Overview on advanced thermal barrier coatings

Robert Vaßen, Maria Ophelia Jarligo, Tanja Steinke, Daniel Mack, Detlev Stöver

PII: S0257-8972(10)00809-1
DOI: doi: 10.1016/j.surfcoat.2010.08.151
Reference: SCT 16121

To appear in: *Surface & Coatings Technology*

Received date: 26 April 2010
Accepted date: 31 August 2010

Please cite this article as: Robert Vaßen, Maria Ophelia Jarligo, Tanja Steinke, Daniel Mack, Detlev Stöver, Overview on advanced thermal barrier coatings, *Surface & Coatings Technology* (2010), doi: 10.1016/j.surfcoat.2010.08.151

Overview on advanced thermal barrier coatings

Robert Vaßen, Maria Ophelia Jarligo, Tanja Steinke, Daniel Mack, Detlev Stöver

Institute of Energy Research (IEF-1), Forschungszentrum Jülich GmbH, Germany

Abstract

During the last decade a number of ceramic materials, mostly oxides have been suggested as new thermal barrier coating (TBC) materials. These new compositions have to compete with the state-of-the-art TBC material yttria stabilized zirconia (YSZ) which turns out to be difficult due to its unique properties. On the other hand YSZ has certain shortcomings especially its limited temperature capability above 1200 °C which necessitate its substitution in advanced gas turbines.

In the paper an overview is tried on the different new materials covering especially doped zirconia, pyrochlores, perovskites, and aluminates. Literature results and also results from our own investigations will be presented and compared to the requirements. Finally, the double layer concept, a method to overcome the limited toughness of new TBC materials, will be discussed.

Keywords:

Thermal barrier coatings, zirconia, pyrochlores, perovskites, aluminates, thermal conductivity

Introduction

Thermal barrier coating (TBC) systems are typically duplex-type which consist of a metallic bond coat and a ceramic topcoat. The bond coat protects the substrates from oxidative and corrosive attack and improves the bonding between ceramic topcoat and substrate. The ceramic topcoat has a significantly lower thermal conductivity than the metallic substrate and by applying an internal cooling of the components it is possible to establish a large temperature drop (several 100 K) across the ceramic layer. Hence, it is possible to either reduce the temperature of the metallic substrates thereby increasing the lifetime of the components, or increase the firing temperature of the turbine leading to the increase in its operation efficiency [1].

The industrial development of TBCs started in the 1950s with the manufacture of the first enamel coatings for military engine components [2]. In the 1960s the first flame sprayed ceramic layers with NiAl bond coats were used in commercial aero engines [3]. Succeeding decades showed continuous improvements in the TBC materials and coatings technology. It was however in the 1980s when the TBCs were significantly improved [4]. During this decade, yttria stabilized zirconia (YSZ) was identified as an exceptional ceramic topcoat material, and has since been established as a standard for the last 30 years [5, 6, 7].

In terms of deposition techniques, two methods have been well established. One is the electron beam physical vapour deposition (EB-PVD) and the other is atmospheric plasma spraying (APS). Coatings deposited by EB-PVD have specifically columnar microstructures and are mainly used for high thermo-mechanically loaded blades of aero engines. The APS process meanwhile boasts of its operation robustness and economic viability compared to EB-PVD, hence more TBCs are now developed with this process. Typically static components such as combustor cans and vane platforms are coated by APS. In stationary gas turbines, also blades are frequently coated by thermal spray processes.

A further improvement of the efficiency of gas turbines is intended by further improvements of the combustion and cooling technology in combination with higher turbine inlet temperatures. This also implies that the standard material YSZ is approaching certain limitations due to sintering and phase transformations at elevated temperatures [8].

PYSZ as formed by the EB-PVD and the APS process consists of the metastable T' phase. When exposed to prolonged exposure at elevated temperatures it decomposes into high yttria and low yttria phases. The latter transforms on cooling to the monoclinic phase with an associated large volume increase, which eventually proves catastrophic and results in failure. The accepted upper limit for use is 1200C [9, 10, 11] In addition to the limited phase stability, also sintering reduces the high temperature capability as it leads to a loss of strain tolerance of the coatings and hence early failure [12].

As a result, within the last decades a number of activities were started to search for even better ceramics than YSZ , a large number of overview articles are covering this topic [13, 14, 15, 16, 17 , 18, 19,]. The present paper will give a summary of the resent developments in the field.

1. Pyrochlores

For application at service temperatures above 1300 °C, TBC materials with pyrochlore structure $A_2B_2O_7$ offer very attractive properties comparable to YSZ. Specifically, a lower thermal conductivity for several zirconate pyrochlores makes this class of materials interesting [20]. Also their thermal stability is excellent which is probably related to the fixed positions of cations in the crystal. Among the widely investigated pyrochlores are the rare-earth zirconates ($Ln_2Zr_2O_7$), where Ln is any or combination of La, Gd, Sm, Nd, Eu and Yb [21, 22, 23, 24, 25, 26, 27, 28, 29, 30,]. Several hafnia ($La_2Hf_2O_7$ and $Gd_2Hf_2O_7$) and ceria ($La_2Ce_2O_7$ and $La_2(Zr_{0.7}Ce_{0.3})_2O_7$) based materials were also found to be interesting TBC materials [31, 32]. In fact, ceria based oxides often show a defect fluorite structure. This structure allows more easily a cation exchange which might explain the higher sintering rates of these materials [33]. Also doping of $La_2Zr_2O_7$ with other elements like Y was tried giving some increase in sintering resistance [34].

Among the pyrochlores, $La_2Zr_2O_7$ (LZ) seems to be one of the most promising for TBC application due to its outstanding bulk properties compared to standard YSZ with high thermal stability up to 2000 °C, the low thermal conductivity of 1.56 W/m K and a low sintering tendency. A drawback however is the relatively low thermal expansion coefficient of about $9 \cdot 10^{-6}$ K^{-1} compared to YSZ with $10\text{-}11 \cdot 10^{-6}$ K^{-1} which leads to higher thermal stresses from thermal expansion mismatch. In this regard, the higher thermal expansion coefficient of $1.1\ 10^{-6}$ K^{-1} of $Gd_2Zr_2O_7$ is advantageous.

