

Thermal fatigue characteristics of $8Y_2O_3$ - ZrO_2 , $La_2Zr_2O_7$, $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ and $La_2Ce_2O_7$ thermal barrier coatings in duplex, multilayer functionally graded and multilayer configurations

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Abstract

La₂Zr₂O₇, La₂(Zr_{0.7}Ce_{0.3})₂O₇ and La₂Ce₂O₇ pyrochlore plasma sprayable powders were synthesized and plasma spray coated on steel plates with NiCrAlY bond coat. Three different configurations were used: duplex, multilayer functionally graded and multilayer, with different combinations of commercial 8% yttria stabilized zirconia (8YSZ) and NiCrAlY (bond coat) layers. The prepared coatings were compared with the standard duplex 8YSZ thermal barrier coatings (TBCs) with a goal to study their suitability to serve as TBCs. TBCs' layer thicknesses and interfaces were studied via SEM on polished cross section metallographic samples removed from the spray coated TBCs. Thermal fatigue resistance was evaluated by directing a gas flame on the ceramic surface at 1200 and 1400 °C, followed by its rapid withdrawal and forced cooling by pedestal fan. The maximum number of thermal shock cycles the coatings could withstand before failure was determined. The multilayered TBCs with lanthanum cerate composition stacked with 8YSZ exhibited the superior thermal fatigue resistance characteristics compared to all other studied TBCs. The findings were correlated with the crystalline phases of the ceramic coatings, obtained via XRD, and discussed in the light of existing literature.

Keywords: thermal barrier coatings, pyrochlore oxides, structure, thermal fatigue

I. Introduction

Research on ceramic coatings began in the aerospace sector, in the early fifties with the ambitious goal of finding some means to protect the metallic gas turbine blades that were getting degraded in service when they encountered a very high temperature (\sim 900 °C) environment. The protection of the metal components from thermal degradation was initially desired to prolong aero-engine service life. The ceramic coatings which were developed during this period (1960's to 1990's) successfully met the stringent technical requirements and specifications that were formulated to suit the service conditions of the gas turbine engines. Later, with the advent of stringent demands related with performance and economy, various materials, configurations

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[#]presently at: National Institute of Technology, Andhra Pradesh, Tadepalligudem 534101, India and coating processes emerged. Generally well-known as thermal barrier coatings (TBCs), 6-8% yttria stabilized zirconia (6-8YSZ) has remained as the most accepted ceramic composition for TBCs. Undoped zirconia $(m-ZrO_2)$ possesses the monoclinic structure which reversibly transforms to tetragonal zirconia (t-ZrO₂) structure between 900 and 1100 °C and to cubic zirconia (c-ZrO₂) at higher temperatures. Stable t-ZrO₂ or c-ZrO₂ are highly favoured phases for industrial applications including TBCs. Suppression of the high temperature transformation by stabilizing the t- ZrO_2 at room temperature by doping with 6-8% Y₂O₃ has facilitated this technological achievement [1-3]. Later, 8% Y₂O₃stabilized ZrO₂ (8YSZ) TBCs were applied on diesel engine components to protect them from combustion chamber heat and more importantly to enhance the engine efficiencies [4–6].

TBCs thermally insulate the metal components by the virtue of the thin layer of ceramic coating they provide. TBC ceramic materials possess low thermal conductivity, high temperature phase stability and other microstructural characteristics to offer long life of the coated gas turbine metal components at the high temperature service environment they operate in. Typically comprised of a ceramic layer (250 to $500\,\mu\text{m}$), they are generally fabricated by an extremely sophisticated and precise process equipment known as electron beam physical vapour deposition (EBPVD). However, atmospheric plasma spray (APS) technique is used most frequently in all engineering applications and for research and material development purposes. While EBPVD employs highly stringent process conditions, APS provides relatively easier but effective research alternative [7]. During TBC fabrication, to obtain good adhesion between the TBC ceramic overlayer and metal substrate, an intermediate bond coat layer, usually fabricated from intermetallic MCrAlY (M = Ni, Co, etc.), is usually applied on the prepared substrate surface prior to depositing the TBC ceramic layers. The role of the bond coat is primarily to reduce the interfacial stress caused by thermal expansion coefficients mismatch between the ceramic top coat and the metal component. 8YSZ ceramic TBCs with NiCrAlY bond coat combination have been well accepted by the engine manufacturers. In APS, the composition to be coated is introduced as free-flowing sprayable powders through the plasma jet. The powder particles partially melt and impinge on the substrate as splats to form a coating that builds layer by layer [8-10]. About 100–150 °C drop in temperature (further enhanced by internal cooling of metal components) is attained across a typically 300 µm thick 8YSZ TBC layer when the ceramic top-coat is subjected to a heating at less than 1200 °C.

