Zirconia based pyrochlore thermal barrier coatings

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Abstract. Improvements in thermal barrier coatings (TBCs) technology, further than what is already in service to enable adequate protection to metallic components from higher (>1100°C) operating temperatures requires newer developments in materials. Many research activities have been undertaken by scientists to seek alternatives after discovering the threshold of Yttria-stabilized zirconia (YSZ) TBCs on standard aero-space materials at elevated temperatures. To increase the thermal performance of gas turbine engines, alternate TBC materials with better sintering resistance and lower thermal conductivity are required. One of the promising candidates for the TBCs is Pyrochlore-type rare earth zirconium oxides (Re₂Zr₂O₇, Re = rare earth). Re₂Zr₂O₇ TBCs have higher phase stability, lower thermal conductivity, lower sintering rate, no phase transformation, and lower coefficient of thermal expansion at elevated temperatures when compared with YSZ. In this work, plasma spray powders of Lanthanum Zirconate (La₂Zr₂O₇) and Lanthanum Ceria Zirconate (La₂(Zr₀.₇Ce₀.₃)₂O₇) were synthesized by the solid-state reaction method with the goal to develop pyrochlore oxide-based coatings with desired properties at high temperatures (>1200°C), better than the YSZ TBCs: currently the most popular choice for TBCs. These TBCs are expected to increase gas turbine efficiencies while protecting the underlying metallic substrate at high operation temperatures. The evaluation of the synthesised TBCs has been carried out by studying their performances at 1200°C. Results of evaluation for phase composition by employing X-Ray Diffractometry (XRD), microstructure via Scanning electron Microscope (SEM) and chemical composition via Energy Dispersive spectroscopy (EDS) also have been included.

1. Introduction

Plasma sprayed thermal barrier coatings (TBC) have been used in modern gas turbines for decades to improve performance [1]. The durability of the component is increased as the thermal barrier coating layer can effectively decrease the temperature of the substance it is coated on (metal substrate). Furthermore, efficiency of the turbines can be increased as higher inlet temperatures can be used. Due to this reason TBCs provide a huge advantage in the daily functioning of aircraft engines, and gas turbines engines [2]. These TBC systems are complex: have multiple layers and materials with many varieties pertaining to composition, processing, and micro-structure. These generally have two layers: an intermediate bond coat and insulated ceramic top coat. The bond coat (NiCrAlY) is mostly inter-metallic

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and protects the metallic substrate from oxidation and corrosion [3]. It also strengthens the bond between the metallic substrate and the top coat. The ceramic top coat is able to provide heat insulation as it has low thermal conductivity.

Turbine engines when operating at high temperatures have high efficiencies, low emissions, and consume less fuel and therefore require pyrochlore oxides that have lower thermal conductivity. These are specially fabricated for advanced TBCs [4]. The corrosion characteristics along with the physical and chemical characteristics limit the performance of the base materials (super alloys, silicon-based ceramics, etc.) at high operational temperature [5]. To further increase operational temperatures of the super alloys or base metals, TBCs are applied in the form of a thin layer or coating. Currently the most commonly used material for TBC is yttria partially stabilized zirconia (YSZ) which is used for coating engine parts by the process of Atomic Plasma Spraying (APS) or electron beam physical vapour deposition (EBPVD). The effectiveness of YSZ decreases at higher temperatures due to the effect of sintering which tends to increase the thermal conductivity [5]. The coating’s durability reduces significantly when the strain tolerance and thermal stress reduces as the coatings are densified and sintered at higher temperatures: these limitations are overcome via advanced TBC materials [6].

6 to 8 by weight% of Yttria (Y₂O₃) in YSZ is the most preferred as TBC material due to its ability to resist fracture and high thermal expansion [7]. YSZ coatings are made with Atomic Plasma Spraying (APS) process; they may consist of a metastable state δ phase. With long duration of exposure to higher temperatures, it decomposes forming stabilized zirconia phases with high or low Yttria content [8]. The zirconia with low Yttria content later gets converted into monoclinic phase with a significant increase in volume. This may be disastrous as it may lead to the failure of TBC at temperature > 1200°C. Also, sintering decreases the high temperature properties as the coatings undergo a loss of strain tolerance which causes an early failure [9]. In addition, the phase stability is also limited. These drawbacks have led researchers to seek ceramic materials with much improved characteristics than YSZ. The most promising materials to be used for TBCs at high temperatures are pyrochlore-type zirconates (Re₂Zr₂O₇, Re = rare earth) [10]. These materials have lower thermal conductivity, high temperature phase stability, low sintering rate, no phase transformation at elevated temperatures and lower Coefficient of thermal Expansion (CTE) than YSZ.

