# Ceramic materials for thermal barrier coatings

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## Abstract

This paper summarizes the basic properties of ceramic materials for thermal barrier coatings. Ceramics, in contrast to metals, are often more resistant to oxidation, corrosion and wear, as well as being better thermal insulators. Except yttria stabilized zirconia, other materials such as lanthanum zirconate and rare earth oxides are also promising materials for thermal barrier coatings.
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## 1. Introduction

During the past decade, research efforts were devoted to the development and manufacturing of ceramic thermal barrier coatings (TBCs) on turbine parts because the traditional turbine material have reached the limits of their temperature capabilities. TBCs are deposited on transition pieces, combustion lines, first-stage blades and vanes and other hot-path components of gas turbines either to increase the inlet temperature with a consequent improvement of the efficiency or to reduce the requirements for the cooling system.[1–3]

The earliest ceramic coatings for aerospace applications were frit enamels developed by the National Advisory Committee for Aeronautics (NACA) and the coating of calcia stabilized zirconia on the exhaust nozzle of the X-15 manned rocket plane in 1960s is believed to be the first use of TBCs in manned flight.[4] The working parts of aircraft jet engines are subjected to serve mechanical, chemical and thermal stresses. Several ceramic coatings such as $Al_2O_3$, $TiO_2$, mullite, $CaO/MgO + ZrO_2$, YSZ, $CeO_2 + YSZ$, zircon and $La_2Zr_2O_7$, etc. have been evaluated as TBC materials.

The selection of TBC materials is restricted by some basic requirements: (1) high melting point, (2) no phase transformation between room temperature and operation temperature, (3) low thermal conductivity, (4) chemical inertness, (5) thermal expansion match with the metallic substrate, (6) good adherence to the metallic substrate and (7) low sintering rate of the porous microstructure.[1,5] The number of materials that can be used as TBCs is very limited. So far, only a few materials have been found to basically satisfy these requirements. This paper is believed to be the first review about the ceramic TBC materials and is helpful to the selection of TBC materials. In Ref. 6 the development of new TBC systems is described. The following are TBC materials under investigation.

Properties of some ceramics that can be used in TBC system are summarized in Table 1. Among those properties, thermal expansion coefficient and thermal conductivity seem to be the most important. These data are collected from different references and hence may not be complete. Metal substrate and bond coats are also included for comparison. The number before yttria stabilized zirconia (YSZ) represents the weight percentage of $Y_2O_3$ in $ZrO_2$. The advantages and disadvantages of other TBC materials are compared with YSZ and listed in Table 2. The improvement techniques of YSZ coatings are also summarized in this table.

## 2. Materials for TBCs

### 2.1. YSZ

7-8YSZ is the most widely studied and used TBC material because it provides the best performance in

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Table 1
Properties of TBC materials

| Materials | Properties | Materials | Properties |
|---|---|---|---|
| $ZrO_2$ | $T_m = 2973$ K[7] <br> $D_{th} = 0.43 \times 10^{-6}$ m$^2$ s$^{-1}$ (1273 K)[8] <br> $\lambda = 2.17$ W m$^{-1}$ K$^{-1}$ (1273 K)[9] <br> $E = 21$ GPa (1373 K)[10] <br> $\alpha = 15.3 \times 10^{-6}$ K$^{-1}$ (1273 K)[11] <br> $\nu = 0.25$[10] | $La_2Zr_2O_7$ | $T_m = 2573$ K[12] <br> $D_{th} = 0.54 \times 10^{-6}$ m$^2$ s$^{-1}$ (1273 K)[5] <br> $C_p = 0.49$ J g$^{-1}$ K$^{-1}$ (1273 K)[5] <br> $\lambda = 1.56$ W m$^{-1}$ K$^{-1}$ (1273 K)[5] <br> $E = 175$ GPa (293 K)[17] <br> $\alpha = 9.1 \times 10^{-6}$ K$^{-1}$ (293–1273 K)[5] |
| 3YSZ | $T_m = 2973$ K[12] <br> $D_{th} = 0.58 \times 10^{-6}$ m$^2$ s$^{-1}$ (1273 K)[5] <br> $\lambda = 2.12$ W m$^{-1}$ K$^{-1}$ (1273 K)[5] <br> $C_p = 0.64$ J g$^{-1}$ K$^{-1}$ (1273 K)[5] <br> $\alpha = 11.5 \times 10^{-6}$ K$^{-1}$ (293–1273 K)[5] | $BaZrO_3$ | $T_m = 2963$ K[12] <br> $D_{th} = 1.25 \times 10^{-6}$ m$^2$ s$^{-1}$ (1273 K)[5] <br> $C_p = 0.45$ J g$^{-1}$ K$^{-1}$ (1273 K)[5] <br> $\lambda = 3.42$ W m$^{-1}$ K$^{-1}$ (1273 K)[5] <br> $E = 181$ GPa (293 K)[17] <br> $\alpha = 8.1 \times 10^{-6}$ K$^{-1}$ (293–1273 K)[5] |
| 8YSZ (plasma-sprayed) | $E = 40$ GPa (293 K)[13] <br> $\alpha = 10.7 \times 10^{-6}$ K$^{-1}$ (293–1273 K)[13] <br> $\nu = 0.22$[13] | | |
| 18YSZ | $\alpha = 10.53 \times 10^{-6}$ K$^{-1}$ (1273 K)[8] | $TiO_2$ | $T_m = 2098$ K[18] <br> $D_{th} = 0.52 \times 10^{-6}$ m$^2$ s$^{-1}$ (1073 K)[8] <br> $\lambda = 3.3$ W m$^{-1}$ K$^{-1}$ (1400 K)[10] <br> $E = 283$ GPa (293 K)[10] <br> $\alpha = 9.4 \times 10^{-6}$ K$^{-1}$ (293–1500 K)[10] <br> $\nu = 0.28$[10] |
| 5 wt.% CaO + $ZrO_2$ | $T_{softening} = 2558$ K[7] <br> $E = 149.3$ GPa (293 K)[7] <br> $\alpha = 9.91 \times 10^{-6}$ K$^{-1}$ (1273 K)[8] <br> $\nu = 0.28$[7] | | |
| Mullite | $T_m = 2123$ K[14] <br> $\lambda = 3.3$ W m$^{-1}$ K$^{-1}$ (1400 K)[10] <br> $E = 30$ GPa (293 K)[15] <br> $\alpha = 5.3 \times 10^{-6}$ K$^{-1}$ (293–1273 K)[16] <br> $\nu = 0.25$[10] | Garnet ($Y_3Al_5O_{12}$) | $T_m = 2243$ K[19] <br> $\alpha = 9.1 \times 10^{-6}$ K$^{-1}$[19] <br> $\lambda = 3.0$ W m$^{-1}$ K$^{-1}$ (1273 K)[19] |
| $Al_2O_3$ | $T_m = 2323$ K[9] <br> $D_{th} = 0.47 \times 10^{-6}$ m$^2$ s$^{-1}$ (1273 K)[8] <br> $\lambda = 5.8$ W m$^{-1}$ K$^{-1}$ (1400 K)[10] <br> $E = 30$ GPa (293 K)[10] <br> $\alpha = 9.6 \times 10^{-6}$ K$^{-1}$ (1273 K, this work) <br> $\nu = 0.26$[10] | Lanthanum aluminate ($LaMgAl_{11}O_{19}$) | $\lambda = 1.7$ W m$^{-1}$ K$^{-1}$ (1273 K)[20] <br> $\alpha = 10.1 \times 10^{-6}$ K$^{-1}$ (298–1473 K)[21] <br> $C_p = 0.86$ J g$^{-1}$ K$^{-1}$ (1273 K)[20] |
| $Al_2O_3$ (TGO) | $E = 360$ GPa (293 K)[13] <br> $\alpha = 8 \times 10^{-6}$ K$^{-1}$ (293–1273 K)[13] <br> $\nu = 0.22$[13] | $LaPO_4$ | $T_m = 2343$ K[22] <br> $\lambda = 1.8$ W m$^{-1}$ K$^{-1}$ (973 K)[22] <br> $\alpha = 10.5 \times 10^{-6}$ K$^{-1}$ (1273 K)[23] <br> $E = 133$ Gpa (293 K)[23] <br> $\nu = 0.28$ (293 K)[23] |
| $Al_2O_3$ + $TiO_2$ | $D_{th} = 0.65 \times 10^{-6}$ m$^2$ s$^{-1}$ (1273 K)[8] <br> $\alpha = 5.56 \times 10^{-6}$ K$^{-1}$ (1073 K)[8] | NiCoCrAlY (bond coat of TBC) | $E = 86$ GPa (293 K)[13] <br> $\alpha = 17.5 \times 10^{-6}$ K$^{-1}$ (293–1273 K)[13] <br> $\nu = 0.3$[13] |
| $CeO_2$ | $T_m = 2873$ K[9] <br> $D_{th} = 0.86 \times 10^{-6}$ m$^2$ s$^{-1}$ (1273 K)[5] <br> $C_p = 0.47$ J g$^{-1}$ K$^{-1}$ (1273 K)[5] <br> $\lambda = 2.77$ W m$^{-1}$ K$^{-1}$ (1273 K)[5] <br> $E = 172$ GPa (293 K)[10] <br> $\alpha = 13 \times 10^{-6}$ K$^{-1}$ (293–1500K)[10] <br> $\nu = 0.27–0.31$[10] | IN737 supperalloy (Substrate of TBC) | $E = 197$ GPa (293 K)[13] <br> $\alpha = 16 \times 10^{-6}$ K$^{-1}$ (293–1273 K)[13] <br> $\nu = 0.3$[13] |

