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Advanced Multi-layered Thermal Barrier Coatings - An Overview

Review Paper

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5 ABSTRACT

6 A new type of thermal barrier coating must be developed to protect the underlying metallic 7 components from higher operating temperatures in order to enhance the fuel efficiency of the 8 gas turbine engine. Yttria stabilised zirconia (YSZ) is a conventionally used top coat material 9 for a thermal barrier coating (TBC) system. However, YSZ cannot work above 1200°C due to its sintering effect. As a replacement of this coating various types of multilayer coatings have 10 11 been developed by researchers. These coatings should fulfil both mechanical and thermal requirements of the TBCs. The current paper focuses on providing an overview regarding 12 advanced multilayer thermal barrier coatings suitable for the future generation gas turbine 13 14 applications.

Keywords: Thermal barrier coating, Multi-layered coating, Functionally graded coating, Gasturbine applications

17 **1. INTRODUCTION**

The gas turbine engine is needed to operate at higher service temperatures in pursuit of 18 19 higher engine efficiency and output. In the 70's, the surface inlet temperature of gas turbine engine was approximately 900°C. But in recent years, the turbine inlet temperature has 20 21 increased to 1380°C for advanced gas turbine engines [1]. This results in an enhanced high temperature corrosion attack on the blade materials like wear, oxidation and erosion etc. 22 23 Various types of coatings have been developed to provide lubrication, stress buffering and 24 thermal insulation to the metallic components [2]. Among these, TBC has the most interesting structure and must operate in the harshest environment of aircraft, marine and industrial gas 25

turbine engines. They are widely employed in the hot sections of the gas turbine to protect the metallic component from high temperature and to extend the lifetime of the engines [3]. TBCs comprising of metal and ceramic multilayers insulate turbine and combustor engine components from the hot gas stream and improve the durability and efficiency of these engines [4]. Improvements in TBCs will require better understanding of the complex changes in structure and properties that occur under operating conditions that lead to their failure. Different types of TBCs are herein reviewed for advanced future application.

33 2. ANATOMY OF TBC

Mostly, TBC is composed of four layers which have specific properties and functions. 34 These layers are (a) substrate, (b) bond coat, (c) thermally grown oxide (TGO) and (d) 35 ceramic top coat [5]. Generally, Ni or Co based super alloys is the substrate used in hot-36 section components of the gas turbine engine [6]. Sometimes, it contains many additional 37 elements to enhance various specific properties such as high temperature strength, ductility, 38 oxidation resistance, hot corrosion resistance and castability. During service at high 39 temperature, diffusion of elements can occur between the super alloy substrate and the bond 40 41 coat. Bond coat is an oxidation resistant metallic layer typically made of NiCrAlY or 42 CoCrAlY, deposited by high velocity oxy fuel (HVOF), atomic plasma spray (APS) or 43 electron beam physical vapour deposition (EB-PVD) technique. It has a thickness of 75-150 44 µm. Other types of bond coats are made of aluminides [7,8] of Pt or Ni deposited by 45 electroplating or chemical vapour deposition (CVD). Glass-ceramic bond coats are also used 46 recently [9]. At high temperature, the bond coat oxidation leads to the formation of a third layer called thermally grown oxide (TGO) which protects the components from oxidation and 47 48 corrosion. But, sometimes increased thickness of TGO leads to spallation of the ceramic top 49 coat [10]. Ceramic top coat is the top layer of TBC which provides thermal insulation. The

basic requirements of a good ceramic top coat are high melting point, low thermalconductivity and high co-efficient of thermal expansion [11].

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3. METHODS FOR TBC DEPOSITION

53 There are various methods to deposit the metallic bond coat and ceramic top coat on 54 the metal substrates. The most common methods are (a) APS, (b) High velocity oxy fuel 55 (HVOF), (c) electron beam physical vapour deposition (EB-PVD) [12]. The MCrAlY [M= 56 Co, Ni] bond coat and ceramic top coat are usually deposited by HVOF/ APS and APS/ EB-57 **PVD methods** [13]. APS-TBCs have less demand in industrial gas turbine application because APS-TBCs generally have shorter thermal cyclic life time than EB-PVD TBCs. EB-PVD top 58 59 coats are produced with columnar structures which reduce the thermal mismatch strain 60 between the metallic substrate and ceramic top coat and thus lead to a longer thermal cycling life. But, EB-PVD technique is complicated as well as expensive. Recently, another technique 61 62 named suspension plasma spray (SPS) has attracted much more attention, fulfilling the 63 desired requirements. A comparative study on the performance of suspension plasma sprayed 64 (SPS) TBCs with different bond coat systems have been investigated by Zou et al. [14]. The 65 SPS TBCs with a rough APS bond coat exhibited a longer lifetime than those with a smooth HVOF bond coat. The microstructure of the SPS YSZ top coat significantly depends on the 66 67 bond coat surface morphology. The failure of SPS TBCs typically occurs at the TGO-bond 68 coat interface.