Since both the substrate and the bondcoat have relatively higher thermal expansion coefficients (about $15 \cdot 10^{-6}$ K^{-1}), cracks can easily grow due to the stresses build up in the TBC close to the bondcoat during operation [35, 23]. This could be the reason for the lower lifetime of the TBC with $La_2Zr_2O_7$ and $Gd_2Zr_2O_7$ as lone ceramic topcoat. In a so-called double-layer system (see Figure 1), with a first layer of YSZ and a top layer made of pyrochlore materials the life time of the coatings tested in thermal gradient cyclic rigs are significantly improved [23]. Within these double-layer structures the YSZ gives a good toughness close to the bondcoat (BC) while the pyrochlore material applied on the top provides low sintering and high thermal stability. These double-layer systems based on pyrochlore/YSZ revealed excellent high-temperature capability significantly better than the one of YSZ and they are expected to improve the thermal capability of gas turbines during application [23]. Figure 2 shows the results of burner rig tests of different new TBC systems with NiCoCrAlY-bondcoated IN738 substrates [23]. Under the given cyclic conditions (5 min heating, 2 min cooling) low porosity YSZ systems (about 12%) show a sharp decrease in lifetime at temperatures above 1350°C. Single layer systems of new TBCs perform even worse due to the reasons given above. Double layer systems prepared from $La_2Zr_2O_7$ powder made by spray-drying in Jülich performed much better and could extend the high temperature capability of the TBC systems by more than 100K. In former experiments, samples prepared by commercial $Gd_2Zr_2O_7$ gave a lower performance [23]. One experiment with a different powder made in Jülich revealed on the other hand a good cyclic life (see Figure 2). It is obvious that the powder morphology and composition has a significant effect on the performance of the coatings.

Although many pyrochlore materials can be rather easily processed by thermal spray methods, especially if compared to perovskite –type materials (see below), some issues still exist. One of these is the loss of constituents during spraying. For $La_2Zr_2O_7$ loss of La_2O_3 was already stated in [36] and it leads to an impurity phase of non-stabilized ZrO_2 which might be detrimental for the coating performance.

Although the high-temperature properties of double layer systems are promising, there might be the need to improve also the performance at moderate temperatures. Chen at al. [37] suggest the use of graded YSZ/ $La_2Zr_2O_7$ which led to a slight improve of the furnace cyclic life. On the other hand, earlier results of R. Vassen et al. [38] suggest a better performance of double layer systems compared to graded structures in a gradient testing. This opposite results might be related to the fact that in a gradient testing the mean stress level and the stored elastic energy in the coating at room temperature is reduced compared to an isothermal test [39].

Chemical stability investigations on a double-layer YSZ and $La_2Zr_2O_7$ system from calcined powder blends (50 % $La_2Zr_2O_7$ and 50 % YSZ) showed no reactions at calcination temperature lower than 1250 °C, implying that $La_2Zr_2O_7$ and YSZ have a good chemical applicability for producing double-layer TBC systems [40].

On the other hand reactions of pyrochlore materials with alumina take place at elevated temperatures [40]. So, during long-term use a reaction between the oxide scale formed on the bondcoat (alumina based scale, so-called thermally grown oxide (TGO)) and the pyrochlore coating is expected. However, this problem is also avoided due to the double layer structure.

Reaction with corrosive species might also be in some cases advantageous. Recently, so-called CMAS attack (Calcium-Magnesium-Aluminc-Silicate) has attracted a lot of attention [41]. At first this kind of damage mechanism was observed in aero engines operated at high engine temperatures. With the intake air fine debris made of CMAS are deposited on the TBCs. At high surface temperature they become liquid and can infiltrate the coating. During cooling they solidify and reduce the strain tolerance of the coatings. Some pyrochlores as $Gd_2Zr_2O_7$ can react with the silicate leading to a crystallization and the penetration of the CMAS is stopped early[42]. Hence, some pyrochlores seem to be more resistant against CMAS than YSZ.

2. Defect cluster TBCs

In this type of new and very promising TBC material zirconia is doped by different rare earth cations. These additions lead to the formation of dopant clusters as in the ZrO_2-Y_2O_3-Nd_2O_3(Gd_2O_3,Sm_2O_3)-Yb_2O_3(Sc_2O_3) system which reduce the thermal conductivity by about 20 to 40 % [43]. For ZrO_2 stabilised with 5.5.mol% Y_2O_3-2.25mol%Gd_2O_3-2.25mol% Yb_2O_3 thermal conductivity is reduced from 2.3-2.6 W/m/K for the baseline ZrO_2-4.5mol%Y_2O_3 to 1.6-1.9 W/m/K. For ZrO_2 stabilised with 8.5.mol% Y_2O_3-0.75mol%Gd_2O_3-0.75mol% Yb_2O_3 values between 1.8 to 2.1 W/m/K are found. Furthermore the additions improve the thermal stability of the coatings. This is demonstrated by a significantly reduced increase of thermal conductivity with time in the cluster TBC compared to the conventional YSZ (e.g. at 1315 °C, rates of 2.9×10^{-7} compared to 2.7×10^{-6} W/m K s [44] are found). The thermal cycling performance increased or was similar to the performance of conventional YSZ at similar dopant levels [45]. Thermal and environmental systems with temperature capabilities up to 1650°C are possible with the defect cluster approach using zirconia or hafnia matrices.

For higher dopant levels the cubic phase is stabilized. A reduced thermal cyclic performance is observed due to the reduced toughness compared to the conventional 7-8 wt.% yttria stabilised zirconia. Similar to the discussion for the pyrochlores, a double layer structure also results in a considerable improvement [49]. In 45 min / 15 min heating / cooling cycles at 1135°C the lifetime could be increased from 300 to 400 cycles to 500 to 800 Cycles.

3. Hexa-aluminates

Lanthanate hexaaluminates with magnetoplumbite structure are already utilized in the fields of laser technology, catalysis, and magnetics [46, 47, 48, 49, 50]. Due to their high melting point, high thermal expansion, low thermal conductivity, excellent longtime sintering resistance and structural stability up to 1800 °C, these materials have also been found advantageous for thermal barrier coating applications. The nominal composition is $(La,Nd)MAl_{11}O_{19}$ where M could be Mg, Mn to Zn, Cr, Sm [51]. Also the addition of Li has been proven to be advantageous [52]. Among these, the most interesting one is $LaMgAl_{11}O_{19}$ which has been extensively investigated in terms of its thermophysical properties and processing issues during air plasma spraying [53, 54, 55, 56]. The plasma sprayed coating is partly amorphous in the as sprayed condition due to the rapid quenching from the molten state. Upon an initial heat treatment recrystallization occurs over the temperature range from ~ 800 °C to 1200 °C which is marked by a large decrease in the volume of the free standing coatings [57].