Symbols in Table 1 have the following meanings: $D_{th}$, thermal diffusivity; $E$, Young's modulus; $\alpha$, thermal expansion coefficient; $\lambda$, thermal conductivity; $C_p$, heat capacity; $\nu$, Poisson's number; $T_m$, melting point; TGO, thermally grown oxide on bond coat.

high-temperature applications such as diesel engines and gas turbines,[27,29,33,35−40] and reports about this material are numerous. YSZ coating has been proved to be more resistant against the corrosion of $Na_2SO_4$ and $V_2O_5$ than the $ZrO_2$ coating stabilized by CaO or MgO.[36] 18-20YSZ coatings has also been studied.[24,41] A

major disadvantage of YSZ is the limited operation temperature ($<1473$ K) for long-term application. At higher temperatures, phase transformations from the $t'$-tetragonal to tetragonal and cubic ($t + c$) and then to monoclinic ($m$) occur, giving rise to the formation of cracks in the coating.[5,42] A practical upper-use tem-

Table 2
TBC materials and their characteristics

| Materials | Advantages | Disadvantages |
|---|---|---|
| 7-8 YSZ | (1) high thermal expansion coefficient<br>(2) low thermal conductivity<br>(3) high thermal shock resistance | (1) sintering above 1473 K<br>(2) phase transformation (1443 K)<br>(3) corrosion<br>(4) oxygen-transparent |
| Mullite | (1) high corrosion-resistance<br>(2) low thermal conductivity<br>(3) good thermal-shock resistance below 1273 K<br>(4) not oxygen-transparent | (1) crystallization (1023-1273 K)<br>(2) very low thermal expansion coefficient |
| Alumina | (1) high corrosion-resistance<br>(2) high hardness<br>(3) not oxygen-transparent | (1) phase transformation (1273 K)<br>(2) high thermal conductivity<br>(3) very low thermal expansion coefficient |
| $YSZ + CeO_2$ | (1) high thermal expansion coefficient<br>(2) low thermal conductivity<br>(3) high corrosion-resistance<br>(4) less phase transformation between m and t than YSZ<br>(5) high thermal-shock resistance | (1) increased sintering rate<br>(2) $CeO_2$ precipitation ($> 1373$ K)<br>(3) $CeO_2$-loss during spraying |
| $La_2Zr_2O_7$ | (1) very high thermal stability<br>(2) low thermal conductivity<br>(3) low sintering<br>(4) not oxygen-transparent | (1) relatively low thermal expansion coefficient |
| Silicates | (1) Cheap, readily available<br>(2) high corrosion-resistance | (1) decomposition into $ZrO_2$ and $SiO_2$ during thermal spraying<br>(2) very low thermal expansion coefficient |

Improvement of YSZ TBCs: (1) post-deposition of the coating with sealants[24,25] or laser irradiation of the coating surface[26] for better corrosion resistance; (2) gradient,[6,27,28] or multilayered,[6,29–32] coatings with other materials; (3) thick TBC for better thermal insulation.[33,34]

perature of 1223 K in gas turbine for the $ZrO_2$ coating stabilized by CaO and MgO was reported.[4] On the other hand, these coatings, possess a high concentration of oxygen ion vacancies, which at high temperature assist oxygen transport and the oxidation of the bond coat at the ceramic–bond coat interface, namely the formation of thermally grown oxide (TGO) on the bond–coat surface. This leads to spallation of the ceramic and such a mode of failure of the TBC is predominant when the coatings are thin as in gas turbines. This problem has been overcome to a large extent by providing oxidation resistant bond coats such as alumina and mullite.[43] A model of life prediction of TBCs has been developed, in which the coating failure was attributed to stresses arising from the formation of TGO,[13] and in Fig. 1 is shown the relationship between the thermal cycling life of TBCs and the substrate temperature.[6]

The silica impurity (even as low as 1 wt.%) in YSZ coating has a strong detrimental effect on the thermal cycling life.[44,45] In bulk zirconia-based ceramics, silica segregates to grain boundaries with excessive amounts collecting at triple points. Silica at the grain boundaries leads to changes in the size and shape of grains and it may dissolve $Y_2O_3$ from the YSZ grain boundary regions leading to localized destabiliza-

tion.[45] Silica can also cause $ZrO_2$ polycrystal superplasticity, dramatic increases in sintering rates, and decreases in electrical conductivity. It may also lead to increased creep rates, as has been observed with silicon-base ceramics.[45] However, silicates have much lower
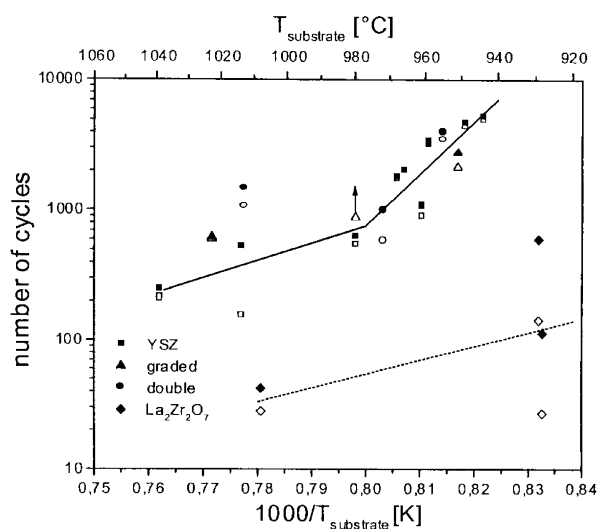