Zirconate pyrochlores generally have lower ability to conduct heat with stability at high temperatures. Lanthanum Zirconate La₂Zr₂O₇ (LZ) is stable up to its melting point i.e. 2700 °C [11]. It also shows a lower sintering tendency and lower thermal conductivity (1.56 Wm⁻¹k⁻¹, bulk material) compared to YSZ. However since its thermal expansion coefficient is low (9.1 x 10⁻⁶ k⁻¹ (300-1000°C)) in relation to bond coats and due to poor toughness [12] pyrochlores are combined with YSZ for better use in TBC systems. YSZ is coated as the first ceramic layer since TBC failure takes place due to crack initiation occurring near the bond coat [13]. This YSZ intermediate layer potentially prevents any possible reactions between the applied pyrochlore and the thermally-grown oxide (TGO) layer formed above the bond coat when subjected to thermal load [14]. However, in the case of rapid solidification considerable amounts of metastable fluorite phases are formed which is typical in plasma spray conditions [15]. The phase transformation of fluorite to pyrochlore takes place at high temperatures (above 1000°C). This transformation does not undergo a significant change in volume and is therefore not critical [16]. Since La₂O₃ is prone to evaporation in plasma spraying, the process of Lanthanum Zirconate composition by APS is still highly challenging.

2. Experimental Procedures

2.1 Powder Preparations

Commercially available raw ceramic powders used such as La₂O₃, ZrO₂ and CeO₂ (all 99.9%, Aldrich) were used in the work. The plasma spray powders of LZ and LCZ was synthesized by the solid-state method [17].Crystallographic structural phases of powders were analyzed using X-ray Diffractometer (XRD). Scanning Electron Microscope (SEM) was used to study the powder particles (morphology and particles size) of the raw and plasma spray powders of LZ and LCZ and its chemical composition was
verified by Energy Dispersive Spectroscopy (EDS) allied with SEM. The zirconia based pyrochlore (LZ and LCZ) were mixed with 10 % PVA (Poly Vinyl Alcohol) and were further processed by using standard ASTM meshes (25 mesh ~ 600 microns; 150 mesh ~106 microns; 300 mesh ~ 53 microns) [18]. Powders pertaining to -106 + 53 microns were the plasma sprayable powder which was used for plasma spray coating on the substrate.

The several steps involved in the plasma sprayable powder preparation and coating of LZ and LCZ is shown in the form of flow chart in Figure 1.

![Flow chart of plasma sprayable powders synthesis](image)

**Figure 1.** Plasma Sprayable Powders Synthesis (Flow chart)

### 2.2 Plasma Spray Coated Specimens

Nickel base super alloy (Inconel 718) were used as substrate of dimensions 80 mm x 80 mm x 5 mm (thickness). Plasma-sprayed coatings were produced by atmospheric plasma spray (APS) method with an 80 Kw Sulzer Metco Triplex gun. Commercially available Bond coat (BC)- AMDRY 962 (Ni-22Cr-10Al-1Y, -106 +52 µm), METCO 204NS (8% Y₂O₃-ZrO₂, -106+11 µm) and laboratory prepared plasma spray powder (LZ and LCZ (-106 +52 µm)) were used for plasma spray coating on the substrate.

The plasma spray parameters used in this work are given in Table 1.
Table 1. Plasma Spray Parameters

| Parameters                  | Bond Coat (NiCrAlY) | Ceramic Top Coat (LZ/LCZ) |
|-----------------------------|---------------------|--------------------------|
| Voltage (V)                 | 60                  | 55                       |
| Current (A)                 | 400                 | 550                      |
| Primary gas, Ar (1/min)     | 57                  | 38                       |
| Secondary gas, H₂(1/min)    | 17                  | 17                       |
| Power feed rate (g/min)     | 45                  | 35                       |
| Spray distance (mm)         | 60                  | 55                       |

2.3 Thermal Shock Tests
The thermal shock test involved exposing the ceramic surface to 1473K (1200°C) for a pre-fixed amount of time (1 minute) and suddenly withdrawing the specimen to rapidly quench the hot ceramic surface for 1 minute. Pt-PtRh thermocouples and non-contact IR thermometers were used to measure the temperatures [19]. The numbers of such heat quench cycles were recorded to evaluate the suitability of the TBC to protect the Inconel substrate from such an extremely harsh thermal environment and further subjected to materials related metrological studies.

2.4 Characterization
Phase analysis of plasma spray powders and as-sprayed coatings of LZ and LCZ were carried out by using the XRD. Scanning electron microscopy (SEM) allied with energy dispersive X-ray analysis (EDXA) was used to study the microstructure and to determine the chemical composition of laboratory prepared plasma spray coatings respectively.

3. Results and Discussion

3.1 Plasma Spray Coated Specimen
Figure 2. shows the photographs of the as-sprayed coatings of LZ and LCZ plasma sprayed powders coated on Inconel718 substrates. The as-sprayed coating surfaces were uniform and smooth.

Figure 2. As sprayed coated specimens

a) LZ
b) LCZ
3.2 Thermal Shock Test Results

The thermal shocked test specimen exhibited significantly varied performance and test results between the conventional YSZ, LZ and LCZ TBC’s. The results pertain to the test when the hot face (ceramic surface) was subjected to the extremely harsh environment (flame surface temperature at ceramic surface 1200°C). The conventional YSZ specimen failed at the end of 90 thermal shock cycles while the specimen with LZ and LCZ failed at 170 and 210 cycles respectively. Failure was recorded when the topmost ceramic layer (visible to naked eye) either cracked or showed signs of degradation such as peeling off. These important results exhibit the highly superior characteristics in zirconia based pyrochlore TBC’S. Figure 3 shows the ceramic topmost surface of the specimen at the end of thermal shock tests at 1200°C.