69 Cold spray (CS) is another superior method for deposition of the bond coat. The 70 oxidation behaviour of TBCs with CS and low pressure plasma spray (LPPS) bond coats were 71 studied by Manap et al. [15] to evaluate the reliability of CS as a method for producing bond 72 coats for TBC. TGO developed in the TBC with the LPPS bond coat was composed of only 73 α -Al₂O₃. On the other hand, TGO developed in the TBC with a CS bond coat was composed 74 of α Al₂O₃ and γ Al₂O₃ and some undesirable spinels which were brittle and porous in texture. 75 α Al₂O₃ transformed into y Al₂O₃ at the expense of mixed oxides. α -Al₂O₃ based TGO 76 exhibited a strong bonding to the YSZ coating while chrome oxide exhibited a poor adhesion 77 to YSZ coating. The direct exposure of cold sprayed bond coat to air at a high temperature of 1150°C led to the formation of fast grown spinel-based mixed TGO at the interface between 78 79 the bond coat and YSZ [16,17]. The high coverage of mixed oxide on the interface led to the 80 early spallation of the YSZ coating. Microstructure and oxidation behaviour of atmospheric plasma sprayed thermal barrier coating was reviewed by Avci et al. [18]. 81

82 4. CONVENTIONAL TBC SYSTEM

83 Hundreds of different types of coatings are used to protect a variety of components 84 used in gas turbine engines such as air propulsion, power generation, marine propulsion etc. Plasma sprayed coatings consist of a metallic bond coat, mostly MCrAlY [M= Co, Ni] 85 applied by HVOF technique and APS 6-8% YSZ top coat [19]. It provides the best 86 performance in high temperature applications because of its low thermal conductivity (2.2 87 W/mK) and very high co-efficient of thermal expansion $(10.7 \times 10^{-6} \text{ K}^{-1})$ [20]. But, standard 88 89 YSZ is not useful for high temperature applications (>1200°C) of gas turbine engine. High temperature capability and longer lifetime are needed for the next generation TBCs. At 90 91 elevated temperature, this coating leads to thermal instability, increased sintering rates and 92 inferior thermal conductivity. At higher temperatures, YSZ undergoes phase transformations 93 from its metastable tetragonal phase to monoclinic phase, promoting volume expansion, stress generation and finally formation of cracks in the coating [21-25] as well as sintering of YSZ 94 95 takes place [26]. Further, growth of crystallites occurs so that the pores in the grain 96 boundaries are gradually filled. It reduces the strain tolerance and thermal cycle lifetime by 97 increasing the young's modulus [27]. This effect will reduce the service life of components 98 and make it inadequate for high temperature gas turbine engine applications. Moreover, YSZ

is also oxygen transparent and allows oxygen diffusion from engine environment and oxidize
the selective elements (i.e. Al, Cr, Ni etc.) within the bond coat during high temperature
applications [28,29]. As a result, TGO forms between the super alloy and ceramic top coat
layer. Stresses generate due to growth of TGO at the interfaces causing localized expansion.
Crack initiates and propagates leading to spallation of the ceramic layer, which is often called
catastrophic failure [30].

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4.1 Compositionally modified bond coat in TBC system

106 A TBC system with a double layer bond coat was developed by Wang et al. [31]using vapour phase coating, HVOF and APS processes. Modification of the TBC processes has 107 been done by Fairbanks and Hecht [32] in 1987 and Bose and Demasi-Marcin [33] in 1997. 108 The earliest TBC consisted of Ni-Al bond coating and MgO-ZrO₂ top coat. APS Ni-Co-Cr-109 Al-Y replaces the Ni-Al bond coat and doubles the performances. Spallation resistance further 110 increases by a factor of 2 by changing to an APS Y2O3- ZrO2 top coat with the same 111 112 NiCoCrAIY bond coat. When the bond coat was deposited by LPPS to avoid oxidation during the air plasma spraying, the resistance to spallation was again doubled. Further were 113 114 improvements accomplished by instituting a more strain-tolerant ceramic top layer using EB-PVD process. Unlike the traditional TBCs, recent TBC systems consist of an aluminide 115 116 diffusion bond coat and a CoNiCrAlY overlay bond coat. The major advantage of the 117 diffusion process is to coat the entire surface of the component. The overlay coating offered 118 good oxidation and corrosion resistance and coating ductility. The HVOF process replaced 119 the LPPS and EB-PVD due to lower cost.