Fig. 1. Thermal cycling lives of TBCs as a function of the substrate temperature. (After Ref. 6. Reprinted with permission of the American Ceramic Society, copyright 2002. All rights reserved.).

oxygen conductivity than YSZ, and a thin layer of silicates on the top of the bond coat as oxygen barrier might improve the oxidation resistance of the bond coat.[46]

## 2.2. Mullite

Mullite is an important ceramic material because of its low density, high thermal stability, stability in severe chemical environments, low thermal conductivity and favorable strength and creep behavior.[47] It is a compound of $SiO_2$ and $Al_2O_3$ with composition $3Al_2O_3 \cdot 2SiO_2$. Compared with YSZ, mullite has a much lower thermal expansion coefficient and higher thermal conductivity, and is much more oxygen-resistant than YSZ. For the applications such as diesel engines where the surface temperatures are lower than those encountered in gas turbines and where the temperature variations across the coating are large, mullite is an excellent alternative to zirconia as a TBC material. Engine tests performed with both materials show that the life of the mullite coating in the engine is significantly longer than that of zirconia.[15,48] Above 1273 K, the thermal cycling life of mullite coating is much shorter than that of YSZ.[43] mullite coating crystallizes at 1023–1273 K, accompanied by a volume contraction, causing cracking and de-bonding.[43] Mullite is the most promising coating material for the SiC substrate because their thermal expansion coefficients are similar.[16]

## 2.3. $Al_2O_3$

$\alpha$-$Al_2O_3$ is the only stable phase among all aluminum oxides. It has very high hardness and chemical inertness. The erosion behavior of vacuum plasma sprayed and air plasma sprayed alumina coatings has been studied and compared with that of bulk material.[49] The addition of a certain amount of alumina into YSZ coatings can improve the hardness and bond strength without substantial modification of Young's modulus and toughness.[50–52] The hardness of the coating can also be achieved by spraying an outer coat of alumina onto YSZ coatings.[52] However, the plasma sprayed coating of alumina contains mainly unstable phases such as $\gamma$ and $\delta$-$Al_2O_3$. These unstable phases will transform into $\alpha$-$Al_2O_3$ during thermal cycling, accompanied by a significant volume change ($\gamma \rightarrow \alpha$, $\sim$15%) which results in microcrack formation in the coating.[53,54] The doping of transition metal oxides such as $Cr_2O_3$, $Fe_2O_3$ and $TiO_2$ into alumina can only partially stabilize the $\alpha$ phase. On the other hand, alumina has relatively high thermal conductivity and low thermal expansion coefficient compared with YSZ.[5] The mechanical properties of alumina coating can be significantly improved by the incorporation of silicon carbide fibers.[55] Even though alumina alone is not a good TBC candidate, its addition to YSZ can increase the hardness of the coating and improve the oxidation resistance of the substrate. A gradient coating of 8YSZ–$Al_2O_3$ has a much longer thermal cycling life than that of 8YSZ coating.[28]

## 2.4. $CeO_2 + YSZ$

$CeO_2$ has higher thermal expansion coefficient and lower thermal conductivity than YSZ, and the addition of $CeO_2$ into YSZ coating is supposed to be effective for the improvement of thermal cycling life. Remarkable improvement of thermal shock tolerability was attained by the addition of $CeO_2$ into YSZ.[56–58] The ceria-doped coating has a better thermal shock resistance because mainly:[59] (1) there is little phase transformation between the monoclinic and tetragonal phase in the $CeO_2 + YSZ$ coating; (2) stress generated by bond coat oxidation is smaller in the $CeO_2 + YSZ$ coating due to better thermal insulation; (3) the thermal expansion coefficient is larger in the $CeO_2 + YSZ$ coating. However, the addition of $CeO_2$ has some negative effects, such as the decrease of hardness and stoichiometry change of the coating due to the vaporization of $CeO_2$,[56] reduction of $CeO_2$ into $Ce_2O_3$ and accelerated sintering rate of the coating.[60,61]

## 2.5. $La_2Zr_2O_7$

$La_2Zr_2O_7$ (LZ) was recently proposed as a promising TBC material.[5,6,12,17,30,62,63] It has a cubic pyrochlore structure which has been discussed in detail by Subramanian et al.[64] The crystal structure consists of the corner-shared $ZrO_6$ octahedra forming the back bone of the network and $La^{3+}$ ions fill the holes which are formed by 6 $ZrO_6$ octahedra. It can largely tolerate vacancies at the $La^{3+}$, $Zr^{4+}$ and $O^{2-}$-sites without phase transformation. Both $La^{3+}$ and $Zr^{4+}$-sites can be substituted by a lot of other elements with similar ionic radii in case the electrical neutrality is satisfied, giving rise to the possibility of its thermal properties to be tailored. It is one of the few oxides with pyrochlore structure (such as $La_2Zr_2O_7$, $La_2Hf_2O_7$, $Pr_2Hf_2O_7$, $Ce_2Zr_2O_7$ and $Sm_2Ti_2O_7$) that are phase-stable up to their melting points (Fig. 2) and this is a major reason that it is believed to have potential as TBC material. On the other hand, $La_2Zr_2O_7$ has even lower thermal conductivity than YSZ. However, the coating of this material did not give a longer thermal cycling life than YSZ coating which might be explained by its relatively low thermal expansion coefficient and poor toughness.[63] By the substitution of $CeO_2$ for $ZrO_2$ (LC), the thermal expansion coefficient of the coating can be increased and its thermal cycling life is largely improved (Fig. 3), comparable with or even better than the standard coating material 8YSZ.[6]
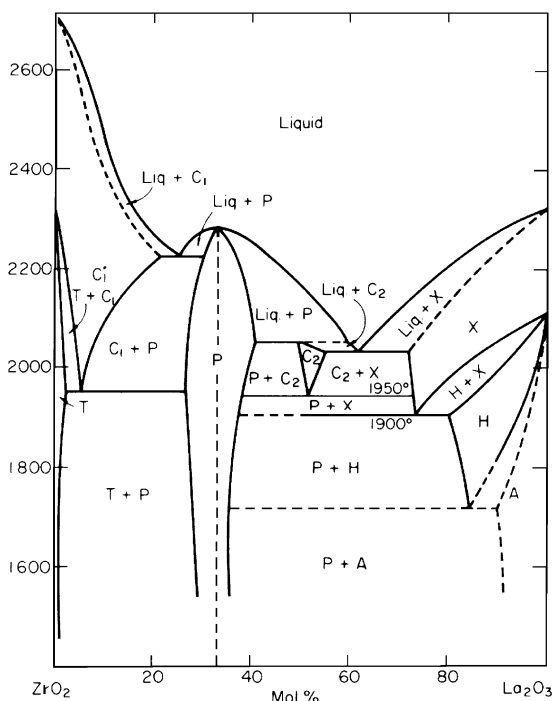
Fig. 2. Phase diagram of $La_2O_3$–$ZrO_2$ system. (After Ref. 65. Reprinted with permission of the American Ceramic Society, copyright 2002. All rights reserved.)