Intensive studies on the thermophysical properties of *A*-site doped hexaaluminates reveal that the thermal expansion behavior of $LnMgAl_{11}O_{19}$ (Ln=La, Gd, Sm, Yb) is independent of the lanthanate species whereas the thermal conductivity can be reduced especially by co-doping on the lanthanate site in similar manner as with the zirconate pyrochlores [58, 59, 60, 61, 62, 63].

The shrinkage behavior attributed to the crystallization of partly amorphous hexaaluminates could be related to a stepwise phase evolution which includes the intermediate formation of secondary phases from the La-Al-Mg oxide system [47, 48, 49]. Typically perovskite phases as $LaAlO_3$ are observed below 1400°C before the hexaaluminate phase formation is finished above 1500°C.

Similar results have been reported for the simpler $LaAl_{11}O_{18}$ hexaaluminate where the formation of the pure hexaaluminate phase has not been found below 1650 °C due to kinetic effects [64, 65]. The low Young's modulus and the high fracture toughness are believed to be the reasons for the long thermal cycling life of these coatings. This is mainly attributed to the random arrangement of lanthanum hexaaluminate platelets which causes a well-balanced microporosity and lowers the thermal conductivity of the ceramics. This platelet morphology was found to be dependent on the sample history as well as composition [47, 49]. The fracture toughness was found to be higher with larger aspect ratio of the platelets.

The recrystallization phenomenon has been considered a major drawback in the plasma spray deposition of hexaaluminate coatings and alternative methods have been sought after. Unfortunately, temperature requirements during calcination in the case of sol gel or dipping techniques and the volatilization of Mg in the case of EB-PVD process, render some difficulties in depositing with these techniques as well [66, 67, 68]. It was found out however that plasma sprayed coatings from most hexaaluminates can develop unusual segmentation crack networks which increase the strain tolerance of the coatings resulting in a reasonable thermal shock resistivity which is advantageous in TBC application (see Figure 3, [69]). This could be attributed to a stress release mechanism within an interlocking network of ceramic blocks similar to that found in flexible sandstone [70]. When utilized as top layer in a double layer TBC system with intermediate YSZ layer a superior lifetime in thermal gradient burner rig tests at temperatures as high as 1350 °C has been reported for plasma sprayed $LaLiAl_{11}O_{18.5}$ [55]. Recently, the use of graded composites from alumina and lanthanum hexaaluminate has also been proposed to increase the ductility and fracture toughness of TBCs [71, 72].

4. Perovskites

This class of ABO_3 crystal structure is rigid with corner-sharing octahedra, and can accommodate a wide variety of ions in solid solution including ions with large atomic mass. Most of these materials are stable at high temperatures making them very attractive candidates for materials development in thermal barrier coating (TBC) applications.

4.1 Zirconates

Among the early candidate materials for TBC application is $BaZrO_3$. Although it has a high melting temperature of 2600 °C, its relatively poor thermal and chemical stability led to early failure of coatings during thermal cycling tests at 1200 °C surface temperature [73]. In contrast, $SrZrO_3$ has been found to exhibit better performance on cycling at surface temperatures higher than 1250 °C, whether as a lone ceramic topcoat or an overlay for YSZ in a double layer system [74]. At intermediate temperature of about 730 °C, $SrZrO_3$ undergoes an undesirable phase transformation from orthorhombic to pseudo-tetragonal. Such transformation could be suppressed by doping with Gd or Yb, which also improves the thermophysical properties of the coatings at elevated temperatures [75]. $CaZrO_3$ on the other hand is the latest material to be considered for TBC application in this group [76]. Although its melting temperature is lower than that of YSZ, it has a promising thermal conductivity of ~ 2 W/m K [77].

4.2 Complex forms

Aside from high melting temperature, an interesting feature of the complex perovskites is the ordering effect in the *B*-site cation which allows for the material properties to be tailored [78, 79, 80]. For instance, $Ba(Mg_{1/3}Ta_{2/3})O_3$ has a disordered cubic phase and an ordered trigonal structure which is promoted with an increase of synthesis temperature up to 1650 °C. During atmospheric plasma spraying, the deposited coatings often exhibit the disordered cubic phase which transforms to the ordered form on annealing at temperatures higher than 1250 °C. Dilatometric investigations up to 1400 °C show, that this type of ordering is not catastrophic to the material structure [61, [81]]. Similar ordering effect is observed with $La(Al_{1/4}Mg_{1/2}Ta_{1/4})O_3$, however, this material shows more promising coating performance due to the presence of vertical crack networks in the plasma sprayed coatings [69]. The microstructure of a coating of such a material applied as a double layer is shown in Figure 4.

Although the bulk properties of perovskites show promising values, their toughness is still inferior compared to YSZ. Differences in vapor pressure of the component oxides also lead to preferential volatilization of the non-zirconia constituents for the zirconates, and magnesia for the complex perovskites during atmospheric plasma spraying [62, 64, [82], 70]. This effect leads to deposition of non-stoichiometric phases which often have detrimental effects to the coating performance. Recent study suggests that this could be minimized by proper optimization of plasma spray parameters to obtain shorter residence time of the particles in the hot plasma plume [[83]].

Volatilization of components is however not observed with the plasma sprayed $BaLa_2Ti_3O_{10}$. This layered perovskite contributes to lowering of thermal conductivity due to its weakly-bonded planes that exist between planes containing rigid polyhedra in layered oxides. The thermal cycling performance of the coating at 1200 °C was found to be superior to the used 7YSZ which is attributed to the presence of segmentation cracks on the atmospheric plasma sprayed coatings without the disadvantage of non-stoichiometric deposition of impurity phases [[84]].

However, further experiments have to demonstrate whether this material with its rather low melting temperature is suitable for high temperature applications beyond 1200°C..

Conclusions

A number of different TBC materials have been investigated in the past. A comparison of the key properties thermal conductivity and thermal expansion coefficient are listed in Table I and plotted in Figure 5. Obviously, the pyrochlore as well as the defect cluster materials cover the most interesting range, i.e. low thermal conductivity and rather high thermal expansion coefficients. As discussed in the paper, these kinds of materials also show no severe problems during processing, indicating that at present these materials seem to be the most suitable ones. However, further development might reveal certain advantages also of the other materials with respect to thermal cyclic performance and thermal stability.

Acknowledgment

Many thanks to Dr. Dongming Zhu, Nasa Glenn Research Center, for his information on defect cluster TBCs. Also the contributions of the colleagues in the IEF-1, Forschungszentrum Jülich, in preparation and testing of TBCs are gratefully acknowledged.

Table I.