Although 8YSZ material has been the state-of-theart TBC material since many decades, it is not without limitations. At ~1200 °C, the stabilized zirconia phase (t-ZrO₂) has the tendency to destabilize (m-ZrO₂) resulting in the development of internal stresses in the ceramics which affects the structural integrity of the coatings [11]. Additionally, these ceramics also suffer from sintering effects which result in the densification of the coated layers. This leads to adhesive or cohesive interlayer failures attributed to reduced thermal fatigue characteristics of the TBCs at the service temperatures. Keeping these restrictions in view, TBC research has continued further from the nineties till date involving newer materials, such as pyrochlores and niobates for example, newer configurations comprising of functionally graded materials (FGM), multilayers (ML) and newer coating processes like cold spray, suspension spray etc. [12–17]. The research efforts have evolved with the aim to: i) find materials and/or systems that protect the engine components from corrosion and oxidation in service, ii) develop simpler and cost-effective coating fabrication processes and iii) attain enhanced engine efficiencies and longer life.

New and alternate TBC ceramic materials (pyrochlores, perovskites etc.) are being investigated worldwide because they possess many characteristics more favoured than 8YSZ. Among them, high thermal stability (crystalline phase remain unchanged between room temperature and high preferred service temperature of ~1500 °C), thermal conductivity and sintering characteristics at >1000 °C being lower than with 8YSZ are the most noteworthy. These properties make the newer materials preferable for use as the next generation gas turbine TBC materials to serve at >1200 °C [18,19].

Several candidates materials such as rare-earth pyrochlores with $A_2^{3+}B_2^{4+}O_7$ structure, specifically $Gd_2Zr_2O_7$ [20,21], $La_2Zr_2O_7$ [22,23], $LaMgAl_{11}O_{19}$ [24,25] La₂(Zr_{0.7}Ce_{0.3})₂O₇ [26,27] and La₂Ce₂O₇ [28– 31] etc. offer the alternative material solution. The advantages are attributed to the relatively higher entropy they possess due to their defect fluorite structure. Hence, they possess low thermal conductivity values: considerably lower than 8YSZ $(1.10-1.37 \text{ W/(m \cdot K)})$, at 25 °C), and correspondingly suitable sintering and stability characteristics at >1200 °C [32]. Composition such as lanthanum zirconate (La₂Zr₂O₇, commonly designated as LZ) has demonstrated high potential to serve as the much-needed alternative to 8YSZ [33-35]. However, a note of caution should be taken into account. Pyrochlores alone do not have the capability to just outperform all the limitations of 8YSZ. LZ is problematic because of its thermal expansion coefficient (9.1- $9.7 \times 10^{-6} \text{ K}^{-1}$ [36] is lower than that of 8YSZ (10.5– $11.5 \times 10^{-6} \text{ K}^{-1}$) at 1000 °C [37,38] which negatively affects the structural integrity of the coating system. Still, the many favourable aspects of LZ and similarly other pyrochlores merit their consideration as the future TBC material, for the reasons described in the following sections.

Among the long list of pyrochlore materials holding promise as TBCs, La₂Ce₂O₇ (LC) ranks high. A solid solution of La_2O_3 in CeO₂ with cubic fluorite structure, thermal conductivity of $1.56 \text{ W/(m \cdot K)}$ at $1200 \,^{\circ}\text{C}$ and thermal expansion coefficient of $12.3-12.6 \times 10^{-6} \text{ K}^{-1}$ at 300-1200 °C, LC has very high potential to serve as the next generation TBC. Nevertheless, more attention has been paid to understanding the thermo-physical characteristics of LC and limited information is available on its behaviour as a TBC. Other than discrete materials, integrated systems also have been reported to exhibit favourable TBC characteristics. They involve incorporation of intermediate FGM layers (ceramic and bond coat blends, such as 8YSZ + NiCrAlY plasma sprayable powders blend in different percentages) applied between the bond coat and ceramic top coat [39]. In the multilayer configuration, the TBCs (ML TBCs) are generally comprised of three or more coated layers with each layer having a specifically beneficial role to enhance the TBC system property. Since being specially designed with different materials in mind from the start, the ML TBCs are expected to offer enhancement in performance, more so in the form of improved life in service due to the enhanced adhesion and gradual variations in layers-interface properties [36,40-43]. Furthermore, 8YSZ and pyrochlores, either as the ordered pyrochlore structure (P-type) or disordered defect fluorite structure (F-type) [12,23,44], are being integrated to realize the benefits of both materials simultaneously in one TBC system. One example of such an amalgamation is the three-layer system which incorporates 8YSZ in between the bond coat and pyrochlore top coat to alleviate the lack of adhesive characteristics of pyrochlores [45]. The combined system is known to improve the high temperature thermal cycling performance of the TBC. Yet another composition being reported to possess good elevated temperature thermal cycling characteristics is lanthanum cerium zirconate $(La_2(Zr_{0.7}Ce_{0.3})_2O_7, designated as LCZ)$. This improvement is attributed to the presence of CeO_2 (ceria) with its capacity to increase the CTEs and lowers the thermal conductivity to $0.79 \,\text{W/(m \cdot K)}$ and sintering-resistance when compared with lanthanum zirconate pyrochlore and the conventional 8YSZ [46,47]. Some of the published papers on multilayered systems and pyrochlore oxide materials follow simulation-based approach with fewer experimental findings [48-51].

