Chapter 4

Experimental Work

4.1 Introduction

The current research aims to develop spray grade powder and plasma spray deposition of lanthanum zirconate based (Lanthanum Zirconium Oxide / LZ / La₂Zr₂O₇) TBCs using plasma heat energy and compare its properties with commercially available Yttria Stabilized Zirconia (YSZ/ZrO₂-8%Y₂O₃) coatings. In particular, microstructural, mechanical, thermal properties and thermal cycling life of the coatings will be compared.

The experimental plan of the present investigation is illustrated in the form of a flow chart as shown in Fig. 4.1 and 4.2. The detailed experimental procedures involved in each stage of the experimental work are elucidated in the following sections.

4.2 Evaluation of Starting Materials Properties

The chemical composition of the polycrystalline super alloy (Supemi C263 substrate material was found by optical emission spectroscopy) is presented in Table 4.1. The chemical composition of commercially available 8YSZ ceramic top coat powder and NiCrAlY bond coat powder (Supplied by M/s.Metallizing Equipment Corporation, Jodhpur, India) used in this investigation are presented in Table 4.1. Powder particle size, evaluated by sieve analysis (conforms ASTM B-214) for the YSZ and NiCrAlY powders are shown in Table 4.2. The optical micrograph of the nickel based super alloy substrate material is displayed in Fig. 4.3. The microstructure consists of equiaxed and columnar grains (Supplied by Gas Turbine Research Establishment (GTRE), Defense Research and Development Organization (DRDO), Bengaluru, India).
Comparative Performance Evaluation of Atmospheric Plasma Sprayed Yttria Stabilized Zirconia and Lanthanum Zirconate Coatings

Synthesis of LZ Powder*

Plasma Spray Deposition of YSZ & LZ

Thermal Spray Deposition of NiCrAlY

Characterization of Synthesized powder for plasma spraying

Optimizing plasma spray parameters

Selection of suitable deposition process with optimized parameters

APS

HVOF

Developing Single, Duplex and DCL* Coatings

As-Sprayed Coatings

Thermal Properties

Co-efficient of Thermal Expansion

Thermal Conductivity

Mechanical Properties

Microhardness & Bond Strength

Young’s Modulus

Evaluation of Thermal Cycling Performance

Comparative Evaluation of YSZ, LZ coatings performance

Results & Discussion

Conclusions

Fig. 4.1 Experimental Plan

*Synthesis procedure in Fig. 4.2

# DCL – Double ceramic layered coatings
Fig. 4.2 Experimental plan for thermal spray grade LZ powder preparation

Table 4.1 Chemical composition (wt %) of substrate and powder materials

<table>
<thead>
<tr>
<th>Elements</th>
<th>Co</th>
<th>Cr</th>
<th>Mn</th>
<th>Mo</th>
<th>Fe</th>
<th>Ti</th>
<th>Al</th>
<th>Zr</th>
<th>Si</th>
<th>Hf</th>
<th>Y</th>
<th>Ni</th>
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<tbody>
<tr>
<td>C263</td>
<td>19.3</td>
<td>19.9</td>
<td>0.4</td>
<td>5.9</td>
<td>0.01</td>
<td>1.95</td>
<td>0.4</td>
<td>0.14</td>
<td>0.22</td>
<td></td>
<td></td>
<td>Bal</td>
</tr>
<tr>
<td>NiCrAlY</td>
<td></td>
<td>23.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.09</td>
<td>10.45</td>
<td></td>
<td></td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>YSZ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.05</td>
<td>0.11</td>
<td>0.12</td>
<td></td>
<td>Bal</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Table 4.2 Powder particle size analysis (percent)

<table>
<thead>
<tr>
<th>Sieve size</th>
<th>+140</th>
<th>-140+200</th>
<th>-200+325</th>
<th>-325</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>7.0</td>
<td>21</td>
<td>40</td>
<td>49</td>
</tr>
<tr>
<td>NiCrAlY</td>
<td>0.4</td>
<td>13.7</td>
<td>37.6</td>
<td>48.3</td>
</tr>
</tbody>
</table>
Commercial grade NiCrAlY (PAC 9620 AMF) powder used was as a bond coat material in this investigation. The powder exhibits a globular shape from gas atomization as can be seen from Fig. 4.4. The feedstock was spray-dried and densified Zirconia-Yttria 8% stabilized powder (Powder Alloy Corporation, USA, PAC 2008P) with a particle size of $\approx 106 \pm 15 \ \mu m$. The SEM image ((Model: JEOL 6410-LV) of the feedstock taken at 200 x magnification with image resolution of 1024 X 768 pixels shows some particles having satellites as shown in Fig. 4.5 (a).