Thermal and mechanical properties of potential dense new TBC materials in comparison to YSZ.

Material	Melting temperature, °C	Coefficient of thermal expansion at 30°C-1000°C, 10^{-6}/K	Thermal conductivity at 1000°C, W/m-K	Young's modulus, GPa	Fracture toughness, MPam$^{1/2}$
YSZ	2680 [72]	11.5 [86]	2.12 [85]	210 ± 10[74]	1-2 [74]
Pyrochlores					
$La_2Zr_2O_7$	2300 [85]	9.1 [85]	1.56 [85]	175 [74]	
$Gd_2Zr_2O_7$		10.4[87]	$1.6_{[800°C]}$ [85]		
Cluster TBCs		11.5-13.5 [88]	1.7 – 2.0 [46]		
Hexaaluminates					
$LaMgAl_{11}O_{19}$		9.5 [58]	2.7 [58]	130 ± 11[53]	
$GdMgAl_{11}O_{19}$		9.6 [58]	2.6 [58]		
$Gd_{0.7}Yb_{0.3}MgAl_{11}O_{19}$		9.6 [58]	1.9 [58]		
$LaLiAl_{11}O_{18.5}$		10 [69]	3.8 [69]		
Perovskites					
Zirconates					
$BaZrO_3$	2690 [74]	7.9 [72]]	3.42 [85]	181 ± 11[72]	
$SrZrO_3$	2800 [74]	10.9 [74]	2.3 [73]	170 ± 4 [73]	1.5 ± 0.1[75]
$CaZrO_3$	2550 [1]	8.4-8.9 [89]	2.0 [63]		
Complex forms					
$Ba(Mg_{1/3}Ta_{2/3})O_3$	3100 [79]	10.9 [81]	2.71 [81]	186 ± 2 [82]	~0.7 [82]
$La(Al_{1/4}Mg_{1/2}Ta_{1/4})O_3$		9.7 [81]	1.82 [81]	174 ± 2 [82]	~0.6 [82]
$BaLa_2Ti_3O_{10}$ [84]		$10\text{-}13_{[200\text{-}1200°C]}$	$0.7_{[1200°C]}$		

Figures:

Figure 1

Optical micrograph of a $La_2Zr_2O_7$/YSZ double layer TBC.

Figure 2

Results of thermal cyclic tests in a gas burner as a function of surface temperature for different thermal barrier coating systems

Figure 3:

Micrograph of a free standing lanthanum-lithium-hexaaluminate APS-coating after isothermal heat treatment at 1200°C with typical segmentation cracks.

Figure 4:

SEM picture of a plasma-sprayed double layer made of $La(Al_{1/4}Mg_{1/2}Ta_{1/4})O_3$ (top) and YSZ (bottom).

Figure 5:

Plot of thermal conductivity and thermal expansion coefficients of dense, new thermal barrier coating materials.

References

V. Arnault, R. Mévrel, S. Alpérine, Y. Jaslier, La Revue Métallurgie – CIT/Science et Génie des Matériaux, 96 [5] (1999) p. 585.

R. A. Miller, J. Therm. Spray Technol., 6 (1997) 35.

S. Bose, J. DeMasi-Marcin, J. of Therm. Spray Technol., 6 (1997) 99.

R. Bürgel, I. Kvernes, edited by W. Betz et. al., D. Reidel Publishing Company, 1986, Dordrecht, NL, pp. 327-356.

S. Stecura, Adv. Ceram. Mater, 1 (1986) 68.

N. Czech. cfi/Ber. DKG 77 [9] (2000) 18.

R. Wing, Materials World, March 2000, p.10.

R. A., Miller, J.L Smialek, R.G Garlick, Advances in Ceramics, Vol. 3, A.H. Heuer and L.W. Hobbs (eds.), The American Ceramic Society, Columbus, OH, USA, (1981) p.241.

J.R.Brandon & R. Taylor Surf & Coatings Tech 46 (1991) 75 -90:

J. R. Vanvalzah & H.E Eaton Surf & Coatings tech 46 (1991) 289 -300 :

R. Taylor, J.R. Brandon & P . Morrell Surf & Coatings Tech 50 (1992) 141-149.

Cipitria, A.; Golosnoy, I.O.; Clyne, T.W., Acta Materialia, Feb. 2009, vol.57, no.4, pp. 980-92,

J. Thornton, Materials Forum 22 (1998) 159-181, V.Arnault, , R. Mévrel, S. Alpérine, and Y.Jaslier, La Revue Métallurgie – CIT/Science et Génie des Matériaux 96 [5] (1999) 585.

M.J. Stiger, N.M Yanar,., M.G. Topping, F.S. Pettit, and G.H. Meier, Zeitschrift für Metallkunde, 90 (1999) 1069.

D. Stöver and C. Funke, Mater. Proc. Technol. 92-93 (1999) 195.

J.R. Nicholls, MRS Bulletin September (2003) 659-670.

C.G. Levi, Curr. Opin. Solid State Mater. Sci., 8 (2004) p.77.

A. Feuerstein, J. Knapp, T. Taylor, A. Ashary, A. Bolcavage, N. Hitchman, J. Therm. Spray Technol. 17 [2] (2008) 199.

C.G. Levi, Curr. Opin. Solid State Mater., 8 (2004) 77.

D.R. Clarke and S.R. Phillpot, Mater. Today, 8 (2005) 22.

N.P. Bansal and D. Zhu, Mater. Sci. Eng. A, 459 (2007) 192.

B. Saruhan, P. Francois, K. Fritscher, and U. Schulz, Surf. Coat. Tech., 182 (2004) 175.

R. Vaßen, F. Traeger, and D. Stöver, Int. J. Appl. Ceram. Tec., 1 (2004) 351.

Z.-G. Liu, J.-H. Quyang, Y. Zhou, J. Li, X.-L. Xia, (Ln0.9Gd0.05Yb0.05)2Zr2O7 Ceramics with Pyrochlore Structure as Thermal Barrier Oxides, Advanced Engineering Materials 10, 8 (2008) 754-758.

M.J. Maloney, European Patent No. EP 0 848 077 A1

J. Wu, X. Wei, j. Wang, C. Wan, L. Qi, H. Miao, Rare-Earth Zirconates Ceramics with Fluorite Structure for Thermal Barrier Coatings, J. Am. Ceram. Soc., 89, 1 (2006) 340-342..