Czech et al. [34] showed that MCrAlY bond coat can be improved by addition of 1.510% rhenium (Re). This overlay coating shows a three phase mixture with better oxidation,
corrosion, thermal, mechanical fatigue behaviour. High temperature strength capability also

increased by the addition of 10% Re in MCrAlY bond coat. Seraffon et al. [35] have 123 124 developed new bond coat compositions for TBC systems operating under industrial gas turbine conditions. A range of Ni-Cr-Al-Co coatings were deposited by physical vapour 125 126 deposition technique by magnetron sputtering through the co-sputtering of one target such as Ni10Cr [Ni-10wt.%Cr], Ni20Cr [Ni-20wt.%Cr], Ni50Cr [Ni-50wt.%Cr], Ni20Co40Cr [Ni-127 128 20wt.%Co-40wt.%Cr], Ni40Co20Cr [Ni-40wt.%Co-20wt.%Cr] with another target e.g. pure Al. During oxidation, Co-rich coating gives non-protective oxides such as spinels wherein 129 with increasing chromium weight percentage of aluminium decreases. The best compositions 130 evaluated were 26Co-22Ni-13Cr-39Al, 14Ni-8Co-18Cr-60Al, 31Ni-8Cr-61Al and 17Ni-131 X 22Cr-61Al. 132

4.2 Two-layered TBC 133

The increasing demands for more efficiency of gas turbines lead to higher service 134 temperature and longer thermal cyclic lifetime. There are large numbers of advanced top coat 135 136 materials reported for advanced TBCs. Recently, some new candidate materials for TBC application at high temperatures such as lanthanum magnesium hexaluminate 137 138 (LaMgAl₁₁O₁₉, LMA) [36,37], La₂Ti₂Al₉O₁₉ [38], metal-glass composite [39], ZrO₂-Y₂O₃- La_2O_3 [40], lanthanum zirconate ($La_2Zr_2O_7$, LZ) [41,42], $La_2C_2O_7$ (LC) [43], La_2 ($Zr_0_7Ce_{0.3}$) 139 140 O_7 (LZ7C3) [44] and other rare earth oxide doped zirconia [45] have been investigated. 141 Among these candidates, the rare earth zirconates and cerates were proposed as a promising 142 TBC material. LZ-pyrochlore has low CTE [46] and LC fluorite has high sintering ability 143 [47]. Doped CeO_2 into LZ results in LZ7C3, which has a higher sintering resistance due to its multiphase structure [48-50]. LZ7C3 is thermally stable after long annealing at 1573K and no 144 phase transformation is observed. The CTE of LZ7C3 is about $10.66 \times 10^{-6} \text{ K}^{-1}$ which is 145 comparable to YSZ. Thermal conductivity of LZ7C3 is 0.87 Wm⁻¹K⁻¹ lower than that of the 146 147 8YSZ and LZ [51]. Some very promising compounds crystallize in the pyrochlore structure,

for example $La_2Zr_2O_7$, $Nd_2Zr_2O_7$ and $Gd_2Zr_2O_7$. These three compounds have high melting points around 2000°C. They are stable up to the melting point without any critical phase transformation and their thermal conductivities are significantly lower than YSZ [52].

Lanthanum magnesium hexaaluminates (LaMgAl₁₁O₁₉, LMA) crystallize in the 151 magnetoplumbite structure. The good phase stability up to the melting point ($T_{mp} > 2000^{\circ}C$) 152 and the thermal conductivity, which is slightly better than YSZ as well as the structural 153 neighbourhood of LMA and TGO (mainly Al_2O_3) increase the high expectations. Lanthanum 154 155 zirconate (rare earth zirconate) TBCs were fabricated by Girolamo et al. [53] using APS technique. Mechanical properties and thermal properties of as sprayed and heat treated 156 lanthanum zirconate TBCs were studied. Partial sintering of porous TBCs occurred after 157 thermal cycling. Elastic modulus increased with increasing test temperature. 158

Many studies have been conducted to reduce the negative effect of TGO growth by 159 changing the bond coat or modifying the chemical composition of the bond coat. Glass-160 ceramic coating was used as bond coat between the substrate and the YSZ top coat by Das et 161 al. [9]. Since the glass-ceramic material is oxide based, bond coat oxidation did not occur. 162 Cao et al. [54] studied thermal stability and failure of lanthanum magnesium hexaluminate. It 163 has long term structural and thermo-mechanical stability up to 1400°C and has higher 164 165 sintering resistance than conventional YSZ. But, during thermal cycling, the plasma sprayed LMA coating undergoes phase transition. The reason why LMA coating has a long thermal 166 cycling life is the plate-like and porous structure, which results in low Young's modulus and 167 168 high stress tolerance of the transformed phase.

A new thermal barrier coating system based on La_{1.7}Dy_{0.3}Zr₂O₇ [LDZ] was investigated by Wang et al. [55] for high temperature application. Compared to conventional 8 wt.% YSZ, it has lower thermal conductivity, excellent antioxidant property, better phase

172 stability. The bond coat NiCrAlY and the ceramic top coat LDZ were deposited by APS 173 method. XRD results showed that it has a single pyrochlore phase and no new phases appeared after ablation at 1573 K and 1773 K. Arai et al. [56] showed that thermal 174 175 conductivity can be reduced by introducing polyester in zirconia powder. As the melting 176 temperature of polyester is very low, polyester sites were evaporated leaving large open pores. 177 Results revealed that the thermal conductivity of polyester incorporated TBC (P-TBC) 178 monotonically decreases with increasing porosity. For conventional TBC, the thermal conductivity is ~ 1.2 [W/(mK)] whereas P-TBC exhibit lower thermal conductivity ~ 0.3 179 180 [W/(mK)].