The traditional TBC system comprise two layers (Fig. 1a), ~75 μ m thick bond coat and ~300 μ m thick ceramic top coat over the substrate. TBC life has been improved by introducing the concept of functionally graded material (FGM) configurations. FGM TBCs possess an additional coating layer which is incorporated in between the bond coat and top coat. A physical blend of bond coat and top coat sprayable powders in desired proportions is plasma spray coated to form the intermediate layers of the FGM TBCs [52,53]. Newer systems including multilayered (ML) configurations with two or more different ceramic overlayers are also engineered for obtaining novel TBC properties [40–43].

The purpose of this work was to study the thermal fatigue characteristics of TBCs synthesized from commercial 8YSZ along with three different pyrochlores synthesized in our laboratory, in duplex, multilayered functionally graded materials (ML FGM) and multilayered (ML) configurations, with commercial NiCrAIY used as the bond coat. The APS fabricated TBCs were subjected to microstructural, thermal fatigue and structural phase analysis. They were bench marked with the commercial duplex 8YSZ TBC. Thermal fatigue resistance data were used to categorize the superiority of the various TBCs with different materials and configurations with respect to one another.

II. Experimental details

2.1. Sample fabrication

Thermal barrier coatings (TBCs) were deposited on Inconel 718 and SS 304L substrates coated with NiCrAlY layer (bond coat, BC) and composed of three functional phases (laboratory synthesized pyrochlores: La₂Zr₂O₇ - LZ, La₂(Zr_{0.7}Ce_{0.3})₂O₇ - LCZ and $La_2Ce_2O_7$ - LC). Three different configurations were used: i) duplex, ii) multilayer FGM and iii) multilayer. The duplex TBCs have the functional phase layer on top of the NiCrAlY layer (Fig. 1a). The multilayer FGM TBCs contained another layer of a mixture of 8YSZ (50%) and NiCrAlY (50%) phases between the NiCrAlY and the functional phase layers (Fig. 1b). The multilayer TBCs have two layers on top of the NiCrAlY - the first is the pure 8YSZ and the second is the functional phase layer (Fig. 1c). For comparison, two additional TBCs were prepared, the first with commercial 8YSZ on top of the NiCrAlY layer (Fig. 1d) and the second with intermediate mixed 8YSZ/NiCrAlY layer and pure 8YSZ top layer (Fig. 1e). Atmospheric plasma



Figure 1. Schematic of: a) Duplex - two layered TBC, b) Multilayer FGM with pyrochlore TBC, c) Multilayer pyrochlore TBC, d) Duplex - two layered commercial 8YSZ and e) Multilayer FGM with commercial 8YSZ

No.	TBCs system	Specimen	Blend or multilayer	Top coat
		designation	thickness	thickness
1	Duplex 8YSZ (Conventional) (BC - 8YSZ)	D-8YSZ	N.A.	~300 µm
2	Duplex LZ (Pyrochlore) (BC - LZ)	D-LZ	N.A.	$\sim 300\mu m$
3	Duplex LCZ (Pyrochlore) (BC - LCZ)	D-LCZ	N.A.	$\sim 300\mu m$
4	Duplex LC (Pyrochlore) (BC - LC)	D-LC	N.A.	$\sim\!300\mu m$
5	Multilayer FGM LZ (BC - (BC/8YSZ) - LZ)	ML-FGM (BC/8YSZ-LZ)	~150 µm	~150 µm
6	Multilayer FGM LCZ (BC - (BC/8YSZ) - LCZ)	ML-FGM (BC/8YSZ-LCZ)	~150 µm	$\sim \! 150\mu m$
7	Multilayer FGM LC (BC - (BC/8YSZ) - LC)	ML-FGM (BC/8YSZ-LC)	~150 µm	~150 µm
8	Multilayer LZ (BC - 8YSZ - LZ)	ML (8ZSY-LZ)	~150 µm	~150 µm
9	Multilayer LCZ (BC - 8YSZ - LCZ)	ML (8ZSY-LCZ)	~150 µm	~150 µm
10	Multilayer LC (BC - 8YSZ - LC)	ML (8ZSY-LC)	~150 µm	$\sim \! 150\mu m$

Table 1. TBC configurations and designations

spray (APS) deposited NiCrAIY was used as the bond coat (BC) with the thickness of \sim 75 µm. The total ceramic layer thicknesses above the bond coat were maintained at 300 µm which were divided into equal thicknesses whenever more than one layer was fabricated.