R. Subramanian, US Patent No. US 6258467

J. Wu, X. Wei, N.P. Padture, P.G. Klemens, M. Gell, E. García, P. Miranzo, and M.I. Osendi, Low-Thermal-Conductivity Rare-Earth Zirconates for Potential Thermal-Barrier-Coating Applications, J. Am. Ceram. Soc., 85 (2002) 3031.

R. Vaßen, D. Stöver, H. Bosch, M. Dietrich, X. Cao, G. Pracht, European Patent 1 38 6017

H. Lehmann, D. Pitzer, G. Pracht, R. Vaßen, D. Stöver, *Thermal conductivity and thermal expansion coefficients of the Lanthanum-Rare Earth Element-zirconate system*, J. Amer. Ceram. Soc., 86, 8 (2003) 1338-44.

W. Ma, Y.- Ma. S. Gong, H. Xu, X. Cao, Thermal Cycling Behavior of Lanthanum-Cerium Oxide Thermal Barrier Coatings Prepared by Air Plasma Spraying, Key Engineering Materials Vols 336-338 (2007) 1759-61.

W. Ma, S. Gong, H. Xu, and X. Cao, Surf. Coat. Tech., 200 (2006) 5113. ???

X. Cao, Development of New Thermal Barrier Coating Materials for Gas Turbines, PhD Thesis Ruhr Universität Bochum 2004 (D294), Berichte des Forschungszentrums Jülich 4127.

Z. Xu, L. He, R. Mu, X. Zhang, Y. Zhang, J. Zhang, and X. Cao, J. Alloy Compd., 473 (2009) 509. ???

X.Q. Cao, R. Vassen, and D. Stoever, J. Eur. Ceram. Soc., 24 (2004) 1.

X.Q. Cao, R. Vassen, W. Jungen, S. Schwartz, F. Tietz, D. Stöver, Thermal Stability of Lanthanum Zirconate Plasma-Sprayed Coating, J. Am. Ceram. Soc. 84, 9 (2001) 2086-90.

H. Chen, Y. Liu, Y. Gao, S. Tao, H. Luo, J. Am. Ceram. Soc. 93, 6 (2010) 1732-1740.

R. Vaßen, G. Pracht, D. Stöver, *New thermal barrier coating systems with a graded ceramic coating,* Proc. of the International Thermal Spray Conference 2002, Verlag für Schweißen und verwandte Verfahren DVS-Verlag GmbH, Düsseldorf, 2001, pp. 202-207.

Vaßen, R.; Giesen, S.; Stoever, D. *Lifetime of Plasma-Sprayed Thermal Barrier Coatings: Comparison of Numerical and Experimental Results,* Journal of Thermal Spray Technology, Vol. 18, No. 5-6, Dec. 2009, pp. 835-845.

H. Dai, X. Zhong, J. Li, Y. Zhang, J. Meng, and X. Cao, Mater. Sci. Eng. A, 433 (2006)1.

C. Mercer, S. Faulhaber, A.G. Evans, R. Darolia, A Delamination Mechanism for Thermal Barrier Coatings Subject to Calcium - Magnesium – Alumino - Silicate (CMAS) Infiltration, Acta Mater. 53 (2005) 1029-1039

S. Krämer, J. Yang, C.G. Carlos, Infiltration-Inhibiting reaction of Gadolinium Zirconate Thermal Barrier Coatings with CMAS Melts, J. Am. Ceram. Soc. 93, 2 (2008) 576-583.

Private communication, D. Zhu, Nasa Glenn Research Center, USA.

D. Zhu, R.A. Miller, Int. J. Appl. Ceram. Technol., 1 [1] (2004) 86.

D. Zhu, R. A. Miller, D. S. Fox, Proc. Of the 48th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, Honolulu, Hawai April 23-26, 2007. pp 1-15.

M. Gasperin, M. C. Saine, A. Kahn, F. Laville, and A. M. Lejus, J. Solid State Chem., 54 (1984) 61.

R. Collongues, D. Gourier, A. Kahn-Harari, A. M. Lejus, J. Thery, and D. Vivien, Annu. Rev. Mater. Sci, 20 (1990) 51.

L. Xie and A. N. Cormack, J. Solid State Chem. 88 (1990) 543

P. Y. Jia, M. Yu, and J. Lin, J. Solid State Chem., 178 (2005) 2734.

H. Inoue, K. Sekizawa, K. Eguchi, and H. Arai. J. Am. Ceram. Soc., 80 (1997) 584.

R. Gadow and G. W. Schäfer, Patent 99-EP982 9942630, WO (1999).

G. Pracht, R. Vassen, D. Stöver, German patent application 10 2005 011 225 Wärmedämmstoff sowie Herstellungsverfahren und Verwendung.

G. Schäfer and R. Gadow. in International Conference on Advanced Ceramics and Composites, (Cocoa Beach, American Ceramic Society, 1999), p. 291.

C. J. Friedrich, R. Gadow, and M.H. Lischka, in 25th Annual Conference on Composites, Advanced Ceramics, Materials, and Structures, (Cocoa Beach, FL, USA, 2001) p. 375.

C. Friedrich, R. Gadow, and T. Schirmer, J. Therm. Spray Technol., 10 (2001) 592.

R. Gadow and M. Lischka, Surf. Coat. Technol., 151(2002) 392.

C. Friedrich, R. Gadow, and T. Schirmer, J. Therm. Spray Technol., 10 (2001) 592.

D. Zhu, D. S. Fox, N. P. Bansal, and R. A. Miller, NASA Briefs (2004).

S. R. Choi, N. P. Bansal, and D. Zhu, in International Conference on Advanced Ceramics and Composites, 11-19 (Cocoa Beach, FL, USA, American Ceramic Society,2005).

N. P. Bansal and D. Zhu, Surf. Coat. Technol., 202 (12) (2008) 2698.

X. Q. Cao, Y. F. Zhang, J. F. Zhang, X. H. Zhong, Y. Wang, H. M. Ma, Z. H. Xu, L. M. He, and F. Lu. J. Eur. Ceram. Soc., 28 (10) (2008) p. 1979.

Y. Zhang, Q. Li, X. Ma, and X. Cao, Mater. Lett., 62 (2008) 923.

J. Zhang, X. Zhong, Y. Cheng, Y. Wang, Z. Xu, X. Chen, H. Ma, Y. Zhao, and X. Cao. J. Alloys Compd., 482 (2009) 376.

R. C. Ropp and G. G. Libowitz, J. Am. Ceram. Soc., 61 (1978) 473.

R. C. Ropp and B. Carroll, Solid-State Kinetics of LaAl11O18. J. Am. Ceram. Soc., 63 (1980) 416.

H. Inoue, K. Sekizawa, K. Eguchi, and H. Arai, Catalysis Today, 47 (1999) 181.

P. Y. Jia, M. Yu, and J. Lin, J. Solid State Chem., 178 (2005) 2734.

B. Saruhan-Brings, U. Schulz, and C.-J. Kröder, Patent EP 1256636 A2, Europe (2002).

G. Pracht, R. Vaßen, and D. Stöver, in the 30th International Conference on Advanced Ceramic and Composites, (Daytona Beach, FL, USA, American Ceramic Society, Westerville, OH, USA, 87, 2007).