181 5. NEW CONCEPT: MULTI-LAYERED TBC

182 5.1 Three-layered TBC

183 In order to have an ideal TBC design the top coat should have some basic 184 requirements such as high melting point, high temperature phase stability, low thermal 185 conductivity, high co-efficient of thermal expansion, high sintering resistance, good chemical compatibility and good adherence to the metallic substrate [57]. No single material could 186 satisfy all these requirements. Multi-layered coatings were introduced as a solution. YSZ has 187 188 low thermal conductivity and relatively high thermal expansion co-efficient but above 1200°C it shows low sintering resistance and phase transformation [21]. LZ has very low co-efficient 189 190 of thermal expansion compared to YSZ and low fracture toughness but high phase stability 191 and sintering resistance at high temperature. It acts as a thermal insulator and protects the 192 underlying YSZ layer [41,42]. Multi-layered thermal barrier coating is composed of different 193 ceramic coating materials having different functions. Various ceramic coatings are deposited 194 to form discrete and homogeneous layers. Distinct compositional interface is formed between 195 each adjacent pair of successive layers.

Xu et al. [58] showed that the double ceramic layer (DCL) $La_2Zr_2O_7$ (LZ) / YSZ 196 197 coating has excellent thermal cycling life compared to the single layered coating of YSZ and LZ. Therefore, this double ceramic layer can be used to improve thermal capability of gas 198 turbines during actual application. LZ has very high phase stability up to the melting point. 199 200 The YSZ coating was used as an interlayer between the bond coat and the LZ top coat. 201 Pyrochlore type rare earth zirconates having low thermal conductivity, high phase stability, reduced sintering rate and moderate thermal expansion co-efficient, are promising candidates 202 as advanced TBC materials used in gas turbine engine. Rare earth oxide doped YSZ/ 203 (gadolinium zirconate, Gd₂Zr₂O₇) DCL coating was successfully established by Rai et al. 204 [59]. Sometimes, trivalent rare earth oxides such as Gd_2O_3 and Yb_2O_3 were doped with ZrO_2 205 to create immobile defect clusters within the structure leading to reduced thermal 206 conductivity, better sintering resistance and increased toughness and phase stability. 207 208 Deposition of standard YSZ was done first before GDO deposition to prevent diffusion of Gd into the TGO layer. Xu et al. [60] reported that lanthanum cerium zirconate [LZ7C3] showed 209 promising thermo physical properties for high temperature applications in gas turbine. But, 210 211 this coating had low thermal expansion co-efficient which led to high thermal stress between LZ7C3 and substrate. Single layer coating of LZ7C3 is not useful in TBC system because of 212 213 its short thermal shock life. In DCL coating, the top ceramic layer should have low thermal 214 conductivity and high phase stability, so that it could protect the inner layer and the substrate 215 alloy. As YSZ has very high thermal expansion co-efficient and thermal shock lifetime, the 216 DCL coating system that consists of LZ7C3/YSZ could act as a potential advanced TBC 217 material.

Xu et al. [61] demonstrated that rare earth cerates also could be used as a significant top coat material for future generation TBCs. The DCL coatings consisting of LZ7C3/ (lanthanum cerate, LC) were deposited by EB-PVD. LC has lower thermal conductivity than 221 YSZ. It has cubic fluorite structure and high temperature phase stability. But, the sintering 222 temperature of this coating is lower than the target service temperature of advanced TBCs. 223 LZ7C3 coating has high sintering resistance [62,63]. Large CTE of LC and low sintering rate 224 of LZ7C3 can make this layered coating more effective. But, the chemical compatibility of 225 LC coating and TGO layer is unstable. LaAlO₃ is formed due to the chemical reaction 226 between LC and TGO layer, which is the primary factor of spallation of DCL coating. Xie et 227 al. [64] proposed and investigated phase stability, mechanical and thermo-physical properties of a new TBC material, LaTi₂Al₉O₁₉ (LTA) for application up to 1300°C. The coating showed 228 excellent phase stability up to 1600°C. Thermal conductivity and CTE values are also 229 comparable to YSZ. However, the fracture toughness value is quite lower than the standard 230 231 YSZ and this was compensated by double ceramic LTA/YSZ layer design. It exhibited desirable thermal cycling life nearly 700 h at 1300°C, thus meeting the demand of advanced 232 233 gas turbine engines.