The plasma sprayable powders used for fabrication of the TBC based coatings were: i) commercial 8YSZ (METCO 204 NS), ii) commercial NiCrAlY (AMDRY 962) and iii) three lab-synthesized pyrochlore oxide materials: lanthanum zirconate, $La_2Zr_2O_7$ (designated as LZ), lanthanum cerium zirconate, $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ (designated as LCZ) and lanthanum cerate, $La_2Ce_2O_7$ (designated as LC).

Based on our experience and the literature data, the intermediate FGM blend layer composition was chosen to be 50% NiCrAlY + 50% 8YSZ as an optimum blend composition found to be favoured for TBC application [54]. In this paper, all further reference to FGM layer would mean that the intermediate layer blend contained 50% NiCrAlY with 50% 8YSZ plasma sprayed together. All TBC configurations and designations are tabulated in Table 1.

Pyrochlore $(La_2Zr_2O_7, La_2(Zr_{0.7}Ce_{0.3})_2O_7)$ and $La_2Ce_2O_7$) plasma sprayable powders were synthesized by mixing stoichiometric weight ratios of the corresponding starting materials, i.e. La₂O₃, CeO₂ and ZrO₂, followed by standard procedures in the solidstate method [26,55]. The plasma sprayable powders were prepared by granulation with polyvinyl alcohol (PVA) organic binder. The stoichiometric amounts of precursors were ball-milled, calcined at 1150 °C for 24 h and thereafter at 1500 °C for 6 h to enable phase forming reactions. Synthesis steps and phases formed at various stages of processing are schematically shown in Fig. 2. The phases, formed during calcination and completion of the processing were confirmed by X-ray diffraction (XRD). Details of the process were reported in our previous papers [43,56].

Traditionally, nickel and cobalt based superalloys have been used as gas turbine engine component metals. Substrates with similar materials compositions such as Inconel 718 and stainless steel (304L) were used in the present work for coatings application. They will be referred to substrates in the rest of this paper. One flat



Figure 2. Schematic representation of synthesis steps and compositions of the formed products for: a) $La_2Zr_2O_7$, b) $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ and c) $La_2Ce_2O_7$ powders

side of the $80 \times 80 \times 5$ mm substrates was used to deposit the coatings. APS process parameters of the commercial 8YSZ (METCO 204 NS) and NiCrAlY (AMDRY 962) were used as per manufacturers guidelines. In the absence of any standard spray parameter for the intermediate FGM layer, modified 8YSZ parameters were used to deposit the FGM blend composition [54]. The plasma spray parameters for the pyrochlores used in this work were initially obtained from the literature which were further optimized by experimentation. The choice of the most suitable parameters used for plasma spray coating pyrochlores has already been reported from this laboratory and all processes (pre-heating spray powders, substrate preparation, spray parameters, number of spray passes, etc.) remained the same as reported [43,57].

2.2. Characterization

To study the coating uniformity, polished metallographic cross-sections were removed from the spray coated TBCs and microstructures were analysed by a Carl Zeiss Gemini column 300-71-34 field emission scanning electron microscope (FE-SEM).

The ceramic top coat surfaces of the TBCs were used for the thermal fatigue test by using oxy-acetylene gas flame as the heating source. The surface was heated with the flame focused on the centre, occupying $\sim 10 \text{ mm}$ in diameter. The sides of the substrate were insulated by ceramic wool to protect the edges from oxidation and degradation that would occur by heat radiation. Thermal shock cycling test consisted of exposure of surface to the flame at 1200 °C for 60 s, followed by rapid cooling facilitated by the removal of the flame source and exposure to a blast of fan air for 60 s. This cycle was termed as one thermal fatigue cycle and the cycles were repeated till the thermal strain induced in the TBC resulted in the visible cracks on the surface. The temperature of the surface during flame exposure was measured by using a non-contact type IR thermometer. The maximum number of thermal fatigue cycles withstood by each sample type (material and configuration) before failure (cracking of ceramic top coat/spallation) was determined. The same test was also performed by maintaining the flame temperature on the ceramic side at 1400 °C. All the TBCs were subjected to the tests under identical conditions (to the extent possible all test parameters were maintained the same). This test was used as a guide to benchmark the newer TBCs with the Duplex 8YSZ TBC.