Doncieux, D. Stagnol, M. Huger, T. Chotard, C. Gault, T. Ota, and S. Hashimoto, J. Mater. Sci., 43 (2008) 4167.

Negahdari, T. Gerdes, and M. Willert-Porada, in Mechanical Properties and Performance of Engineering Ceramics and Composites III, (2008) 15.

B. R. Lawn, N. P. Padture, H. Cait, and F. Guiberteau, Science, 263 (1994) 1114.

R. Vassen, X. Cao, F. Tietz, D. Basu, and D. Stoever, J. Am. Ceram. Soc., 83 (2000) 2023.

W. Ma, D.E. Mack, J. Malzbender, R. Vassen, and D. Stöver, J. Euro. Ceram. Soc., 28 (2008) 3071.

W. Ma, M.O. Jarligo, D.E. Mack, D. Pitzer, J. Malzbender, R. Vassen, and D. Stöver, J. Therm. Spray. Technol., 17 (2008) 831..

J. E. Garcia, C. Cano, T.W. Coyle, M.I. Osendi, and P. Miranzo, J. Therm. Spray. Technol., 17 (2008) 831. .

P. Srirama Murti and M.V. Krishnaiah, Mater. Chem. and Phys., 31 (1992)347.

R. Guo, A.S. Bhalla, and L.E. Cross, J. Appl. Phys., 75(1994) 4704.

R. Tarvin and P.K. Davies, J. Am. Ceram. Soc., 87 (2004) 859.

C. Tsai and H. Teng, J. Am. Ceram. Soc., 87 (2004) 2080.

M.O. Jarligo, D.E. Mack, R. Vassen, and D. Stöver, J. Therm. Spray. Technol., 18 (2009) 187.

M.O. Jarligo, D.E. Mack, R. Vassen, and D. Stöver, J. Therm. Spray. Technol., 19 (2010) 303.

Y. Zhang, D.E. Mack, M.O. Jarligo, X. Cao, R. Vaßen and D. Stöver, J. Therm. Spray. Technol., 18 (2009) 694.

H. Guo, H. Zhang, G. Ma and S. Gong, Surf. Coat. Technol., 204 (2009) 691.

R. Vassen, F. Tietz, G. Kerkhoff, and D. Stoever. in Proceedings of the 6th Liege Conference on Materials for Advanced Power Engineering, ed. by J. Lecomte-Beckers, F. Schuber and P. J. Ennis, (Forschungszentrum Jülich GmbH, Jülich, Deutschland, 1998) p.1627.

W. Pan, Q. Xu, L. Qi, J. Wang, H. Miao, K. Mori and T. Torigoe, Key Eng. Mater. 280-283 (2005) p. 1497.

H. Lehmann, D. Pitzer, G. Pracht, R. Vassen, and D. Stöver, J. Am. Ceram. Soc., 86 (2003) 1338.

D. Zhu, J.A. Nesbitt, C.A. Barrett, T. R. McCue, R.A. Miller, Journal of Thermal Spray Technology 13 (1) (2004) 84-92.

Dudek, M.; Rog, G.; Bogusz, W.; Kozlowska-Rog, A.; Bucko, M.; Zych, L., Calcium zirconate as a solid electrolyte for electrochemical devices applied in metallurgy, Materials Science, 2006, vol.24, no.1, pp. 253-60,