Han et al. [65] have done a parametric study of LZ7C3/8YSZ DCL thermal barrier 234 coating. Heat insulation behaviour of this DCL-TBC system has been mainly studied. 235 236 Calculation was done based upon two structural parameters of DCL-TBC system: the thickness of top ceramic layer and the total thickness of two ceramic layers. Results indicate 237 238 that too large or too small values of these two parameters are unfavourable to the temperature 239 in the whole DCL-TBC and a temperature safe region has been evaluated. The temperature 240 safe region obtained in this study is a theoretical safe region. Therefore, further study is 241 needed. Liu et al. [66] introduced a new coating which has great potential as a next generation 242 of high performance TBC top coat material. $Sm_2Zr_2O_7/YSZ$ and $(Sm_{2/3}Yb_{2/3})_2 Zr_2O_7/YSZ$ DCL thermal barrier coatings were prepared by plasma spraying to evaluate their 243 244 microstructure and thermal shock behaviour. $Sm_2Zr_2O_7$ exhibits pyrochlore type [Ln₂Zr₂O₇ 245 type, Ln- lanthanum] structure and show promising thermo-physical properties at high

temperature. $(Sm_{2/3}Yb_{2/3})_2 Zr_2O_7$ has defect fluorite structure. At 1250°C, the number of thermal shock failure of $Sm_2Zr_2O_7/YSZ$ and $(Sm_{2/3}Yb_{2/3})_2 Zr_2O_7/YSZ$ coatings are 52 and 33, respectively. But, the failure of zirconate/YSZ DCL coating mainly occurs inside the ceramic top coat and TGO layer is not responsible for this failure.

250 Zhang et al. [67] investigated the effect of Al-deposition on erosion resistance of plasma sprayed TBC. A columnar Al film was deposited on the top of 7YSZ in TBC system by 251 252 magnetron sputtering technique. On heat treatment, Al formed a loose surface layer and a 253 dense sub-layer. The dense sub-layer consisted of Al₂O₃ and Al₃Zr which in situ formed Al and ZrO₂ under heat treatment and the loose surface layer contained α -Al₂O₃. The porosity of 254 7YSZ top layer was also decreased because of pore filling by α -Al₂O₃ phases. Functional 255 performance of Gd₂Zr₂O₇/YSZ multi-layered thermal barrier coatings deposited by 256 257 suspension plasma spray was reported by Mahade et al. [68]. At higher temperature (above 1200°C) YSZ is susceptible to calcium magnesium alumino silicate (CMAS) infiltration 258 along with phase stability and sintering effect. In this study, double layer TBC comprising of 259 gadolinium zirconate and YSZ [GZ/YSZ] and triple layer TBC [GZ dense/GZ/YSZ] 260 comprising of relatively denser GZ top layer on GZ/YSZ were deposited by suspension 261 plasma spray technique. Single layer 8YSZ TBC was suspension plasma sprayed to compare 262 263 its functional performance with the multi-layered TBCs. The multi-layered GZ/YSZ TBCs 264 were shown to have lower thermal conductivity and longer thermal cycle life compared to the 265 single one. Erosion performance of gadolinium zirconate based thermal barrier coating was studied by Mahade et al. [69]. 266

The as sprayed GZ based multi-layered TBCs were subjected to erosion test at room temperature and their erosion resistance was compared with the single layer 8YSZ. It was observed that the erosion resistance of 8YSZ single layer TBC was higher than GZ based multi-layered TBCs. Among the multi-layered TBCs triple layer TBC was slightly better than double layer in terms of erosion resistance. Micro-structural characterization and thermal shock test of $Gd_2Zr_2O_7$ / ceria–yttria stabilized zirconia (GD/CYSZ) were also done by Gok et al. [70]. In this study, first $Gd_2Zr_2O_7$ /CYSZ TBCs having multi-layered and functionally graded designs were subjected to thermal shock test. The functionally graded coating showed better result than the multi-layered and single TBCs.

276 Jonnalagadda et al. [71] studied the corrosion resistance of multi-layer gadolinium 277 zirconate (GZ) /YSZ and YSZ single-layer suspension plasma sprayed TBCs. Typical single 278 layer, double layer and three layered TBC systems are shown in Fig. 1 [71]. When exposed to a mixture of vanadium pentoxide and sodium sulfate at 900 °C, multi-layer gadolinium 279 zirconate-based coatings demonstrated lower reactivity with the corrosive salts. Significant 280 281 salt penetration occurred into the coating through the columnar gaps due to the columnar 282 microstructure of the coatings and low reactivity of the GZ. Dense third layer on the top did 283 not improve the corrosion resistance as the second layer was degraded on account of salt 284 infiltration into the coating through the vertical cracks. The single-layer YSZ coating showed lesser damage than the multi-layer coatings partly due to the corrosive species being 285 restrained in the upper portion of the coating. The corrosive products were formed inside the 286 pores whereas they were formed at the columnar gaps of GZ [71]. 287

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289 5.2 Multi-layered TBC

Researchers are looking to improve the conventional TBC system for long term high temperature application. A new approach using composite layer was conceived by Ramachandran et al. [72]. This coating architecture had five layers with two intermixed interlayers, which had much longer lifetime than the other TBC systems. In the DCL system, generation of high residual stress between two ceramic layers resulting from thermal expansion mismatch still remain a serious problem. Hence, coating architecture with intermixed interfacial layer was introduced. The duplex coating showed a sharp interface between ceramic coat and bond coat. On the contrary, no clear interface was displayed in case of four and five layered coating due to the introduction of a layer with intermixed materials of the top and bottom layers. This five layered coating revealed excellent high temperature capability, high thermal cycle life, low oxygen transparency, high thermal stability, low thermal conductivity and low sintering ability.