The plasma sprayable powders, the outermost TBC layers (top most coated surface), in form of plasma spray coating and after being subjected to thermal fatigue tests, were subjected to phase analysis by X-ray diffraction (XRD) method. PANalytical X-ray diffractometer (X'Pert Highscore plus) with Cu-K α radiation ($\lambda = 1.5418$ Å) in the range 20–90° at a scanning rate of 1 °/min was used. Any signs of destabilization or phase non-stoichiometry were analysed from the XRD results.

III. Results and discussion

3.1. Microstructural analysis by SEM

SEM micrographs of the polished metallographic cross-sections of the spray coated TBCs are shown in Fig. 3. They represent four typical TBCs from each of the materials and configurations: Duplex 8YSZ, Duplex pyrochlore (LZ), ML FGM pyrochlore (with LZ top coat) and ML pyrochlore (with LC top coat).

All TBCs as expected contained a consistent (about 60 to 70 μ m thick) layer of bond coat. The total top coat thicknesses of all coatings were between 280 and 370 μ m, which were not aligned with the expected layer thicknesses of 300 μ m. Notably, thickness adjustment was achieved very efficiently in the case of the commercial 8YSZ. The 8YSZ coating thickness (>350 μ m) in the D-8YSZ configuration was much higher compared



Figure 3. SEM micrographs of as spray coated TBCs representing: a) Duplex 8YSZ, b) Duplex pyrochlore, c) ML-FGM with pyrochlore top coat and d) ML with pyrochlore top coat (on polished metallographic cross sections)



Figure 4. Photographs of: a) spray coated and b) failed specimen of a typical pyrochlore based TBC (representative - LC)

with the duplex pyrochlore, i.e. D-LZ TBC (thickness $<300 \,\mu$ m). This discrepancy was attributable to the variable properties of plasma sprayable powder (the commercial 8YSZ and laboratory synthesized pyrochlores).

Two layers over the bond coat in the ML-FGM and ML TBCs, i.e. the intermediate (8YSZ + NiCrAlY) FGM layer or in 8YSZ ML layer, were as thick as the top ceramic coat over them (140 to $180 \,\mu$ m). The substrate-bond coat interface and the ceramic coating layer interfaces were smooth, as well as defect free. Voids and defects, present in the coatings most likely due to the incomplete contact between lamellae and micro-cracks induced by thermal stresses, along with ~11% porosity (determined via image analysis on SEM micrographs), were expected to aid the thermomechanical resistance properties.

3.2. Thermal fatigue test results

Figure 4 shows the photographs of the freshly spray coated and failed specimen of a typical pyrochlore based TBC (representative - LC). It has already been reported in the previous section that a specimen had failed when one or more upper layers were chipped off at the end of thermal fatigue cycles. The thermal fatigue behaviour (numbers of cycles before failure) of the TBCs for all configurations and materials was analysed and the results are presented in Table 2.

 Table 2. Thermal fatigue data (number of cycles withstood before failure)

		Number	of cycles	
No.	Designation	withstood/to failure		
		at $1200^{\circ}\mathrm{C}$	at 1400 °C	
1	D-8YSZ	160	130	
2	D-LZ	315	170	
3	D-LCZ	410	185	
4	D-LC	440	210	
5	ML-FGM (BC/8YSZ-LZ)	470	246	
6	ML (8ZSY-LZ)	430	310	
7	ML-FGM (BC/8YSZ-LCZ)	505	350	
8	ML (8ZSY-LCZ)	630	380	
9	ML-FGM (BC/8YSZ-LC)	545	420	
10	ML (8ZSY-LC)	720	450	

The bar graph shown in Fig. 5 represents the number of thermal shock cycles withstood by all the TBCs at failure (or test stopped prior to failure). They include findings from TBCs tested between 1200 °C (Fig. 5a) and 1400 °C (Fig. 5b) and ambience. Depending upon the four different pyrochlores, i.e. 8YSZ, LZ, LCZ and LC, the test results depicted in Fig. 5 are shaded differently for ease in identification.

A short glance at two figures is sufficient to recognize the enhanced thermal fatigue characteristics offered by the pyrochlore TBCs. The LC and LCZ based TBCs performed better than the Duplex 8YSZ, but also over the LZ-based TBCs among all the three categories of TBCs that were studied here (D, ML-FGM and ML). The trend for the LC-based TBCs to offer the most thermal fatigue resistance under the experiments carried out was consistent when the thermal fatigue test temperature was at 1400 °C as well (Fig. 5b). The failure at the test temperature of 1400 °C occurred sooner than at 1200 °C as expected. When the analogy was extended slightly further, all the configurations comprised of cerium and zirconium (LCZ based), were a close second to the thermal fatigue resistance offered by the LC-based TBCs in all three (FGM, ML-FGM and ML) configurations.