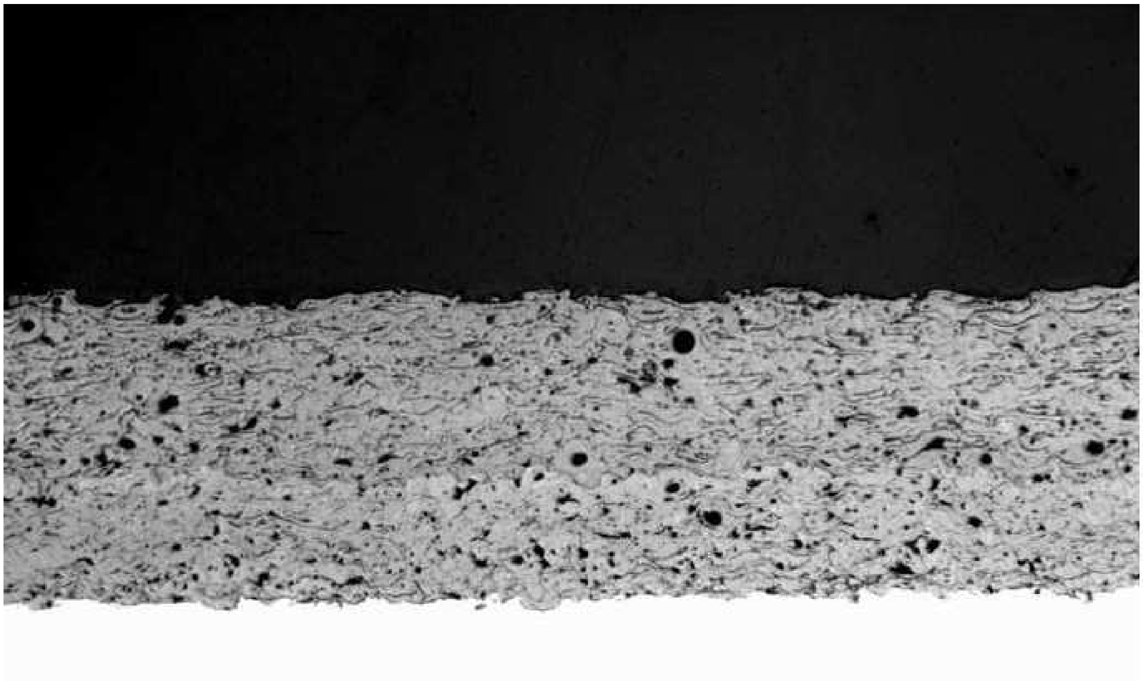

Fig. 1

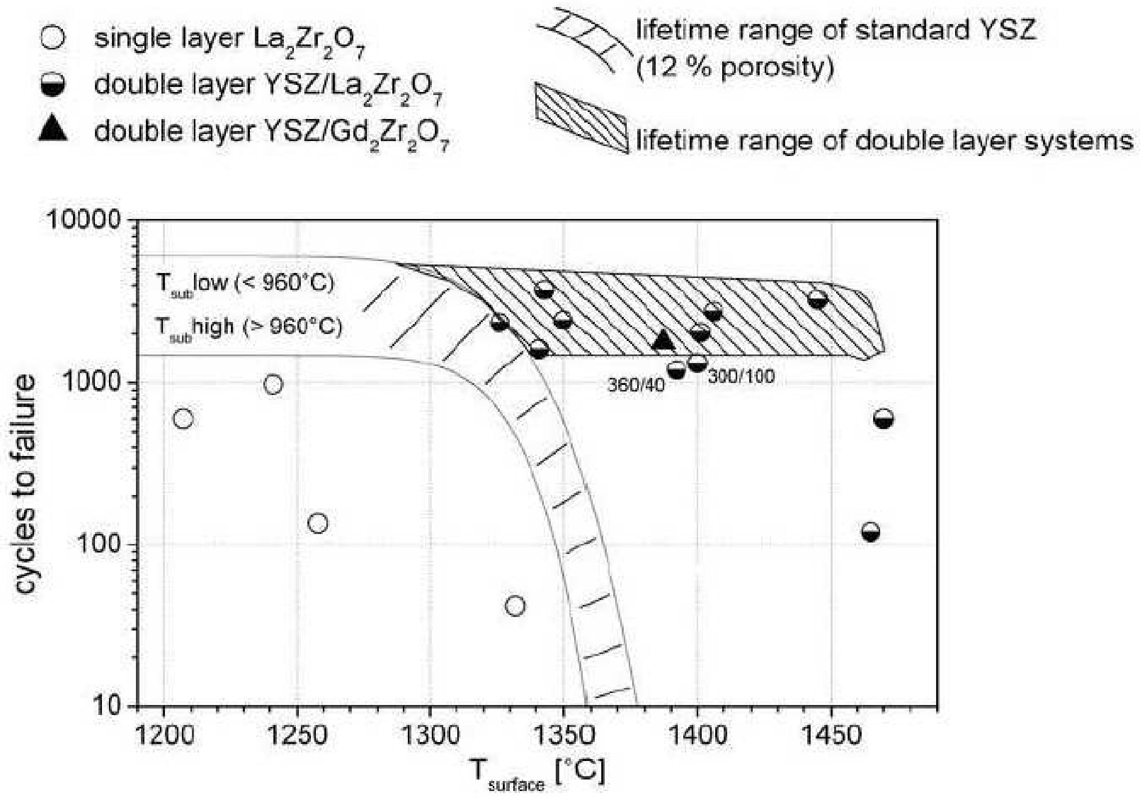
single layer $La_2Zr_2O_7$
double layer YSZ/$La_2Zr_2O_7$
double layer YSZ/$Gd_2Zr_2O_7$
lifetime range of standard YSZ (12 % porosity)
lifetime range of double layer systems
T_{sub} low (< 960°C)
T_{sub} high (> 960°C)
360/40
300/100
cycles to failure
10000
1000
100
10
1200
1250
1300
1350
1400
1450
$T_{surface}$ [°C]

