PROCESSING, CHARACTERIZATION, AND PROPERTIES OF SOME NOVEL THERMAL BARRIER COATINGS

DISSERTATION

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By

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ABSTRACT

The efficacy of ceramic thermal barrier coatings (TBCs) used to protect and to insulate metal components in engines increases with the thickness of the TBCs. However, the durabilities of thick TBCs deposited using conventional ceramic-coating deposition methods have not been adequate. Here the feasibility of depositing highly durable thick TBCs (1.5 to 4 mm thickness) of ZrO$_2$-7 wt.% Y$_2$O$_3$ (7YSZ) on bond-coated superalloy substrates using the solution-precursor plasma spray (SPPS) method has been demonstrated. Thermal cyclic durabilities of the thick SPPS TBCs have been shown to be much superior compared to TBCs deposited using the conventional air-plasma-spray (APS) process. To evaluate the performance of thick APS and SPPS TBCs, mechanical properties of free-standing coatings and coating/substrate interfaces have been determined experimentally. Additional evaluation of TBC performance has been obtained from studies of damage and development of thermally grown oxide (TGO) at the interface as a result of thermal cycling. The later results are used to suggest mechanisms of chemical failure of TGO in thick plasma-sprayed TBCs. Based on the experimental results and numerical analysis of the TBC residual stresses, the dramatic
improvement in the thermal cycling life in the SPPS TBCs is attributed to superior mechanical properties of SPPS coatings. The presence of the strain tolerant vertical cracks in SPPS TBCs reduces the driving force for TBC spallation under mode-II loading. Additionally, high in-plane fracture toughness in the SPPS TBCs under mode-I loading delays the TBC spallation significantly. Finally, thermal conductivity of the SPPS TBCs has been reduced by microstructural tailoring. Analytical and object-oriented finite element (OOF) models have been used to analyze the experimental thermal conductivity data, and to predict thermal conductivities of engineered TBCs.
Dedicated to my parents
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CHAPTER 1

OVERVIEW OF THERMAL BARRIER COATINGS

1.1 Introduction

Continuous development of gas turbine engines is aided by efforts in various areas of engineering and science. These include design of modern and efficient turbines, better understanding and utilization of combustion processes, advances in manufacturing and the materials technology, etc. Developments in materials technology have further been classified in three subcategories [1, 2]: (i) substrate alloy development to facilitate more high temperature strength and corrosion resistance; (ii) improvements in materials manufacturing (especially casting technology) to produce directional solidification of blades, single crystal blades to improve creep resistant structural components, and intricate cooling channels on these blades to facilitate better heat transfer and; (iii) application of ceramic coatings on superalloy components to provide thermal insulation [3-5]. These coatings are well-known today as thermal barrier coatings (TBCs). Even though first two approaches have resulted in enhanced performances, they are associated with high cost of development and manufacturing, and have almost reached their
saturation of further development. The advances and developments in these two areas have been reviewed in the literature [6-8]. This chapter will review important research work done in the field of TBCs over the last three decades.

Due to their superior high temperature properties, superalloys comprise more than half of the modern day aero-gas turbine engines by weight. The low thermal conductivity and high melting-point TBCs offer very good thermal insulation along with protection against oxidation and hot-corrosion above 850 °C to the superalloys [9]. This concept has found widespread use in hot-sections of gas turbine engines. The coatings can extend the hot-section component life by reducing the temperature of metallic components. In gas turbines, they can be used to permit higher operational temperatures or reduce the air-cooling required, thereby improving the efficiency. The amount of improvement in fuel economy can be up to 20%, in addition to reduced emissions [1, 2]. Typical gas turbine engine components protected by use of TBCs are blades, vanes, combustors, transition ducts, exhaust nozzles and afterburners. TBCs also hold an exciting promise in the development of diesel engines [10-12]. Most diesel engine manufacturers today are developing so-called low heat rejection engines, with thermal insulation of the combustion valves, pistons and exhaust passages. This minimizes the heat loss through the combustion chamber components. Thus the performance of the diesel engines can be improved in terms of reduced emission, reduced fuel consumption and prolonged life of the metallic substrate. Additional advantages of TBCs arise from their ability to provide protection against rapid thermal transients that occur in turbine and diesel engine
environment. This approach helps to simplify the turbine blade design in many instances [1, 2].