Satellites are finer particles embedded over coarser particles in spray dried powders. In spray drying, atomized coarser and finer powder particles interacts with each other under turbulent atomization condition, which leads to formation of satellites in spray dried powders [66]. Figure 4.5(b) shows the EDS results of YSZ
powder and it conforms the presence of zirconia and yttria as major elements and no other traceable elements.

4.3 Procedure to Prepare Thermal Spray Grade Lanthanum Zirconate Powder

This part of the report deals with the preparation of thermal spray grade lanthanum zirconate (LZ) powder by solid state sintering (SSS) route, transferred arc plasma (TAP) melting technique followed by crushing, ball milling and sieve analysis. The procedures involved in thermal spray grade LZ powder preparation is shown in Fig. 4.2.

4.3.1 Preparation of lanthanum zirconate powder

To prepare lanthanum zirconate powder, solid state reaction technique was adopted for initial investigations to understand and compare the phases exist in the developed powders. The lanthanum oxide and the zirconium oxide powders with 99.9% purity (Sigma Aldrich, India) were used as a starting material. The scanning electron microscope (Make: JEOL, Japan; Model: 6410-LV) was used to analyse the size and morphology of the starting materials are presented in Figs. 4.6 and 4.7. Both the powders have a blocky and angular morphology with a size distribution ranging between 2-8 μm.

The X-Ray diffraction (Make: Rigaku, Japan; Model: ULTIMA-III) patterns of the raw lanthanum oxide and zirconium oxide is shown in Fig. 4.8. The XRD pattern of the lanthanum oxide exhibits cubic phase only, whereas the XRD pattern of the zirconium oxide shows tetragonal as well as monoclinic phases. Presence of lanthanum oxide and zirconium oxide in the green pellets was confirmed by EDS analysis as shown in Fig. 4.9 and major element is La₂O₃ followed by ZrO₂. Figure 4.10 shows the procedure followed to prepare LZ powder by conventional sintering route. The stoichiometry was two moles of zirconium oxide + one mole of lanthanum
oxide being the stoichiometric mix leading to the formation of the lanthanum zirconate cubic pyrochlore phase. The powder mixtures were mixed in a ball mill (Make: VBCC; India, Model: LVBPBM-11 High energy ball mill) for 4 hours with water and zirconia balls as the mixing medium. The mixtures were then dried and blended with a suitable amount of polyvinyl pyrrolidone (binder) and stearic acid (lubricant) additions. These powder mixtures were then compacted by cold pressing (Make: VBCC; India, Model: VBHPCC-18, Hydraulic press) at 420 Kg/cm² to form pellets. The cold pressed pellets (Fig.4.11) were calcinated at a temperature of 800 °C in open air using a tubular furnace (Fig. 4.12; Make: VBCC India Model: VBHTSF-1800MF12) for 4 hours to remove the volatile compounds from the pellets. The calcined pellets then sintered at a temperature of 1600 °C in open air for 12 hours and this ensured complete sintering of the pellets (Fig. 4.13). Fig. 4.14 shows the optical micrograph of the sintered pellet contains visible pores.

4.3.2 Transferred Arc Plasma (TAP) melting

In this investigation, transferred arc plasma (TAP) melting was used to prepare lanthanum zirconate powder to reduce the processing time and cost. This system consists of a water cooled graphite crucible / anode (diameter 76.2 mm, height 101.6mm, wall thickness 25.4 mm) a graphite rod / cathode (diameter 25.4 mm, height 304.8 mm solid rod with 3 mm centre hole for the passage of argon) and a cooling system capable of circulating chilled water. The system has manually operated up down mechanism to lower or retract the anode from the crucible. 40 kW Insulated Gate Bipolar junction Transistor (IGBT) based power supply system was connected to the electrode and crucible. The pellet preparation procedure is same as discussed in section 4.3.1.
Fig. 4.6 Lanthanum oxide powder shows irregular morphology with particle size in submicron range