The thermal fatigue test results at 1200 and 1400 °C shown in Fig. 5 are placed into one bar graph for enhanced clarity and shown in Fig. 6. This was done to illustrate the leaning of ceria containing pyrochlores, i.e. the LC- and LCZ-based TBCs (within 10–15% variation between them), towards exhibiting improved thermal fatigue characteristics compared with either 8YSZ or LZ-based TBCs. The trend was especially visible in ML-FGM and ML configurations.

The results are not very surprising when we consider published data in the literature. There are many reasons to explain the advantages offered by pyrochlore structured compounds with cerium oxides (CeO2) in their composition, such as: i) phase structure stability (cubic fluorite) from room temperature up to its melting point and during the transit in plasma, ii) no variation in properties even when associated with significant variation from stoichiometry (deviation in lattice parameter)



Figure 5. Results of thermal fatigue tests on 8YSZ and pyrochlore TBCs of all configurations at: a) 1200 °C and b) 1400 °C



Figure 6. Bar graph showing data shown in Figure 5 (a and b) combined in one plot for enhanced clarity

and iii) negligible influence of generation of deposition defects in its microstructure (such as porosity) on the properties of coatings [58,59].

3.3. X-ray diffraction - Duplex 8YSZ TBCs

XRD patterns of the Duplex 8YSZ TBCs before and after thermal fatigue cycling tests at 1200 and 1400 °C were studied and published in our previous paper [54]. While the spray coated D-8YSZ contains 100% cubic/tetragonal zirconia (c/t-ZrO₂), after thermal fatigue test cycling (even without failure) transition to monoclinic zirconia (m-ZrO₂) occurred and about 16% m-ZrO₂ was formed. Transformation of c/t-ZrO₂ to m-ZrO₂ is only one of the many mechanisms that lead to TBC failures. Microstructural changes caused by longer exposure to high temperatures also cause failures of TBCs [60].

3.4. X-ray diffraction - LZ based TBCs

Figure 7 shows XRD patterns of the lanthanum zirconate (LZ) powder and LZ-based D-LZ coating. The main phase of the LZ powder and D-LZ coating is py-



Figure 7. XRD patterns of LZ powder and D-LZ coating

rochlore with the (222) plane having the highest intensity and $d_{222} = 3.12$ Å (ICDD standard data). The cubic pyrochlore structure was confirmed by the presence of all peaks of La₂Zr₂O₇. However, in the sprayed coating, the peak shift of the (222) plane to a lower 2 θ value indicates on some amount of lattice strain that corresponds to an increase of *d* value from 3.12 Å to 3.14 Å. The slight shift in the *d* value may be attributed to the coating fabrication methods. All the material studied here are plasma-sprayed coatings, while the standard patterns are obtained on perfectly crystalline materials.

XRD pattern of the thermal shock cycled D-LZ sample (after 315 cycles at 1200 °C) shown in Fig. 8a closely matched with the standard LZ pattern (including the minor shift in peak position), but has a small kink belonging to c/t-ZrO₂ (111) at $d_{111} = 2.96$ Å. This confirms the retention of cubic pyrochlore structure, even after being subjected to the thermal fatigue cycling at 1200 °C. A weak (333) peak of the LZ pyrochlore was observed, which was not found in the untreated D-LZ TBC. Sivakumar et al. [61] have reported the phase structure of heat-treated LZ APS coatings without and with water vapour environment at 1100 °C for 50 and 100 h. They also mentioned decomposition with appearance of weak peaks of t/m-ZrO₂. The reason for the appearance of the weak (333) LZ pyrochlore peak (2.08 Å) was not clear. However, since the peak pertained to LZ family itself and there was no inadvertent influence on the environment, the finding did not warrant any further studies. It was concluded that failure did not occur due to any structural phase changes in the outermost layer.



Figure 8. XRD patterns of LZ-based TBCs configurations after thermal cycling at: a) 1200 °C and b) 1400 °C

XRD pattern of the ML-FGM (BC/8YSZ)-LZ TBC, failed after completing 470 thermal fatigue cycles at 1200 °C, is shown in Fig. 8a. Noticeable in this pattern was the shift in the *d* (towards lower values) of the LZ peaks up to $2\theta < 45^{\circ}$ (higher 2θ values). Other than this small deviation, the pattern showed cubic pyrochlore structure, and no destabilization or structural phase changes were found. The resulting small changes in crystal interplanar spacings d_{hkl} are expected to occur due to the stoichiometric variations in the materials, which do not play any role in the thermal performance of LZ.