## 2.6. Silicates

From the whole wide group of silicates, only the spraying of zircon $(ZrSiO_4)$[66] or natural zircon sand[67] is occasionally reported. Zircon has a low thermal expansion coefficient $(4.99 \times 10^{-6}$ $K^{-1}$, 300–1700 K) and high thermal conductivity $(3.46$ W $m^{-1}$ $K^{-1}$, 365–1810 K).[7] It is chemically very stable, particularly at lower temperatures. With the exception of concentrated hydrofluoric acid, zircon is not generally attacked by acids but by basic materials at elevated temperatures. Zircon has no true melting point as it dissociates before melting. The thermal decomposition of zircon occurs at 1949 K or even as low as 1558 K depending on the purity.[68] During plasma spraying, zircon dissociates and consequently coatings are composed of a mixture of crystalline $ZrO_2$ and amorphous $SiO_2$. When using zircon as TBC for diesel engines, the decomposed $SiO_2$ in the coating may cause problems due to the evaporation of SiO and $Si(OH)_2$.[69] The barrier effect is supposed to be due to the $ZrO_2$ phase in the coating.[67] Quite a few other silicates are relatively cheap and readily available and have potential as TBC materials, such as garnet almandine $Fe_3Al_2(SiO_4)_3$, garnet pyrope $Mg_3Al_2(SiO_4)_3$, garnet andradite-grossular $Ca_3Al_2(SiO_4)_3$, basalt (glass).[66] The coating of composite oxides $2CaO \cdot SiO_2$-10 to 30 wt.% $CaO \cdot ZrO_2$ shows excellent thermal shock resistance and hot corrosion.[26]

## 2.7. Rare earth oxides

The mixture of rare earth oxides is readily available and very cheap. The coatings of rare earth oxides $(La_2O_3, CeO_2, Pr_2O_3$ and $Nb_2O_5$ as main phases) have lower thermal diffusivity and higher thermal expansion coefficient than $ZrO_2$, and they have the potential as thermal barrier coatings.[70] No further reports about this material are available. Most of the rare earth oxides are polymorphic at elevated temperatures,[71] and the phase instability will certainly to some extent affect the thermal shock resistance of their coatings.

## 2.8. Metal–glass composite

This is totally a new TBC system.[72,73] The powder mixture of metal and normal glass can be plasma-sprayed in vacuum. For a suitable composition this TBC material has similar thermal expansion coefficient with metal substrate and its thermal conductivity is about a factor of 2 larger than that of YSZ. There are basically three reasons for the long thermal cycling life of metal-glass TBC, namely high thermal expansion coefficient $(12.3 \times 10^{-6}$ $K^{-1})$, good adherence to the bond-coat and the absence of open porosity. Such a coating does not have open pores, preventing the oxidation of bond-coat
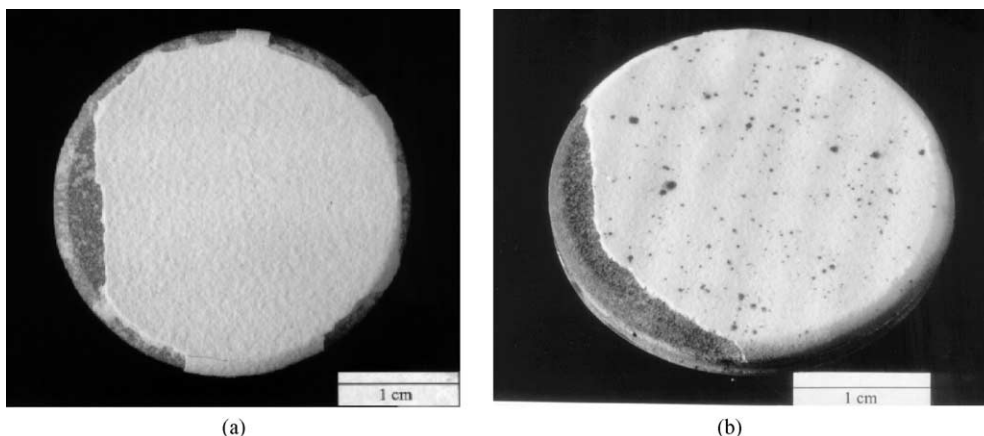


Fig. 3. Coatings after thermal cycling: (3a) LZ, $T_{surf.}$1200 °C/$T_{sub.}$960 °C, 775 cycles; (3b) LC, $T_{surf.}$1225 °C/$T_{sub.}$965 °C, 3238 cycles.

from corrosive gases. Fig. 4 shows the microstructure of such a coating after thermal treatment.

### 2.9. $Y_3Al_xFe_{5-x}O_{12}$

Garnet ceramics with compositions of $Y_3Al_xFe_{5-x}O_{12}$ ($x = 0$, 0.7, 1.4 and 5) have been proposed as TBC materials.[19] YAG ($Y_3Al_5O_{12}$), in particular, has superior high-temperature mechanical properties, excellent phase/thermal stability up to the melting point (2243 K) and low thermal conductivity. The oxygen diffusivity in YAG is about 10 orders of magnitude lower than that in zirconia, implying that it is more oxygen-resistant than the latter and can give a better protection to the bond coat. However, the relatively low thermal expansion coefficient ($9.1 \times 10^{-6}$/K) and low melting point of this material seem to be the major problem.

### 2.10. $SrZrO_3$ and $BaZrO_3$

So far, only two materials with perovskite structure have been studied, i.e. $SrZrO_3$ and $BaZrO_3$.[17] They have very high melting points (3073 and 2963 K, respectively), their thermal expansion coefficients ($10.9 \times 10^{-6}$ K$^{-1}$ and $7.9 \times 10^{-6}$ K$^{-1}$, respectively, 303–1273 K) are comparatively lower than that of YSZ. A former work about the TBC of $BaZrO_3$ proved that this coating did not show better thermal-shock resistance than YSZ. $SrZrO_3$ shows a phase instability, which is expected to be detrimental to its thermal shock resistance.

### 2.11. Lanthanum aluminates

A newly developed alumina-based ceramic coating consisting of $La_2O_3$, $Al_2O_3$ and MgO ($MMeAl_{11}O_{19}$,
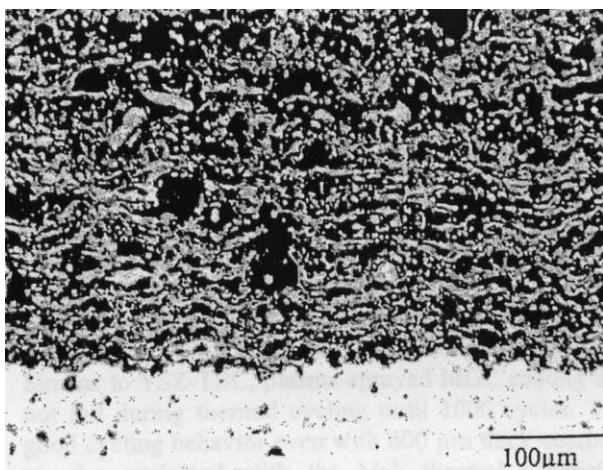


Fig. 4. Plasma-sprayed metal–glass thermal barrier coating after annealing at 1000 °C for 300 h without cracks and spalling. White and gray strips are metal and glass, and the black spots are pores. (After Ref. 73. Reprinted with permission of Wiley-VCH, STM-Copyright & Licenses.)