Fig. 4.7 Zirconium oxide powders shows irregular morphology and particles in submicron size range

Fig. 4.8 XRD pattern of starting powders

Fig. 4.9 EDS analysis LZ green pellet
Fig. 4.10 Graphical representation of powder preparation by sintering route

Fig. 4.11 Stoichiometrically prepared cold pressed pellets

Fig. 4.12 Furnace used to sinter the powders

Fig. 4.13 Photograph of sintered samples

Fig. 4.14 As sintered powder samples
The cold pressed pellets were charged in the crucible of the transferred arc plasma (TAP) ceramic melting unit (Model: TAPCMU-II, Make: Ion arc Technologies; India) and were fired (Fig. 4.15 (a-d)). The optimum TAP operating parameters were input power: 7 kW, Argon flow rate: 9 l/min, Cooling water temperature & flow rate: 18 °C & 38 l/min, Melt time: 12 minutes for 50 g of pellets, Cooling time: 5 Minutes, Cooling medium: Water cooled crucible. The above mentioned process parameters enabled a complete melting of the pellets to form a lanthanum zirconate nugget with minimum porosity and powder wastage (Fig. 4.15 (e)). Fig. 4.15 (f) shows the optical micrograph of the TAP melted nugget forms equiaxed grains and no visible pores were seen. Further, these TAP melted powders were crushed manually, ball milled and subjected sieve analysis for further plasma spray deposition.

4.4 Thermal Spray Deposition of Ceramic and Metallic Powders

In this investigation, multi objective optimization of APS process parameters was performed using response surface methodology (RSM) to tailor the properties of the commercial YSZ and laboratory prepared fused and crushed LZ powder coatings. The TAP melted and crushed LZ powders were again sieved and the particles having -106+10 μm size were separated and used for plasma spray deposition. Plasma spray deposition was carried out using an atmospheric plasma spray (APS) system (Model: APSS-II Make: Ion Arc Technologies, India) shown in Fig. 4.16 (a). The same 40 kW IGBT based power supply system, which was used in TAP melting to supply D.C. power to the non-transferred arc plasma spray troch. The ceramic powders were plasma sprayed over NiCrA1Y (Ni-22Cr-10Al-1Y, Make: PAC 9620 AMF, size: 10-45 μm) bond coat (BC), which was previously deposited using HVOF (Model: MEC HIPOJET 7100, Make: MEC: India.) process on to the grit blasted Superni C263 (Substrate). The HVOF spraying system used to deposit metallic bond coat is shown in Fig. 4.16 (b).
(a) Powder charged in the form of pellet
(b) TAP melting of powders
(c) At the end of melting
(d) After cooling
(e) TAP melted nugget of cold pressed pellet
(f) Optical micrograph of the melted nugget

Fig. 4.15 TAP melting process
Grit blasting was carried out by suction blasting equipment (M/s. Metallizing Equipment Corporation Pvt. Ltd., India) using corundum grits of size of 500 ± 320 μm and subsequently cleaned using acetone in an ultrasonic bath and dried. After grit blasting, the average surface roughness was measured using the surface roughness tester (Model: Surftest 301, Make: Mitutoyo, Japan). The average roughness was found to be ~ 5 μm.

(a) Plasmatron spray unit used to deposit coatings

(b) HVOF spraying system used to deposit metallic bond coat

Fig. 4.16 Thermal spray facility used in this research
The YSZ and LZ powders were directly sprayed on to the grit-blasted substrate to a thickness of 350 ± 10 μm and bond coat was not used for initial investigations. Thickness of the coating was measured by 0.001 accuracy digital micrometer (Make: Mitutoyo, Japan). Area to be coated kept perpendicular to the spray torch axis, the stream of spray particles should impact the target surface as close to normal (90°) as possible. The gun traverse rate was constant for all experiments; it was 300 mm s⁻¹, and the coating track overlap was 30%. Lanthanum zirconate was plasma sprayed without restriction into an open, ambient environment and artificial cooling system was not used and also no preheating of the substrate.

Fig. 4.17 Photograph of coated specimens
The cracks and delamination of the coating, the thickness developed per pass, and avoiding markedly seeing open pores by naked eye were inspected to identify the working limits of the operational plasma spray parameters.