Ceria-yttria stabilized zirconia/alumina (CYSZ/Al₂O₃) and CYSZ/Al₂O₃+YSZ multi-302 layered ceramic coatings were produced in 4, 8 and 12 layers using HVOF and APS 303 techniques. Microstructure, thermal and mechanical properties were investigated [73]. 304 305 Thermal conductivity values of the CYSZ/Al₂O₃ and CYSZ/Al₂O₃+YSZ coatings were in the 306 range of 0.99 to 1.50 W/mK. The bonding strength of as-sprayed coatings was increased from 307 5.4 to 10.1 MPa for CYSZ/Al₂O₃ and 8.7 to 11.5 for CYSZ/Al₂O₃+YSZ coatings with increasing number of layers. Existence of phase transformation $[y-\alpha]$ for Al₂O₃ coating was 308 observed after the thermal cyclic test. The result indicated that the thermal conductivity and 309 thermal cyclic strength of CYSZ/Al₂O₃+YSZ TBCs were higher than CYSZ/Al₂O₃ based 310 thermal barrier coating. Bonding strength of both coatings decreased after thermal cyclic test 311 312 consisting of 300 and 500 cycles. Total thickness of the ceramic top coat was unchanged. The 313 thickness of the individual layer was decreased with increasing number of layers. Thermal 314 conductivity of CYSZ/Al₂O₃ coating showed an increase with increasing number of layers whereas $CYSZ/Al_2O_3 + YSZ$ coating did not show any significant changes with increasing 315 number of layers. 316

The microstructural, mechanical and thermal properties of Al₂O₃/CYSZ functionally graded thermal barrier coating were studied by Kirbyik et al. [74]. In that study CYSZ/ Al₂O₃ ceramic TBCs were produced in double layered and functionally graded designs having 4,8 and 12 layers by high velocity oxy fuel and atmospheric plasma spray processes. Thermal
conductivity of the coating having 8 layered CYSZ/ Al₂O₃ functionally graded design were
lowest compared to CYSZ/ Al₂O₃ double layered and CYSZ single layered designs at 835°C.
Thermal cyclic performance and bonding strength of CYSZ/ Al₂O₃ functionally graded TBCs
were superior to those of single layered CYSZ and double layered CYSZ/ Al₂O₃ coatings.

325 Thermal conductivity is one of the most important properties of the TBCs used in gas 326 turbine blades. Ravichandran et al. [75] have also studied the microstructure, texture and 327 thermal stability of single and multi-layered TBCs of YSZ and Al₂O₃ made by physical 328 vapour deposition. Bulk 8YSZ coating exhibits columnar textured microstructure. But, in multi-layered coating, intensity of textured structure decreases with decreasing thickness of 329 330 individual 8YSZ layer. Thermal conductivity of these coatings was measured using the laser 331 flash method. The multi-layered coating consisted of 2, 8 alternating layers of Al_2O_3 and 332 YSZ. In all the coatings, the total thickness was maintained at $\sim 100 \ \mu m$. The thermal conductivity data of the multi-layered coatings of Al₂O₃ and 8YSZ matched to the predicted 333 data. The interlayer interfaces between Al₂O₃ and 8YSZ did not appear to contribute to 334 thermal resistance. This was also supported by the progressive dilution of the texture of the 335 8YSZ layers by Al_2O_3 with increasing number of layers. 336

Gupta et al. [76] investigated different multi-layered TBCs consisting of advanced topcoat materials fabricated by suspension plasma spraying (SPS). These samples were evaluated by thermal cyclic fatigue (TCF) testing and thermal shock testing. The experimental results showed that YSZ/gadolinium zirconate (GZO) had the best lifetime results considering both TCF test and burner rig test (BRT). This is due to high fracture toughness of YSZ combined with low thermal conductivity and comparable thermal expansion coefficient of GZO. Fig. 2 shows the thermal cyclic fatigue lifetime results and burner rig testing lifetime results.

345 **5.3 Functionally graded TBC**

Plasma sprayed thermal barrier coatings often have some problems like spallation and cracking during service due to their poor bond strength and residual stresses. This thermal stresses are induced due to thermal expansion mismatch between ceramic top coat and metallic bond coat. To overcome this problem a new concept of functionally graded materials has been introduced. The concept is to make a composite material by varying the microstructure from one material to another material with a specific gradient [77]. This enables the composite material to achieve the best property of both materials.