XRD pattern of ML (8YSZ-LZ) TBC, failed after completing 430 thermal fatigue cycles at 1200 °C is also shown in Fig. 8a. The outermost LZ layer exhibited the maximum deviation in 2θ values, which shifted to lower values than their corresponding standard. The equivalent *d* values were higher and the (222) plane reflection shifted from 3.12 Å to 3.20 Å. Yet, the TBC withstood a significantly higher number of thermal fatigue cycles, signifying and reconfirming the importance of reported superiority of LZ pyrochlores by Cao *et al.* [55]. Furthermore, the intermediate 8YSZ layer in the ML configuration appeared to retain the adhesive integrity of the TBC system while the outermost LZ layer contributed towards the thermal fatigue resistance characteristics at high temperature (1200 °C).

In summary, the LZ-based sprayable powder and TBCs have pyrochlore structure throughout the tests and temperatures, showing no destabilization for all configurations after thermal shock cycling from 1200 °C. Lanthanum zirconate can accommodate greater variations in stoichiometry changes that get reflected in the form of peak shifts. In the ML-FGM and ML configurations' thermal shock cycling data, it was observed that with the increase in the thermal fatigue life, the lattice parameters began to increase during the thermal shock cycling time.

Figure 8b shows XRD patterns of the same system, except for the thermal fatigue test temperature (1400 °C). These patterns also showed a similar trend observed for the samples tested between 1200 °C and ambient: major difference being the number of shock cycles to failure. They were all correspondingly lower as expected to be, considering an increase of 200 °C in the fatigue test temperature.

The observed salient features, i.e. i) cubic pyrochlore structure with no phase transformation due to thermal cycling; ii) kink of the most intense (111) peak of t-ZrO₂; iii) presence or absence of the small (333) peak ($d_{333} = 2.08$ Å) and iv) shift in the values in the (222) peak ($d_{222} = 3.12$ Å) in some specimen (attributed to the most likely non-stoichiometry with no deterioration in performance) were found to be near identical to the findings in the previous case (Fig. 8a). The findings were also similar to the report by Ramachandran *et al.* [62], who studied the thermal cycling behaviour of LZ APS coatings at 1280 °C with five different coating architectures and the patterns did not exhibit any phase transformation due to the thermal shock cycling.

3.5. X-ray diffraction - LCZ based TBCs

Figure 9 shows XRD patterns of the lanthanum cerium zirconate (LCZ) powder and LCZ-based D-LCZ coating. The LCZ sprayable powder comprised of both pyrochlore and fluorite phases, since in the series of $La_2(Zr_{1,r}Ce_r)_2O_7$, LCZ is a mixture of pyrochlore and fluorite structure [47,63]. The main phase in the LCZ powder is LZ with a small solubility of LC, which retains the pyrochlore structure. The second phase is a solid solution of LZ and LC in a fluorite structure. The peaks pertaining to the pyrochlore structure are stronger than those which belong to fluorite structure. The D-LCZ coating shows a solid solution of LZ and LC with a predominantly pyrochlore structure (Fig. 9). Our results are also in line with that reported by Cao et al. [64] and Ma et al. [65]. The fluorite peak from (111) plane was reduced to merely a kink, signifying the complete conversion to pyrochlore attributable to the high temperature plasma.

At the end of thermal shock cycling tests at 1200 °C, the D-LCZ TBCs withstood ~410 thermal shock cycles



Figure 9. XRD patterns of LCZ powder and D-LCZ coating



Figure 10. XRD patterns of LCZ-based TBCs configurations after thermal cycling at: a) 1200 °C and b) 1400 °C

prior to failure. XRD patterns (Fig. 10a) show that the thermal fatigue test cycles induced shift in peak positions (change of lattice parameters). This may be due to local variation in the composition, or also due to different vapour pressures of La_2O_3 , CeO_2 and ZrO_2 which could partially lead to the chemical composition deviation of LCZ. It was observed that only these small deviations in lattice parameters occurred, but without phase transformation (the top coats have cubic pyrochlore structure only). This finding supports the credence that phase change had no role to play in the failures of the TBCs.

From XRD patterns of the ML-FGM (BC/8YSZ)-LCZ (505 cycles) and ML (8YSZ-LCZ) (630 cycles), shown in Fig. 10a, both TBCs not only withstood much higher number of shock cycles but also exhibited complete phase transformation from pyrochlore to defect fluorite structure. The high-test temperature along with longer duration of thermal fatigue cycling most likely induced the phase transformation. Transformation from the pyrochlore to other structures, especially defect fluorite structure has been commonly observed to occur at high temperatures in these systems [44]. Defects in the atomic level introduced in the crystal structure are the primary cause for phonon scattering resulting in lowered thermal conductivity. The fundamental crystal structure and the related chemistry of phase transformations occurred from an ordered pyrochlore to disordered defect fluorite structure and yet failure did not occur.