The coating experiments were carried out as per experimental design matrix. The selection of the experimental design matrix, the manipulation of process parameters, the evaluation of responses, and the formulation of empirical relationships are developed based on Central Composite Design (CCD) concept in Response surface methodology approach using Design Expert (V.8.0) software.

To evaluate the coating properties, four geometries of coated substrates were used: (i) 25.4x 12.7 mm coupons for metallographic examination and microhardness measurement (Fig. 4.17 (a&c)) (ii) 100 x 25.4 x 2 mm coupons for Young’s modulus measurement test (Fig. 4.17 (b&d)) and (iii) 25.4 mm x 25.4 mm (diameter x height) cylindrical specimens for tensile bond strength (ASTM C 633) test.

4.5 Characterization of Coated Specimens

4.5.1 Metallographic preparation

Metallographic cross sections of the coatings were prepared for the porosity and microhardness measurements. The coated specimens were first carefully cut to the specific dimensions (10 X 10 X 2 mm³) using a slow speed metallurgical sample saw (Make: Ducom, India; Model: MSS-10) equipped with resin bonded diamond cutting disc. They were then mounted with low viscosity epoxy resin under vacuum environment. The mounted samples were successively ground with 600, 800, 1000 and 1500 grit SiC papers and eventually polished using diamond slurries of 10-8, 8-5, 5-2, 2-0.5, 0.5-0 μm during 5, 5.7, 10 and 10 min, respectively. Because of pullouts in brittle materials, it is difficult to establish and evaluate true porosity in a metallographically prepared spray coating. As metallographic grinding and polishing,
if not carried out correctly, can introduce artifacts which are not part of the coating structure. Ceramic coatings are brittle and particles break out of the surface during grinding. If not polished thoroughly, these breakouts leave an incorrect impression of a high porosity [67, 68].

4.5.2 Porosity analysis

Porosity measurement was carried out using an image analysis method on the metallographic cross sections according to the ASTM B276 standard [69] on the polished cross-section of the coating, using optical microscope (Make: Meiji; Japan, Model: MIL-7100) equipped with image analyzing system (Metalvision version 6). While carrying out image analysis proper magnification has to be selected in order to reveal the features of images like open pores and network of cracks. In this investigation 400 X magnifications of optical micrographs with image resolution of 1024 X 768 pixels were chosen for porosity analysis. Initially, a 200 μm square area was selected on the polished cross-section of the coating, and the image was analyzed. The same procedure was repeated at five random locations to find out the average percentage volume of porosity. Previous studies [70, 71] shows that depending on the purpose, comparisons are usually based on micrographs taken at magnifications ranging from 50 to 500 times. It is evident from the porosity analysis, images captured at 400X magnification revealed the intricate features of plasma sprayed coatings such as, Type A and Type B pores.
Fig. 4.18 Steps involved in image analysis; (a) Binary image of the selected image; (b) Selected area to be analyzed (c) Color coded image after porosity analysis.
(a) Schematic diagram

(b) Experimental setup

Fig. 4.19 Details of Three point bend test
Costil et al. [72] also discussed about resolution of images and predicted responses. They opined that image resolution have uncertainties such as, high resolution leads to overvaluation in predicting values and hence the analyzed results have to be considered indicative rather than exact. The steps involved in image analysis are shown in Fig. 4.18 and results shows the presence Type A and Type B pores usually formed in plasma sprayed coatings.

Pore size and pores classified from 0 to 10 µm as Type A and designated as A02, A04, A06 and A08. Pores Classification in the range from 10 to 25 µm as Type B and designated as B02, B04, B06 and B08. Type A pores may be formed as a result of interaction between material particles and the gaseous media [73]. The type B pores are caused by the splashing of particles on impact with deposited material; or it may be due to voids resulting from the poor deformation of partially melted particles. These pores can have different sizes and exceedingly intricate shapes. Moreover, results shows that coating consists of type A and type B pores and distributed as A08 and B08 form which is evidence of the characteristics of plasma sprayed coating.