Functionally graded NiCrAlY / YSZ coating was successfully fabricated by Khoddami 353 et al. [78] using plasma spray co-injection of two different powders in a single plasma torch. 354 The amounts of ZrO_2 in this coating were gradually increased from 30 to 100 vol. %. The 355 microstructure, porosity, composition and other properties vary gradually in functionally 356 graded coatings. Coatings were free from cracks and no distinct interfaces were found 357 between two successive layers. The results also show that the average bond strength of the 358 graded coating is superior to that of the duplex coating of same materials. Functionally graded 359 360 yttria stabilised ZrO₂/ NiCoCrAIY coating were prepared by Khor et al. [79] and thermal properties of the coating were studied. The duplex and five layer functionally graded (FG) 361 362 coating were heated and cooled between 25° C and 1300° C cyclically to determine the thermal 363 cyclic resistance of coating. Experimental results showed that the thermal diffusivity and 364 thermal conductivity increased with increasing NiCoCrAIY content and temperature. The thermal cycling resistance of functionally graded coating was five times better than that of the 365 366 duplex coating having same thickness. Results also showed that the bond strength decreased with increasing thickness of the coating [80]. 367

368 Zhao et al. [81] prepared five layer ceramic-ceramic functional graded thermal barrier 369 coating (FG-TBC) using La₂ (Zr_{0.7}Ce_{0.3})₂O₇ [LZ7C3] and 8YSZ by APS technique. The functionally graded coatings consisted of 100% 8YSZ, 75% YSZ + 25% LZ7C3, 50% YSZ + 370 371 50% LZ7C3, 25% YSZ + 75% LZ7C3 as interlayers and 100% LZ7C3 as the top coat. The 372 thermal properties and microstructure were gradually changed from the top layer to the inner 373 layer. The average co-efficient of thermal expansion was found to be increased from top layer 374 to inner layer gradually. Chen et al. [82] prepared a six-layered TBC composed of YSZ and La₂Zr₂O₇ [LZ] using plasma spraying method. Thermal shock tests were conducted and the 375 376 results show that the thermal shock resistance of the graded YSZ/ LZ coating was better than that of the conventional double layer coating. Morphology of specimen before and after 377 378 thermal shock was also measured. Spallation was observed after ~ 21 cycles on the surface of the functionally graded coating. On the other hand, delamination was observed for the double-379 380 layer coating after six to seven cycles. Another new functionally graded TBC system was studied by Chen et al. [83]. This coating based on LMA/ YSZ was prepared using the APS 381 technique and microstructure, mechanical and thermal properties of the TBC were 382 investigated. Excellent thermal cycle life, superior sintering resistance, high CTE and good 383 chemical compatibility between LMA and YSZ make this coating a promising candidate for 384 high temperature application. A five layered ceramic [LMA]-ceramic [YSZ] FG-TBCs in the 385 386 weight ratios of 0%, 25%, 50%, 75% and 100% were deposited on the Ni-based super alloy 387 with a conventional bond coat MCrAlY using APS method. Fig. 2 shows the typical 388 microstructures of monolayer, multilayer and functionally graded coatings [84].

389 **5.4 Nano-structured TBC**

Nano-science and technology offer the potential for significant advances in the performance
 of new and established materials based on improvements in physical and mechanical
 properties resulting from reducing the grain size by a factor of 100 - 1000. Nano structured

393 materials exhibit very small grain sized particles and very high surface area. The nano 394 coatings have a high porosity of ~ 25% than the conventional coating, which is mainly attributed to the large amount of inter-splat gap in the nanostructured TBC. Lima et al. [85] 395 396 showed that the nanostructured YSZ coatings represent an alternative to improve the performance of TBCs. In this study, nanostructured and conventional YSZ particles were 397 398 thermally sprayed using APS. The produced coatings were heat treated in air at 1400°C for 1, 5 and 20 h. The microstructural characteristics, porosity, thermal diffusivity and elastic 399 modulus values of the as sprayed and heat treated coatings were evaluated. They 400 401 demonstrated that nanostructured YSZ coatings can be engineered to neutralize sintering effects and reveal significantly lower increase of thermal diffusivity and elastic modulus 402 403 values in high temperature environments compared to those of conventional YSZ coating. The coating microstructure consisted of bimodal features, which affected the mechanical 404 405 property of the coating.

The deposition of dense alumina layer over YSZ can significantly reduce the TGO 406 induced spallation of coating. Thermal shock behaviour of layer composite of ceria-stabilized 407 zirconia (CSZ)/nano alumina has been studied by Netaji et al. [86]. Alumina is not a reliable 408 material as an alternative for YSZ for advanced TBC application. But, due to its high melting 409 410 point, hardness and oxygen diffusion resistance, it can be used as a top layer over YSZ to 411 improve the thermal cycle life of usual TBCs. Plasma sprayed nano structured TBCs have 412 high bond strength [87], high corrosion resistance [88], low thermal conductivity [89, 90-92] and long thermal cycling life as compared to conventional TBCs. It reduces the growth of 413 414 TGO leading to less stress generation at the TGO/CSZ interface.