Fig. 2

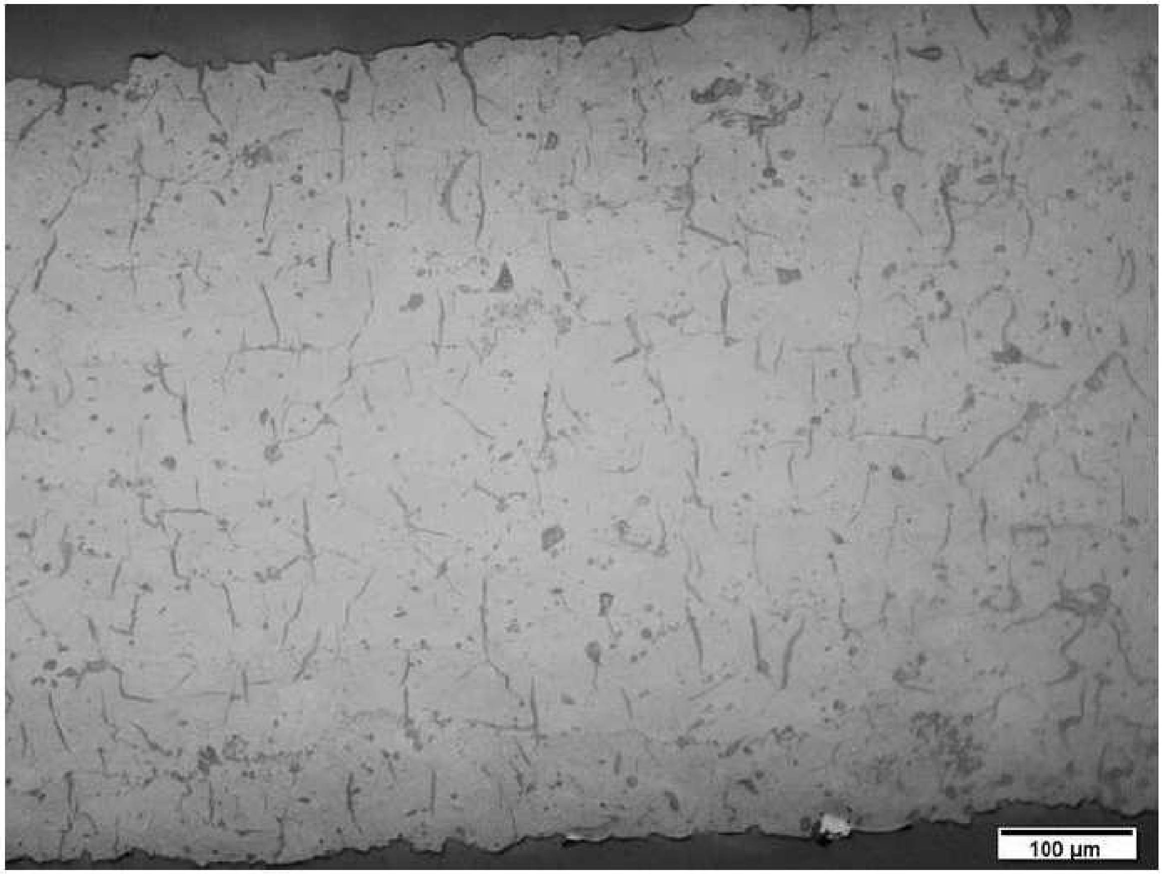

Fig. 3

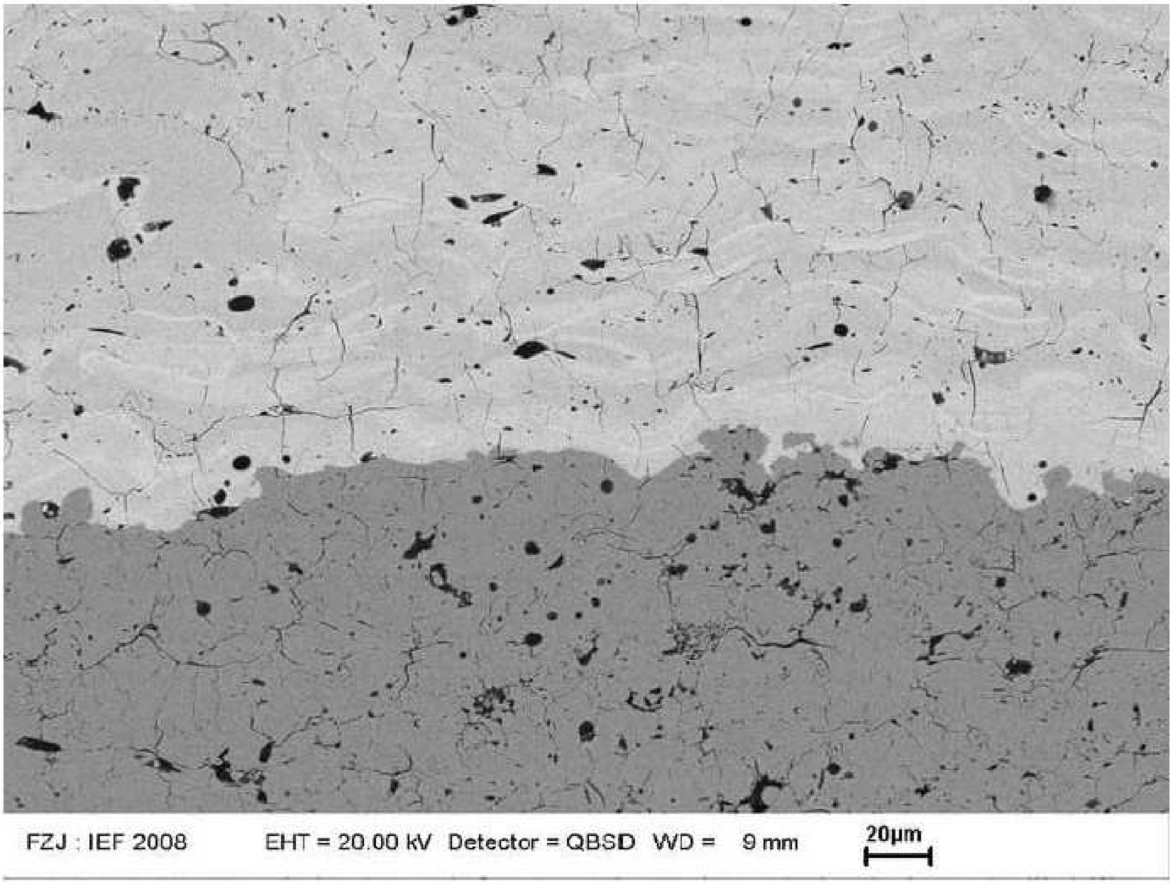

Fig. 4

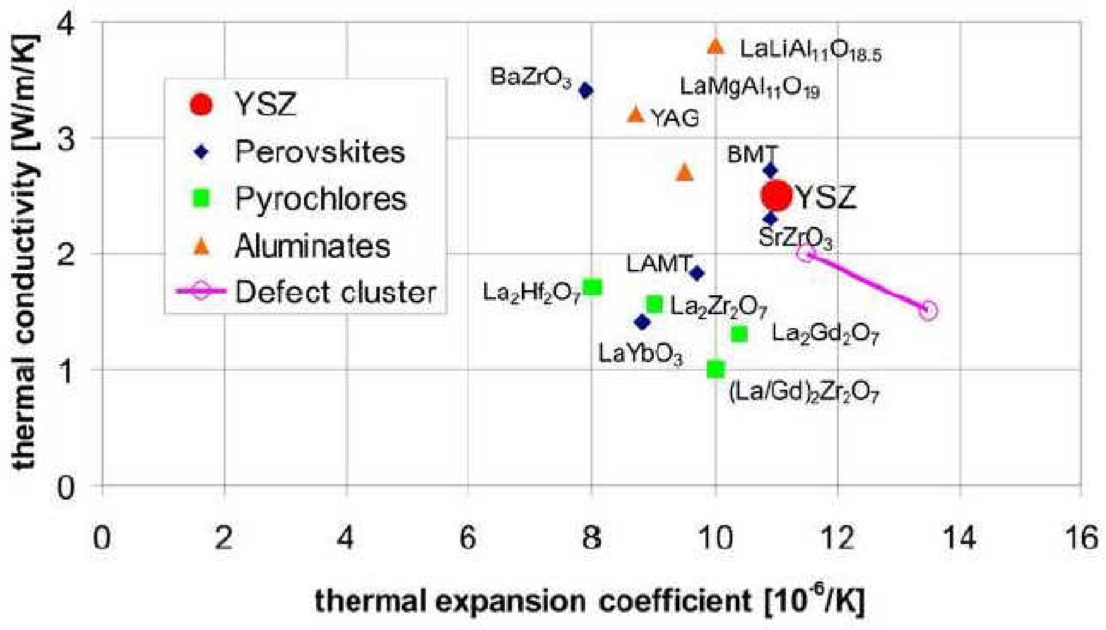
thermal conductivity [W/m/K]
0
1
2
3
4
thermal expansion coefficient [10^{-6}/K]
0
2
4
6
8
10
12
14
16
YSZ
Perovskites
Pyrochlores
Aluminates
Defect cluster
$LaLiAl_{11}O_{18.5}$
$BaZrO_3$
$LaMgAl_{11}O_{19}$
YAG
BMT
YSZ
$SrZrO_3$
LAMT
$La_2Hf_2O_7$
$La_2Zr_2O_7$
$La_2Gd_2O_7$
$LaYbO_3$
$(La/Gd)_2Zr_2O_7$

Fig. 5