4.5.3 Microhardness measurements

Microhardness measurements were made by indenting the indenter on the metallographic cross sections under 300 g load for 15 s using a Vickers microhardness tester (Make: Shimadzu, Japan; Model: HMV-2T). For each coating sample, the measurement series comprised 20 random indentations. Distance between indentations was kept three times longer than the indentation diagonal to prevent the effects of the stress field of nearby indentations.
4.5.4 Determination of Young’s modulus

Figure 4.19 (a) shows the schematic diagram of 3 point bend test setup for the coating system. Three point bend test was carried out in 20-kN servo controlled horizontal tensometer (Fig. 4.19 (b); Kudale instruments, Pune). The specimen was loaded at the rate of 0.5 mm/min until the visible crack is observed.

After assuming the symmetry during the bending test in relation to Fig. 4.19(a), the Young’s modulus can be written as

\[ Eclc + Esls = PL^3/48d \]  

(4.1)

Where Is and lc are the moment of inertia of the substrate material and the coating, P is the applied load, L is the distance between the supports, and d is the displacement of the substrate material and coating during the bending tests [50]. The moment of inertias are,

\[ Ic = \int_{-hc/2}^{hc/2} y^2 \, dy \]  

(4.2)

and

\[ Is = \int_{-hs/2}^{hs/2} y^2 \, dy \]  

(4.3)

Where, hs and hc are the height of substrate and coating.

4.5.5 Tensile bond strength analysis

The procedures prescribed in ASTM- C633-01 (Fig. 4.20) standard was used to evaluate for adhesion bond strength of as sprayed coatings [74]. The bonding of coated and uncoated was done by using commercially available epoxy adhesive, (HTK ULTRA BOND 100, bond strength of epoxy was found to be 85 MPa,) which was self-adhesive at 190 °C for 35 min. Then bonded samples were loaded with a loading rate of 1mm/min using a universal tensile testing machine (Model: UNITEK-
94100; Make: FIE Blue Star, India) until fracture and the corresponding fracture stress was recorded for analysis.

(a) Schematic diagram of tensile bond testing as per ASTM C-633-01

(b) Coated specimens

(c) Bonded specimens

Fig. 4.20 Details of tensile bond test

4.5.6 Surface roughness analysis

Surface roughness profiles of the as sprayed coatings were measured using a Rank Taylor Hobson contact profilometer (Rank Taylor Hobson Limited, Leicester, England). Three measurements of 5 mm length were made at random locations on coatings top surface using a stylus with a 2.0 mm tip radius. The as-sprayed coatings surface roughness values were analyzed and results were plotted as 2-D and 3- D images using image J analysis software.
4.5.7 Thermal expansion measurements

The thermal expansion behavior of free standing coatings of Yttria stabilized Zirconia, Lanthanum Zirconate and Ni-22Cr-12.5Al-1Y coatings, as well as the C263 superalloy, was measured to assess the relative influence of substrate and bond coat thermal expansion behavior on TBC durability. The super alloy specimen and YSZ and LZ freestanding coating of 12 mm diameter 2 mm length specimens were used. Thermal expansion measurements were made from 25 to 1200 °C, using a High Temperature dual push rod differential dilatometer (VB Ceramic Consultants, Chennai, India). Expansion measurements were made using a computerized data acquisition system, while the samples were heated and cooled at a rate of 3 °C/min. Data sets were continuously stored at online using Labview software. Fig. 4.21 shows the dilatometer setup to measure the thermal expansion co-efficient values of coatings

![Dilatometer setup](image)

Fig. 4.21 Dilatometer setup

4.5.8 Acoustic emission analysis

The schematic diagram of three-point bend test and coated specimens are shown in Figs. 4.22 (a and b). The samples were subjected to three-point bend tests with a span length of 100 mm using a servo-hydraulic testing machine (Instron 8801,
100 KN) at a cross-head speed of 1 mm/min. Load and displacement were recorded for each measurement. Two piezo electrical acoustic emission sensors (Physical Acoustic Corporation (PAC), R15 resonance frequency 150 kHz) were attached at the ends of the coated bottom side as shown in Fig. 4.22 (c).