415 Weber et al. [93] have presented a thick nanostructured mono- and multi-layered 416 lanthanum zirconate TBC deposited using spray pyrolysis from aqueous nitrate based 417 precursor solution. The resulting mono- and multi-layered coatings with a thickness of ~200 418 µm were porous and crystalline and the coatings showed good adhesion to the substrate. The 419 multi-layered coating results in higher thermal conductivity compared to the mono-layered 420 one. But, lower thermal diffusivity, smaller features in the nanostructure and unique crack 421 pattern of multilayer coating made it suitable for TBC application. Researchers have 422 demonstrated the advantages of nano-sized YSZ for TBCs. As compared with conventional 423 YSZ coatings, higher co-efficient of thermal expansion, lower thermal diffusivity, higher 424 hardness and toughness and better wear resistance have been reported for nanostructured 425 TBCs. Heat transfer through TBCs composed of alternating nanostructured thick layers of 426 aluminium oxide and 7YSZ was studied by Josell et al. [94] at the temperatures in the range 427 of 1275K to 1375K.

428 Zhong et al. [95] have shown that thermal shock resistance of gadolinium zirconate 429 (GZ) coating can be improved by the addition of nanostructured 3 mol% YSZ. By introducing 430 nanostructured YSZ the fracture toughness of the composite of 90 mol% GZ-10 mol% YSZ (GZ-YSZ) was increased compared to the monolithic GZ resulting in enhancement of thermal 431 cyclic lifetime. GZ has excellent thermal stability, low sintering rate, low thermal 432 433 conductivity and high CTE. Hence, it is a promising advanced coating material for high 434 temperature application. However, fracture toughness of GZ is low leading to short thermal cycling lifetime, which is one of the main reasons for the failure of the GZ coating. 435 436 Nanostructured YSZ was incorporated into GZ matrix in order to improve the fracture 437 toughness of the GZ. The failure of GZ-YSZ composite coating was due to thermal expansion 438 mismatch between bond coat and ceramic top coat.

Zhai et al. [96] investigated the creep phenomenon of the functionally graded
materials by the computational micromechanical method (CMM). They showed that the creep
phenomenon was obvious for the ceramic-rich interlayers depending on the properties of the
ceramic. The creep strain rate of the ceramic/metal interlayer was larger than that of pure

metal under same load when the modulus of the ceramic component was lower than one of 443 444 the metal component. Carpio et al. [97] studied double-layer and graded composite coatings of yttria-stabilized zirconia on metallic substrates. The coating was fabricated by using two 445 different feedstocks (micro and nano). The coating layer formed from the nanostructured 446 feedstock adversely affects the mechanical properties of the composite. Adhesion and scratch 447 448 tests showed undesirable effect on the coating adhesion of layer obtained from the nanostructured feedstock on the bond coat. The poor integrity of this layer led to lower 449 normal stress needed to delaminate the coating during adhesion testing and minor critical load 450 451 during the scratch testing.

452

453 6. CONCLUSIONS

Researchers are looking for YSZ replacement because at elevated temperature (> 454 455 1200°C) it shows low phase stability, increased sintering rates and inferior thermal 456 conductivity. Advanced high temperature TBCs should have high temperature phase stability, high thermal expansion co-efficient, sintering resistance, low oxygen diffusivity and low 457 thermal conductivity. Researchers have found a number of suitable candidates such as rare 458 459 earth oxides, pyrochlore oxides, fluorite oxides, glasses, nano crystalline materials etc. But, 460 their low thermal expansion co-efficient leads to high stress if applied directly on bond coat. Therefore, multi-layered coatings have been developed to reduce the residual stress and 461 462 improve the mechanical and thermal properties. Subsequently, researchers have established 463 that functionally graded coating can be also used to reduce the mismatch effect, difference of 464 thermal expansion and interlayer stresses.

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- 754 **List of abbreviations**
- 755 **1.** Thermal barrier coating (TBC)
- 756 2. Yttria stabilised zirconia (YSZ)
- 757 **3.** Ceria-stabilized zirconia (CSZ)
- 758 4. Ceria–yttria stabilized zirconia/alumina (CYSZ
- 759 **5. Thermally grown oxide (TGO)**
- 760 6. High velocity oxy fuel (HVOF)
- 761 **7.** Atomic plasma spray (APS)
- 762 8. Electron beam physical vapour deposition (EB-PVD)
- 763 9. Chemical vapour deposition (CVD)
- 764 10. Suspension plasma spray (SPS
- 765 **11.** Cold spray (CS)
- 766 **12.** Low pressure plasma spray (LPPS)
- 767 13. Lanthanum magnesium hexaluminate (LaMgAl₁₁O₁₉, LMA)
- 768 14. Lanthanum zirconate ($La_2Zr_2O_7, LZ$)
- 769 **15**. La₂C₂O₇ (LC)
- 770 **16.** La₂ ($Zr_{0.7}Ce_{0.3}$)O₇ (LZ7C3)
- 771 **17.** $La_{1.7}Dy_{0.3}Zr_2O_7$ (LDZ)
- 772 18. Polyester incorporated TBC (P-TBC)

Figure captions

Fig. 1. Typical single layer, double layer and three layered TBC systems [71].

Fig. 2. (a) Thermal cyclic fatigue lifetime results and (b) burner rig testing lifetime

- results [76].



Fig. 1. Typical single layer, double layer and three layered TBC systems [71].





results.