M = La, Nd; Me = alkaline earth elements, magnetoplumbite structure) that possesses long term structural and thermochemical stability up to 1673 K is presented in Refs. 6,20,74. This coating has significantly lower sintering rate than zirconia-based TBCs. The low thermal conductivity of LHA is caused by its microstructure, i.e. a random arrangement of LHA platelets that build up a microporous coating and the insulating properties of the material with its crystallographic feature itself. A study describing the development of an optimized procedure for the processing, manufacturing and application of LHA as TBCs is reported in Ref. 20.

### 2.12. $(Ca_{1-x}Mg_x)Zr_4(PO_4)_6$

It is reported that this material has lower thermal conductivity than zirconia and the thermal expansion coefficient is near zero.[75] On the other hand, this material is less dense than $ZrO_2$ with theoretical density 3.2 g/cm$^3$ vs. 5.8 g/cm$^3$. Furthermore, no strength-loss after air quenching from temperatures up to 1773 K was observed, showing a good thermal shock resistance. It is not clear if this material can really be used for thermal barrier coatings because of its low thermal expansion coefficient. No further results about this coating are reported.

### 2.13. $LaPO_4$

Lathanum phosphate is monoclinic with four formula units of $LaPO_4$ in the $P2_1/n$ unit cell.[23] It is considered as a potential material for thermal insulation coating on Ni-based superalloys owing to its high-temperature stability (melting point 2345±20 K), its high thermal expansion and low thermal conductivity (comparable with properties of dense zirconia).[22] In addition, lanthanum phosphate is expected to have good corrosion resistance in environments containing sulfur and vanadium salts. It does not react with alumina, which is a positive attribute, but bonds poorly to it, which is a limitation for the application. On the other hand, $LaPO_4$ is a line compound that melts congruently but small deviations from stoichiometry change its solidus temperature from 2343 to 1853 K on the La-rich side or to 1323 K on the P-rich side. From this point of view, it is very hard to make coating of this material by plasma spraying, and it is expected that the coating made from this material can hardly be used for high temperature applications. No thermal cycling tests about this coating are reported.

## 3. Summary

In the periodical table of elements, the elements whose oxides find applications in TBCs are mainly dis-
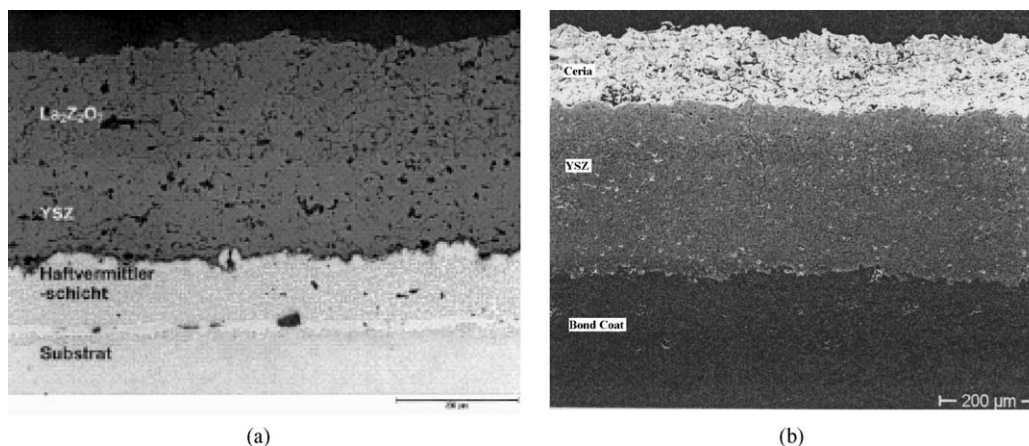
Fig. 5. Double-ceramic-coating system. [After Ref. 77 (6a) and Ref. 78 (6b). Reprinted with permission of Wiley-VCH, STM-Copyright & Licenses.].

tributed in IIIB (rare earth elements), IVB (Ti, Zr and Hf), IIIA (Al) and IVA (Si). The IIA elements (Mg and Ca) can only be used as stabilizers of zirconia. Rare earth oxides are promising materials for TBCs because of their low thermal conductivity, high thermal expansion coefficients chemical inertness. By the doping of certain elements, the thermal expansion coefficient of $La_2Zr_2O_7$ can be increased. When its thermal expansion coefficient is increased to a value similar to that of YSZ, the $La_2Zr_2O_7$ coating can be hopefully used in high temperature applications. On the other hand, as the dual layer MCrAlY/YSZ system seems to reach their optimum performance, the development of TBCs must shift towards different materials combinations and deposition processes. It seems that the concept of multilayer is effective for the improvement of the thermal shock life of TBCs[29,76] because no single material satisfies all requirements for TBCs. The multilayer includes an erosion resistant layer as the outer layer, a thermal barrier layer, a corrosion-oxidation resistant layer, a thermal stress control layer and a diffusion resistant layer. Based on the multiplayer system, a double-ceramic-coating system is newly developed as shown in Fig. 5. On the top of 8YSZ coating, another coating whose thermal conductivity is lower than that of 8YSZ is formed. The top ceramic layer acts as thermal insulator to protect the 8YSZ layer. As reported by the authors, the thermal cycling performance of $La_2Zr_2O_7$/ 8YSZ coating is excellent,[77] and the $CeO_2$/8YSZ coating showed a good thermal shock resistance.[78] Taken in total, several decades of TBC development indicate that when all of the necessary properties for successful TBCs considered, YSZ remains difficult to be replaced.

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## References

1. Cernuschi, F., Bianchi, P., Leoni, M. and Scardi, P., Thermal diffusivity/microstructure relationship in Y-PSZ thermal barrier coatings. *J. Therm. Spray Technol.*, 1999, **8**(1), 102–109.

2. DeMasi-Marcin, Jeanine T. and Gupta, Dinesh K., Protective coatings in the gas turbine engine. *Surf. Coat. Technol.*, 1994, **68/69**, 1–9.

3. Wigren, J. and Pejryd, L., Thermal barrier coatings-why, how, where and where to. In *Proceedings of the 15th International Thermal Spray Conference: Thermal Spray Meeting the Challenges of the 21st Century* (Nice, France, May 1998), ed. Christian Coddet. ASM International, Materials Park, OH, USA, 1998, pp. 1531–1542.

4. Miller, R. A., Thermal barrier coatings for aircraft engines: history and directions. *J. Therm. Spray Technol.*, 1997, **6**(1), 35–42.

