systems and should therefore be followed in parallel.

ACKNOWLEDGEMENT

The authors would like to thank Mr. K.H. Rauwald and Mr. R. Laufs (both IWV1, FZ Jülich) for the manufacture of the plasma-sprayed coatings and Dr. F. Traeger and Mrs. A. Lemmens for assistance during the thermal cycling of the specimens. The authors also gratefully acknowledge the work of Mrs. S. Schwartz-Lückge and Mr. M. Kappertz (both IWV1, FZ Jülich) who performed the characterization of most of the specimens. Also the coating of samples by Sulzer Metco, Wohlen, CH, within the COST 522 program is gratefully acknowledged.

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