![Figure 3. Specimen Thermal shock tested at 1200°C (a through c)](image)

3.3 Microstructural Analysis and Chemical Composition of LZ

Figure 4 shows the LZ plasma spray coated surface microstructure obtained by using SEM at magnifications of 3000 X and 10000 X. The grains in the spray-coated surfaces were only a few microns sized and were determined to be in the range of 1-5 microns, depicting an extremely fine-grained microstructure. Similar microstructures have been reported by other workers as well [20].

![Figure 4. SEM Micrograph of LZ plasma spray-coated surface](image)
SEM (EDS) was used to analyse the chemical composition on selected surface of LZ coated specimen and the EDS pattern and chemical composition is shown in Fig.5. Peaks pertaining to Lanthanum (La), Zirconium (Zr), Cerium (Ce) and Oxygen (O) were present in the EDS patterns. Figure 6 shows the chemical composition of the selected area of LZ as-spray coated specimen.

**Figure 5.** EDS pattern of LZ coated surface showing Elemental composition and the spray-coated surface (selected area SEM Image)

### Chemical Composition

| Element | Weight % | Atomic % |
|---------|----------|----------|
| O K     | 23.51    | 69.37    |
| ZrL     | 26.05    | 13.48    |
| LaL     | 50.45    | 17.15    |

3.4. Crystallographic Structural Phase Analysis of LZ spray coated specimen

Figure 6 (a thru e) shows the XRD patterns of LZ powders and coatings that have undergone different heat treatments during processing. The changes in the patterns show the various phases formed during the various stages of processing of \( \text{La}_2\text{O}_3, \text{ZrO}_2 \) (mixing, calcination and plasma spraying). The final phase (lanthanum zirconate pyrochlore structure) has not yet formed at 1000°C while a completely crystalline phase is formed at 1500°C. Plasma spray processing appears to have introduced some amount of glassiness to the structure (broadened peaks) which was evident in the microstructure analysis as well. The peaks were observed to shift towards the right, which reveals the LZ formation of metastable phase.

**Figure 6.** XRD patterns of LZ powders a) Raw mixed b) Calcined at 1000°C c) LZ Sintered at 1500°C d) Plasma Spray Powders e) LZ Plasma spray coated on Inconel 718 substrate.
3.5. Microstructural Analysis and Chemical Composition of LCZ spray coated specimen

Figure 7 shows LCZ plasma spray coated surface microstructure obtained by using SEM at magnifications of 3000 X and 10000 X. The microstructure was as expected glassy, with almost 100% melting achieved via the process of plasma spray coating. The grain sizes of the melted particles on the glassy matrix of the coatings were found to no larger than the range of 1 to 10 microns, a fine grained microstructure.

![Figure 7. SEM Micrograph of LCZ plasma spray-coated surface](image)

SEM (EDS) was used to analyse the chemical composition on selected surface of LCZ coated specimen which is shown in Figure 8 shows the chemical composition of the selected area of LCZ as-spray coated specimen.

![Figure 8. Elemental composition of SEM Image on The LCZ spray-coated surface on selected area](image)

### Chemical Composition

| Element | Weight % | Atomic % |
|---------|----------|----------|
| O K     | 20.97    | 67.02    |
| ZrL     | 20.37    | 11.42    |
| LaL     | 46.41    | 17.08    |
| CeL     | 12.25    | 4.47     |

3.6. Crystallographic Structural Phase Analysis of LCZ spray coated specimen

The phase formation of LCZ (lanthanum ceriate zirconate pyrochlore structure) is similar to the LZ formation as discussed in section 3.4. XRD patterns of LCZ powders and coatings that have undergone different heat treatments during processing which are seen in figure 9 (a thru e). The changes in the patterns show the various phases formed during the various stages of processing of La2O3, CeO2, ZrO2 (mixing, calcination and plasma spraying) and a complete crystalline phase is formed at 1500°C. The LCZ broadening peaks exhibited characteristics similar to LZ.
Conclusion
Plasma sprayable powders of LZ and LCZ were synthesized from La$_2$O$_3$, ZrO$_2$, and CeO$_2$ raw material composition. Organic binder (PVA) was used to synthesis these composition by manual methods such as grinding, oven drying and different sieves mesh were used in order to get good flowability of plasma spray powders. Inconel 718 were used as substrate, bond coat (NiCrAlY) layer were sprayed followed by plasma spray powders LZ and LCZ using APS method. Crystal Structural Phase analysis, microstructure and chemical composition confirmed the presence of pyrochlore phases in the LZ and LCZ coatings. The zirconia based pyrochlore (LZ and LCZ) TBC’s exhibited superior thermal shock cycle resistance over conventional Yttria stabilized TBCs.

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