5. Vassen, R., Tietz, F., Kerkhoff, G. and Stoever, D., New materials for advanced thermal barrier coatings. In *Proceedings of the 6th Liége Conference on Materials for Advanced Power Engineering (Universite de Liége, Belgium, November 1998)*, ed. J. Lecomte-Beckers, F. Schuber and P. J. Ennis. Forschungszentrum Jülich GmbH, Jülich, Deutschland, 1998, pp. 1627–1635.

6. Vassen, R., Cao, X., Dietrich, M. and Stoever, D., Improvement of new thermal barrier coating systems using layered or graded structure. In *The 25th Annual International Conference on Advanced Ceramics and Composites: An Advanced Ceramics Odyssey (Cocoa Beach of Florida, Jan. 2001)*, ed. Mrityunjay Singh and Todd Jessen. American Ceramic Society, 2001, pp. 435–442.

7. Garvie, R. C., Zirconium dioxide and some of its binary systems. In *High Temperature Oxides, Vol.5-II*, ed. Allen M. Alper. Academic Press, New York and London, 1970, pp. 133–157,175.

8. Ding, C. and Tong, Z., Laboratory report-thermal spraying at the Shanghai Institute of Ceramics. *J. Therm. Spray Technol.*, 1992, **1**(3), 205–210.

9. Samsonov, G. V., *The oxide Handbook, 2nd edn*. IFI/Plenum, New York, 1982.

10. Lackey, W. J., Stinton, D. P., Cerny, G. A., Schaffhauser, A. C. and Fehrenbacher, L. L., Ceramic coatings for advanced heat

engines—a review and projection. *Adv. Ceram. Mater.*, 1987, **2**(1), 24–30.

11. Mesrati, N., Ajhrourh, H., Du, Ng. and Treheus, D., Thermal spraying and adhesion of oxides onto graphite. *J. Therm. Spray Technol.*, 2000, **9**(1), 95–99.

12. Vassen, R., Cao, X., Tietz, F., Kerkhoff, G. and Stoever, D., La$_2$Zr$_2$O$_7$—a new candidate for thermal barrier coatings. In *Proceedings of the United Thermal Spray Conference'99 (Düsseldorf Germany, March 1999)*, ed. E. Lugscheider and P. A. Kammer. ASM International, Verlag für Schweißen und Verwandte Verfahren, Düsseldorf, 1999, pp. 830–834.

13. Vassen, R., Kerkhoff, G. and Stoever, D., Development of a micromechanical life prediction model for plasma sprayed thermal barrier coatings. *Mater. Sci. Eng.,*, 2001, **A303**, 100–109.

14. Davis, R. F. and Pask, J. A., Mullite. In *High Temperature Oxides, vol.5-IV*, ed. Allen M. Alper. Academic Press, New York and London, 1970.

15. Kokini, K., Takeuchi, Y. R. and Choules, B. D., Surface thermal cracking of thermal barrier coatings owing to stress relaxation: zirconia vs mullite. *Surf. Coat. Technol.*, 1996, **82**, 77–82.

16. Lee, K. N., Miller, R. A. and Jacobson, N. S., New generation of plasma-sprayed mullite coatings on silicon carbide. *J. Am. Ceram. Soc.*, 1995, **78**(3), 705–710.

17. Vassen, R., Cao, X., Tietz, F., Basu, D. and Stoever, D., Zirconates as new materials for thermal barrier coatings. *J. Am. Ceram. Soc.*, 2000, **83**(8), 2023–2028.

18. Beals, M. D., Single-crystal titanates and zirconates. In *High Temperature Oxides, Vol.5-II*, ed. Allen M. Alper. Academic Press, New York and London, 1970.

19. Nitin, P. P. and Klemens, P. G., Low thermal conductivity in garnets. *J. Am. Ceram. Soc.*, 1977, **80**(4), 1018–1020.

20. Friedrich, C. J., Gadow, R. and Lischka, M. H., Lanthanum hexaaluminate thermal barrier coatings. In *The 25th Annual International Conference on Composites, Advanced Ceramics, Materials, and Structures: B (Cocoa Beach of Florida, Jan. 2001)*, ed. Mrityunjay Singh and Todd Jessen. American Ceramic Society, Westerville, OH, USA, 2001, pp. 372–375.

21. Schäfer, G. W. and Gadow, R., Lanthanum aluminate thermal barrier coating. In *The 23rd Annual International Conference on (Cocoa Beach of Florida, 1999)*, ed. David E. Clark. American Ceramic Society, Westerville, OH, USA, 1999, pp. 291–297.

22. Sudre, O., Cheung, J., Marshall, D., Morgan, P. and Levi, C. G., Thermal insulation coatings of LaPO$_4$. In *The 25th Annual International Conference on Composites, Advanced Ceramics, Materials, and Structures: B (Cocoa Beach of Florida, Jan. 2001)*, ed. Mrityunjay Singh and Todd Jessen. American Ceramic Society, Westerville, OH, USA, 2001, pp. 367–374.

23. Morgan, P. E. D. and Marshall, D.B., Ceramic composites of monayite and alumina. *J. Am. Ceram. Soc.*, 1995, **78**(6), 1553–1563.

24. Troczynski, T., Yang, Q. and John, G., Post-deposition treatment of zirconia thermal barrier coatings using Sol-Gel alumina. *J. Therm. Spray Technol.*, 1999, **8**(2), 229–234.

25. Knuuttila, J., Sorsa, P. and Maentylae, T., Sealing of thermal spray coatings by impregnation. *J. Therm. Spray Technol.*, 1999, **8**(2), 249–257.

26. Mifune, N., Harada, Y., Taira, H. and Mishima, S., Field evaluation of 2CaO-SiO$_2$-CaO-ZrO$_2$ thermal barrier coating on gas turbine vanes. In *Proceedings of the 1st United Thermal Spray Conference: Thermal Spray, A United Forum for Scientific and Technological Advances (Indiana USA, Sept. 1997)*, ed. C. C. Berndt. ASM International, Materials Park, 1997, pp. 299–303.

27. Lima, C. R. C. and Exaltação Trevisan, R. da, Temperature measurements and adhesion properties of plasma sprayed thermal barrier coatings. *J. Therm. Spray Technol.*, 1999, **8**(2), 323–327.

28. Xu, H., Guo, H., Liu, F. and Gong, S., Development of gradient thermal barrier coatings and their hot-fatigue behaviour. *Surf. Coat. Technol.*, 2000, **130**, 133–139.

29. Tamura, M., Takahashi, M., Ishii, J., Suzuki, K., Sato, M. and Shimomura, K., Multilayered thermal barrier coating for land-based gas turbines. *J. Therm. Spray Technol.*, 1999, **8**(1), 68–72.

30. Vassen, R. and Stoever, D., Conventional and new materials for thermal barrier coatings. In Functional Grandient Materials and Surface Layers Prepared by Fine Particles Technology, ed. M.-I. Baraton and I. Uvarova. Kluwer Academic Publishers, Netherlands, pp. 199–216.

31. Yoshiba, M., Abe, K., Aranami, T. and Harada, Y., High-temperature oxidation and hot corrosion behaviour of two kinds of thermal barrier coating systems for advanced gas turbines. *J. Therm. Spray Technol.*, 1996, **5**(3), 259–268.