(a) Schematic diagram of coated specimens for three point bend test with AE sensors

(b) NiCrAlY coated specimens for bend test

(c) Specimens during bend test
(d) Acoustic Emission (AE) recorder

Fig. 4.22 Three point bend test setup with AE recorder
(a) Schematic diagram of thermal conductivity meter

(b) Photograph of guarded heat flow thermal conductivity meter

(c) Photograph of specimens prepared to measure thermal conductivity

Fig. 4.23 Details of thermal conductivity measurement
Roller bearing grease was used for acoustic coupling, while the sensors were secured by the use of tape during the experiment. The sensor positions were chosen for minimizing acoustic emission emerging from deformation of the specimen. The frequency response of the sensors is roughly 50–520 kHz for transient (burst) signals. This overlaps with the results, which have shown that 90% of the acoustic emission emerging from material deformation is within the frequency band of 10–550 kHz. The sensors are connected to an amplifier/filter with a gain of 40 dB. Acoustic emission signals were continuously recorded through acoustic emission recorder as shown in Fig. 4.22(d).

4.5.9 Thermal conductivity measurements

The thermal conductivity was measured, using the experimental arrangement shown in Fig. 4.23 (a). According to the ASTM standard, E-1530-04 Guarded Heat Flow Meter Technique, [52] the equipment was designed. Electric heating coils were used to provide the required heat and allowed to flow through the flux meter and coated samples. On the radial faces of the flux meter, 1 mm diameter drills were made to insert the thermocouples. Thermocouples were used to monitor the simultaneous heat transfer through the flux meters and across the coated samples. Steady state was determined by data-logging of the thermocouple output as shown in Fig. 4.23(b).

The pair of coated C263 samples, cylinders with 30 mm diameter and 30 mm height) were placed back to back, in order to double the coating thickness and hence improve the accuracy. Nimonic C263 (Supplied by GTRE, Bengaluru) was used in the present work (Fig. 4.23(c)). Unidirectional heat flow is assumed, the system is allowed to flow the heat from lower hot plate to upper copper sink, where heat is taken away through chiller unit. A dead load of ~0.7 MPa was applied over the specimens. Temperature variations in flux meters and across the coating were
measured through thermocouples, which are connected with Lab View software. These steady state temperature data were used to calculate the thermal conductivity of the coated specimens (Fig. 4.23(c)).

By assuming one-dimensional heat flow across the setup, and by taking into account changes in thermal conductivity of the blocks with temperature, the mean heat flux, Q, can be found using Eqns. (4.4) – (4.8):

\[
Q = \frac{1}{6} \sum_{j=2}^{4} \sum_{h=1}^{3} K_{sub} \left( \frac{T_{f,j} - T_{k,h}}{x_{j} - x_{h}} \right) (T_{f,j}^{ave}) (4.4)
\]

\[
Q = \frac{1}{6} \sum_{j=6}^{8} \sum_{h=7}^{9} K_{sub} \left( \frac{T_{f,j} - T_{k,h}}{x_{j} - x_{h}} \right) (T_{f,j}^{ave}) (4.5)
\]

\[
(T_{f,j}^{ave}) = \left( \frac{T_{j} + T_{k}}{2} \right) (4.6)
\]

where j and k designate locations of thermocouples, while \( K_{sub}, (T_{f,j}^{ave}) \) is the temperature-dependent thermal conductivity of the Nimonic C263 substrate, at the average temperature.

The mean flux can be written as:

\[
Q = \left( \frac{Q_{upper} + Q_{lower}}{2} \right) (4.7)
\]

The conditions are presumed to approximate to one dimensional heat flow when:
Fig. 4.24 shows a schematic diagram of the one dimensional heat flow, which assumes similar heat flow throughout the thickness direction under steady state conditions. Assuming no lateral heat losses, the same flux flows through coating and interfaces [52], so that the relationships established to determine the heat flow across substrate are given in the following Eqns-4.9-4.11

\[
\frac{Q_{\text{upper}} - Q_{\text{lower}}}{Q_{\text{upper}}} \leq 10\%
\]  \hspace{1cm} (4.8)

\[
Q = K_{\text{eff}} \frac{\Delta T}{\Delta x}
\]  \hspace{1cm} (4.9)

\[
Q = h\Delta T_i
\]  \hspace{1cm} (4.10)
\[ Q = K_{\text{true}} \frac{\Delta T_c}{\Delta x} \]  

(4.11)

Where,

\( K_{\text{eff}} \) is the effective thermal conductivity of the coating, \( \Delta T \) is the total temperature drop, \( \Delta x \) is the coating thickness, \( h \) is the interfacial thermal conductance (assumed the same for both interfaces) and \( K_{\text{true}} \) is the actual coating thermal conductivity. The subscripts \( i \) and \( c \) denote interface and coating, respectively.