XRD patterns of the LCZ TBCs, after thermal fatigue tests at 1400 °C are shown in Fig. 10b. Pyrochlore to defect fluorite transformation occurred after thermal cycling in the D-LCZ and ML-FGM (BC/8YSZ-LCZ) TBCs (Fig. 10b). Thus, the D-LCZ TBC failed at number of thermal shock cycles as low as 185 at 1400 °C, however the pyrochlore to fluorite transformation occurred only at >500 thermal shock cycles at 1200 °C. It can be concluded that pyrochlore to fluorite transformation occurred in these materials at lower temperature (1200 °C) with higher number of shock cycles or at higher temperature (1400 °C) even with lower number of shock cycles. However, this is not the case for ML (8YSZ-LCZ) TBC (Fig. 10b) and the reason for the non-occurrence of this transformation in this TBC that failed after 380 cycles when tested at 1400 °C is not understood at this time.

The pyrochlore to defect fluorite phase transformations did appear to contribute favourably towards enhanced life of the TBC, and most likely enhanced atomic scattering was facilitated by phase transformation that resulted in the enhanced life. The LZ-based TBCs did not exhibit any defect fluorite pattern at any stage of processing or testing. On the other hand, both pyrochlore and fluorite phases appeared in the LCZ TBCs patterns during the various stages of synthesis and thermal fatigue testing. Nevertheless, the LCZ-based TBCs undoubtedly performed better than the LZ-based TBCs under the present thermal fatigue test conditions.

3.6. X-ray diffraction - LC based TBCs

Figure 11 shows XRD patterns of the lanthanum cerate (LC) powder and D-LC coating while XRD patterns of the thermal shock cycled LC-based TBCs are shown in Fig. 12. All the patterns, without any exception, confirm presence of defect fluorite structure. The role of cerium ions in the lattice in stabilizing the defect fluorite phase was evident. The sprayed D-LC coating exhibited cubic defect fluorite phase and no obvious decomposition, but the diffraction peaks broadened and shifted towards the higher diffraction angles. The changes due to the rapid cooling during spraying led to the imperfect crystallization. Previous studies have found that the much higher vapour pressure of CeO_2 than La_2O_3 leads to the composition deviation (non-stoichiometry) of the sprayed coating from corresponding spray powder [29,58,66].



Figure 11. XRD patterns of LC powder and D-LC coating

The best thermal fatigue resistance among all the TBCs studied in this work was exhibited by the LCbased TBCs which established the definitive role played by the defect fluorite phase in enhancing thermal fatigue resistance when the outermost layers were exposed to gas flame at 1200 °C. The resulting minor changes in lattice parameters (or *d*-values) are expected to occur due to the stoichiometric variation in the compositions or due to the process mechanisms, and do not negatively



Figure 12. XRD patterns of LC-based TBCs configurations after thermal cycling at: a) 1200 °C and b) 1400 °C

affect thermal performance of the LC-based TBCs, or rather they appear to have accommodated higher thermal strains.

At the end of thermal fatigue tests and after failure, the D-LC and ML (8YSZ-LC) TBCs exhibited maximum deviation in 2θ values, i.e. significant shifts towards higher *d*-values. Thus, the *d*-values of the (111) peak increased from 3.21 Å to 3.28 Å and 3.29 Å for the D-LC and ML (8YSZ-LC) TBCs, respectively. However, for the ML-FGM (BC/8YSZ)-LC TBC, the same peak moved toward higher 2θ value, corresponding to d = 3.18 Å. Despite the significant changes in the lattice parameters, cubic fluorite phase was maintained well without any structural phase transformation.

IV. Conclusions

 $La_2Zr_2O_7$ (LZ), $La_2(Zr_0 Ce_{0.3})_2O_7$ (LCZ) and $La_2Ce_2O_7$ (LC) powders were synthesized by the solidstate method from La₂O₃, ZrO₂ and CeO₂. The synthesized powders were used for fabrication of TBCs via APS in duplex, multilayer functionally graded and multilayered configurations, with different combination of commercial 8% yttria stabilized zirconia (8YSZ) and NiCrAlY (bond coat) layers. All TBCs were tested for thermal fatigue resistance via thermal shock cycling between ambiance and 1200 or 1400 °C (gas flame heating sources) followed by rapid air cooling, till they failed. XRD was used to analyse the coating stability after the thermal fatigue tests. The cerium containing (i.e. LCZand LC-based) TBCs exhibited enhanced thermal shock resistance properties when compared with the LZ and 8YSZ TBCs. Among these, the LC-based TBCs exhibited the best thermal fatigue properties in all configurations studied at both test temperatures, but especially for the ML configuration where the intermediate layer comprised of commercial 8YSZ.

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