32. Wilden, J., Wank, M., Steffens, H. D. and Brune, M., New thermal barrier coating system for high temperature applications. In *Proceedings of the 15th International Thermal Spray Conference: Thermal Spray Meeting the Challenges of the 21st Century (Nice, France, May 1998)*, ed. Christian Coddet. ASM International, Materials Park, OH, USA, 1998, pp. 1669–1673.

33. Bengtsson, P., Ericsson, T. and Wigren, J., Thermal shock testing of burner cans coated with a thick TBC. *J. Therm. Spray Technol.*, 1998, **7**(3), 341–348.

34. Steffens, H.-D., Babiak, Z. and Gramlich, M., Some aspects of thick thermal barrier coating lifetime prolongation. *J. Therm. Spray Technol.*, 1999, **8**(4), 517–522.

35. Babiak, Z., Bach, Fr.W., Bertamini, L., Hindryckx, F., Krugers, J. P., Mertens, C., Michel, B., Sturlese, S. and Unterberg, W., Innovative plasma sprayed 7% YSZ-thermal barrier coatings for gas turbines. In *Proceedings of the 6th Liége Conference on Materials for Advanced Power Engineering (Universite de Liége, Belgium, November 1998)*, ed. J. Lecomte-Beckers, F. Schubert and P. J. Ennis. ASM International, 1998, pp. 1611–1618.

36. Kaspar, J. and Ambroz, O., Plasma spray coatings as thermal barriers based on zirconium oxide with yttrium oxide. In *The 1st Plasma-technik-symposium, Vol.2, (Lucerne Switzerland, 18–20 May 1988)*, ed. H. Eschnauer, P. Huber, Andrew R. Nicoll and S. Sandmeier. Plasma-Technik AG, Wohlen, Switzerland, 1988, pp. 155–166.

37. Steffens, H. D., Babiak, Z. and Brandl, W., Thermal barrier coatings: some aspects of properties design. In *Proceedings of the 4th national thermal spray conference: Thermal Spray Coatings–Properties, Processes and Applications (Pennsylvania USA, May 1991)*, ed. Thomas F. Bernecki. ASM International, Materials Park, Ohio, 1991, pp. 289–294.

38. Matejícek, J., Sampath, S. and Dubsky, J., X-ray residual stress measurement in metallic and ceramic plasma sprayed coatings. *J. Therm. Spray Technol.*, 1999, **7**(4), 489–496.

39. Wallace, J. S. and Ilavsky, J., Elastic modulus measurements in plasma sprayed deposits. *J. Therm. Spray Technol.*, 1999, **7**(4), 521–526.

40. Slifka, A. J., Filla, B. J., Phelps, J. M., Bancke, G. and Berndt, C. C., Thermal conductivity of a zirconia thermal barrier coating. *J. Therm. Technol.*, 1998, **7**(1), 43–46.

41. Voyer, J., Gitzhofer, F. and Boulos, M. I., Study of the performance of TBC under thermal cycling conditions using acoustic emission rig. *J. Therm. Spray Technol.*, 1998, **7**(2), 181–190.

42. Thornton, J. and Majumdar, A., Ceria precipitation and phase stability in zirconia based thermal barrier coatings. In *Proceedings of the 14th International Thermal Spray Conference: Thermal Spray–Current Status and Future Trends (Kobe Japan, May 1995)*, ed. A. Ohmori. ASM International, 1995, pp. 1075–1080.

43. Ramaswamy, P., Seetharamu, S., Varma, K. B. R. and Rao, K. J., Thermal shock characteristics of plasma sprayed mullite coatings. *J. Therm. Spray Technol.*, 1999, **7**(4), 497–504.

44. Goedjen, J. G., Brindley, W. J. and Miller, R. A., Sintering of plasma-sprayed sol-Gel zirconia-yttria as a function of silica content. In *Proceedings of the 8th National Thermal Spray Conference: Advances in Thermal Spray Science and Technology*

(*Texas USA, Sept. 1995*), ed. C. C. Berndt and S. Sampath. ASM International, Materials Park, Ohio, 1995, pp. 73–77.

45. Miller, R. A., Brindley, W. J., Goedjen, J. G., Tiwari, R. and Mess, D., The effect of silica on the cyclic life of a zirconia-yttria thermal barrier coating. In *Proceedings of the 7th National Thermal Spray Conference: Thermal Spray in Industrial Applications (Massachusetts USA, June 1994)*, ed. C. C. Berndt and S. Sampath. ASM International, Materials Park, Ohio, 1994, pp. 49–54.

46. He, Y., Lee, K. N., Tewari, S. and Miller, R. A., Development of refractory silicate-yttria stabilised zirconia dual-layer thermal barrier coatings. *J. Therm. Spray Technol.*, 2000, **9**(1), 59–67.

47. Brunauer, G., Frey, F., Boysen, H. and Schneider, H., High temperature thermal expansion of mullite: an in-situ neutron diffraction study up to 1600°C. *J. Eur. Ceram. Soc.*, 2001, **21**, 2563–2567.

48. Yonushonis, T. M., Overview of thermal barrier coatings for diesel engines. *J. Therm. Spray Technol.*, 1997, **6**(1), 50–56.

49. Kingswell, R., Scott, K. T. and Bull, S., Erosion behaviour of plasma sprayed alumina coatings. In *The 2nd Plasma-technik-symposium, Vol.3 (Lucerne Switzerland, June 1991)*, ed. S. Sandmeier, H. Eschnauer, P. Huber and A. R. Nicoll. Plasma-Technik AG, Wohlen, Switzerland, 1991, pp. 367–375.

50. Foujanet, M. C., Lumet, J. P. and Derep, J. L., Structural analysis of zirconia-alumina plasma sprayed coatings. In *The 1st Plasma-technik-symposium, Vol.2 (Lucerne Switzerland, May 1988)*, ed. H. Eschnauer, P. Huber, A. R. Nicoll and S. Sandmeier. Plasma-Technik AG, Wohlen, Switzerland, 1988, pp. 357–366.

51. Sainte-Catherine, M. C., Derep, J. L. and Lumet, J. P., Zirconia-alumina plasma sprayed coatings: correlation between microstructure and properties. In *The 2nd Plasma-technik-symposium, Vol.2 (Lucerne Switzerland, June 1991)*, ed. S. Sandmeier, H. Eschnauer, P. Huber and A. R. Nicoll. Plasma-Technik AG, Wohlen, Switzerland, 1991, pp. 131–140.

52. Krishnamoorthy, P. R., Ramaswamy, P. and Narayana, B. H., Evaluation of multilayer $ZrO_2$ and $Al_2O_3$ thermal barrier coatings. In *The 2nd Plasma-technik-symposium, Vol.3 (Lucerne Switzerland, June 1991)*, ed. S. Sandmeier, H. Eschnauer, P. Huber and A. R. Nicoll. Plasma-Technik AG, Wohlen, Switzerland, 1991, pp. 263–272.

53. Chráska, P., Dubsky, J., Neufuss, K. and Písacka, J., Alumina-base plasma-sprayed materials—part I: phase stability of alumina and alumina-chromia. *J. Therm. Spray Technol.*, 1997, **6**(3), 320–326.

54. Ilavsky, J., Berndt, C. C., Herman, H., Chraska, P. and Dubsky, J., Alumina-base plasma-sprayed materials—part II: phase transformations in alumina. *J. Therm. Spray Technol.*, 1997, **6**(4), 439–444.