4.6 Evaluation of Thermal Cycling Life of Coatings

For the evaluation of thermal cycling behavior of coatings, the considered dimensions of the substrate superalloy C263 material coupons were 25.4 x 12.7 x 2 mm. The corners and the edges of the substrate coupons were chamfered and rounded prior to grit blasting. The coatings were made on the single side of the grit blasted substrate coupons. The investigation was started to compare the thermal cycling lives of the duplex YSZ and LZ coatings. But, the intrinsic low coefficient of expansion and the low fracture toughness of the LZ coating, compared to YSZ coatings as inferred in the literature [75], made it try DCL coating architectures to find whether the thermal cycling life of the LZ coatings could be improved.

The various coating architectures considered for the investigation, are shown in Fig. 4.25. Specimens without bond coat were used for initial investigations and specimens with bond coat were used for thermal cycling studies. At elevated temperatures, bond coat behaves as a substrate [17, 19], hence the TBCs could be considered as a substrate and ceramic layer structure. The thermal stress due to the mismatch between the ceramic layer and the substrate. Thermal stress was resulting from difference of the CTE of coating and substrate during substrate and coating
cooled together from spraying temperature to the room temperature [17, 61]. For two-
dimensional analysis, the thermal stress in the coating can be expressed as:

\[ \sigma_{tm} = \frac{E_c}{1 - \nu} \Delta \alpha \Delta T \]

where \( E_c \), \( \Delta \alpha \), \( \Delta T \) and \( \nu \) were the elastic modulus of coating, CTE difference
between the substrate and coating, temperature difference upon cooling and the
Poisson’s ratio of coating, respectively [60-62]. Coated specimens are shown in Figs.
4.26 and 4.27. The total thickness of all the coatings, were kept constant at 500 \( \mu \)m
for thermal cycling studies. The porosity levels of the ceramic coatings were
maintained at 14 vol. % by appropriately modifying the APS process parameters,
which are given in Chapter 5, 6 and 7.

4.6.1 Thermal cycling test method

The thermal cycling test was carried out, using a 1700 °C automated thermal
cycling furnace (Make: VBCC; India, Model: VBTCF-1). The test condition and
procedures were followed as per the guidelines provided by the funding agency of this
project (Gas Turbine Research Establishment, DRDO Labs, Ministry of Defence,
Govt. of India). The coupons for thermal cycling were placed on a zircar plate and
inserted directly into the hot zone (150 X 150 mm) having a temperature of 1050 °C,
in which the coupons were exposed to the aforesaid temperature for 45 minutes,
followed by cooling the coupons for 15 minutes under forced air cooling arrangement
leading to 50 °C temperature. This one hour cycle was repeated until an area of 20%
of the coating got peeled off and the corresponding number of cycle was recorded as
the life time of the coating. The equipment used to carry out thermal cycling studies is
shown in Fig. 4.28.
Fig. 4.25 Coating architecture considered for thermal cycling test

Fig. 4.26 TCL specimens of YSZ

Fig. 4.27 TCL specimens of LZ

Fig. 4.28 Automated twin chambered thermal cycling furnace used for thermal cyclic studies
4.7 Evaluation of Isothermal Oxidation Behaviour of Coatings

In this investigation, an attempt was made to compare the isothermal oxidation behavior of various specimen types with bond coat (Fig. 4.25) are subjected to a temperature of 1150 °C until the visible cracks appeared. The results of the isothermal oxidation tests are presented in the VII Chapter. The Further, isothermal oxidation test, the specific weight gain of the coatings were measured once in every 50 hours, by means of a precision weighing machine with 0.01 mg of resolution. The specimen dimensions and the coating procedures are the same as mentioned under the Section 4.6.1.

4.8 Microstructural analysis

The scanning electron microscopes (Model: 6410LV, Make: JEOL, Japan) was used to carry out the microstructural and elemental analysis studies, respectively. The X-ray analysis was carried out to confirm compound formation and phase analysis was carried out using X-ray diffractometer (Model: Ultima –III, Make: RIGAKU, Japan)

4.9 Concluding Remarks

The details about substrate material, bond coat material and top coat materials are presented in this chapter. The processing steps involved in indigenous development of spray quality LZ powder employed and testing methods are described briefly. The results obtained from this experimental work are presented and analyzed in the following chapters.