55. Steffens, H. D., Brune, M., Müller, E. and Dittrich, R., The manufacture of SiC fibre reinforced $Al_2O_3$ coatings by plasma spraying. In *The 9th national thermal spray conference: Thermal Spray-Practical Solutions for Engineering Problems (Cincinnati USA, Oct. 1996)*, ed. C. C. Berndt. ASM International, Materials Park, Ohio, 1996, pp. 311–316.

56. Sodeoka, S., Suzuki, M., Inoue, T., Ueno, K. and Oki, S., Thermal and mechanical properties of plasma sprayed $ZrO_2$–$CeO_2$–$Y_2O_3$ coatings. In *Proceedings of the 9th national thermal spray conference: Thermal Spray-Practical Solutions for Engineering Problems (Cincinnati USA, Oct. 1996)*, ed. C. C. Berndt. ASM International, Materials Park, Ohio, 1996, pp. 295–302.

57. Holmes, J. W. and Pilsner, B. H., Cerium oxide stabilised thermal barrier coatings. In *Proceedings of the National Thermal Spray Conference: Thermal Spray-Advances in Coatings Technology (Orlando USA, Sept. 1987)*, ed. D. L. Houck. ASM International, Materials Park, Ohio, 1987, pp. 259–270.

58. Heintze, G. N. and McPherson, R., Fracture toughness of plasma-sprayed zirconia coatings. In *Proceedings of the National Thermal Spray Conference: Thermal Spray-Advances in Coatings Technology (Orlando USA, Sept. 1987)*, ed. D. L. Houck. ASM International, Materials Park, Ohio, 1987, pp. 271–275.

59. Kim, H. K., Choi, H. S. and Lee, C. H., Failure analysis of plasma sprayed $ZrO_2$–$CeO_2$–$Y_2O_3$ thermal barrier coatings. In *Proceedings of the United Thermal Spray Conference (Duesseldorf Germany, March 1999)*, ed. E. Lugscheider and P. A. Kammer. Verlag für Schweißen und Verwandte Verfahren, Düsseldorf, 1999, pp. 740–746.

60. Thornton, J., Majumdar, A. and McAdam, G., Enhanced cerium migration in ceria-stabilized zirconia. *Surf. Coat. Technol.*, 1997, **94/95**, 112–117.

61. Rouanet, A., Peraudeau, G., Sibieude, F., Priem, T., Ranc, R., Rigal, E. and Cornu, A., Chemical and structural characterisation of quenched ceria (yttria) stabilised zirconia or hafnia ceramics for plasma coatings. In *The 14th international thermal spray conference: Thermal Spray-Current Status and Future Trends (Kobe Japan, May 1995)*, ed. A. Ohmori. High temperature society of Japan, Osaka, 1995, pp. 507–512.

62. Maloney, M. J., Thermal Barrier Coating Systems and Materials. European Patent EP 0848077 A1, 1998.

63. Cao, X., Vassen, R., Tietz, F., Jungen, W. and Stoever, D., Thermal stability of lanthanum zirconate plasma-sprayed coating. *J. Am. Ceram. Soc.*, 2001, **84**(9), 2086–2090.

64. Subramanian, M. A., Aravamudan, G. and Subba Rao, G. V., Oxide pyrochlores—a review. *Prog. Solid State Chem.*, 1983, **15**, 55–143.

65. Rouanet, A., Fig. 5232-System $ZrO_2$-$La_2O_3$, p.133. In *Phase Diagrams for Ceramists Vol. IV*, ed. S. Roth, Taki Negas and Lawrence P. Cook. The Am. Ceram. Soc. Inc, Ohio, 1981.

66. Chráska, P., Neufuss, K., Kolman, B. and Dubsky, J., Plasma spraying of silicates. In *Proceedings of the 1st United Thermal Spray Conference: Thermal Spray—A United Forum for Scientific and Technological Advances (Indiana USA, Sept. 1997)*, ed. C. C. Berndt. ASM International, Materials Park, 1997, pp. 477–481.

67. Ramaswamy, P., Seetharamu, S., Varma, K. B. and Rao, K. J., Thermal barrier coating application of zircon sand. *J. Therm. Spray Technol.*, 1999, **8**(3), 447–453.

68. Pavlik, R. S. Jr., Holland, H. J. and Andrew Payzant, E., Thermal decomposition of zircon refractories. *J. Am. Ceram. Soc.*, 2001, **84**(12), 2930–2936.

69. Kvernes, I., Lugscheider, E. and Ladru, F., Lifetime and degradation processes of TBCs for diesel engines. In *Proceedings of the 6th Liége Conference on Materials for Advanced Power Engineering (Universite de Liége, Belgium, November 1998*, ed. J. Lecomte-Beckers, F. Schuber and P. J. Ennis. Forschungszentrum Jülich GmbH, Jülich, 1998, pp. 997–1001.

70. Ding, C., Xi, Y., Zhang, Y., Qu, J. and Qiao, H., Thermophysical properties of plasma sprayed rare earth oxide coatings. In *The 2nd Plasma-technik-symposium (Lucerne Switzerland, June 1991)*, ed. S. Sandmeier, H. Eschnauer, P. Huber and A. R. Nicoll. Plasma-Technik AG, Wohlen, Switzerland, 1991, pp. 27–32.

71. Warshaw, I. and Roy, R., Polymorphism of the rare earth sesquioxides. *J. Phys. Chem.*, 1965, **65**, 2048–2051.

72. Verlotski, V., Stoever, D., Buchkremer, H. P. and Vassen, R., *Wärmedämmende Glas–metall/Keramik-Schichten*. German Patent No. 198 52 285, 3 May 2000.

73. Dietrich, M., Verlotski, V., Vassen, R. and Stoever, D., Metal-glass based composites for novel TBC-systems. *Mater. Sci. Eng. Technol.*, 2001, **32**(8), 669–672.

74. Gadow, R. and Schäfer, G. W., *Thermal insulating materials and method for producing SAME*. German Patent No. WO 99/42630, 1999.

75. Hirschfeld, D. A., Liu, D. M. and Brown, J. J., CMZP-a new high temperature thermal barrier material. In *The 4th International Symposium on Ceramic Materials and Components for Engines*, ed. R. Carlsson, R. Johansson and L. Kahlman. Elsevier Applied Science, London, 1992, pp. 370–372.

76. Takahashi, M., Itoh, Y. and Miyazaki, M., Thermal barrier coatings design for gas turbine. In *Proceedings of 14th International Thermal Spraying (ITSC'95), Vol. 1 (Kobe, Japan, May 1995)*, ed. A. Ohmori. High Temperature Society of Japan, Kobe, Japan, 1995, pp. 83–88.

77. Vassen, R., Dietrich, M., Lehmann, H., Cao, X., Pracht, G., Tietz, F., Pitzer, D. and Stoever, D., Development of oxide ceramics for an application as TBC. *Mater. Sci. Eng. Technol.*, 2001, **32**(8), 673–677.

78. Wilden, J. and Wank, A., Application study on ceria based thermal barrier coatings. *Mater. Sci. Eng. Technol.*, 2001, **32**(8), 654–659.