1.2 Components of TBC System

A schematic illustration of a general TBC system can be seen in Figure 1.1. In general, the TBC system comprises of four main constituent layers: a superalloy substrate—the metal being protected by the coating, an intermetallic bond-coat coated on the substrate, and a ceramic topcoat (the outermost layer) - the actual ceramic coating. A bond-coat will typically consist of a ~100-150 µm thick alloy. The TBC top-coat is applied on top of the bond-coat. A typical top-coat for turbine engine application is ~200-600 µm thick. A thin layer of the thermally grown oxide (TGO), a reaction product, is developed at the interface of the bond-coat and the top-coat. It is mainly comprised of α-Al₂O₃, which is also considered as one of the TBC constituents [3]. Thickness of TGO varies between 1-10 µm at the time of failure of TBC. A brief description of all four components of the TBC is given in the following paragraphs.

1.2.1 Substrate

Ni (or Co) based superalloy is used as the substrate material. The superalloy components are investment-cast in single-crystal or polycrystalline forms. They contain several elements that are added for the enhancement of specific properties, such as high-temperature strength, ductility, oxidation resistance, hot-corrosion resistance, and castability [13]. At the high temperature of operation in gas-turbine engines, diffusion of elements of high relative concentration can occur between the superalloy substrate and
the bond-coat. These diffusing elements can occasionally be found in the TGO and the top-coat as well [3]. This interdiffusion, which results in formation of impurities in top-coat/ bond-coat interface, is expected to have a negative effect on the spallation failure of the TBC. Typically, the superalloy components are air-cooled from the inside or through internal hollow channels. Temperature reduction is established by this route, which helps to improve the component durability [3].

1.2.2 Bond-Coat

The main role of the bond-coat is to provide oxidation resistance to the substrate (by serving as an Al reservoir), in addition to enhancing the adhesion of the top-coat to the superalloy [3]. It also reduces the interface stresses in the TBC by providing intermediate expansion properties, and lessens the thermal-expansion mismatch between the substrate and the TBC [2]. Bond-coat is made either of MCrAlY (M=Ni or Co or both) alloy or of aluminides of Ni and Pt [3, 14, 15]. PtNiAl is used in applications where oxidation resistance is sought at working temperatures higher than that of the MCrAlY bond-coats [2]. For NiCrAlY systems, the base element, Ni and/ or Co, both minimize interdiffusion. Al forms $\alpha$-Al$_2$O$_3$, which protects the base from high temperature oxidation. While Ni depresses chemical activity of Al, Co increases it [16]. The amount of Al in the alloy can be reduced by Cr addition. Cr also helps in the formation of Cr$_2$O$_3$, protects the base against hot corrosion and oxidation up to 900°C [1, 16]. Finally, Y improves adherence of alumina and chromia scales on Ni and Co base alloys [17].
MCrAlY is typically deposited by using the plasma-spray or the electron-beam physical-vapor deposition (EB-PVD) method, depending on the final application of TBC and cost of manufacturing. The plasma spray process is much cheaper than EB-PVD process, and thus it can be useful in depositing thicker bond-coats. Pt/Ni-aluminides are deposited by electroplating in conjunction with diffusion-aluminizing or chemical-vapor deposition. Bond-coats used for plasma-sprayed TBCs are typically roughened (average roughness of 5-15 µm) for better mechanical interlocking [1].

1.2.3 Thermally Grown Oxide (TGO)

As mentioned earlier, TGO, predominantly consisting of $\alpha$-Al$_2$O$_3$, forms between the top-coat and the bond-coat. Defect-free TGO has a very low oxygen ionic diffusivity, and it provides an excellent diffusion barrier, retarding further bond-coat oxidation. [18-20]. During thermal cycling, the TGO develops very high compressive stresses (~3-6 GPa) due to thermal expansion mismatch [20]. Another source of relatively smaller compressive stresses is lateral growth of TGO (~1 GPa). Very high energy density in the TGO leads to its and subsequently the TBC failure. Thus it has major influence on TBC durability [20].

1.2.4 Top-Coat

Top-coat material is needed to fulfill certain requirements [1]: (i) high melting point, (ii) low thermal conductivity, (iii) coefficient of thermal expansion close to substrate, (iv) low density, (v) high erosion resistance, (vi) high surface emissivity, (vii) good oxidation resistance and (viii) thermal shock resistance. Zirconia (ZrO$_2$) has
emerged as the preferred material, stabilized into its cubic/tetragonal forms by the addition of yttria in solid solution. Several ceramics other than zirconia, including Ca$_2$SiO$_3$, MgAl$_2$O$_4$ and CaTiO$_3$, have been tried for this purpose. However, zirconia ceramics have emerged as the most suitable one for use in harsh environments because it demonstrates a superior combination of strength, toughness, and chemical resistance when compared to other ceramic materials [1].

Pure zirconia exhibits three polymorphs: monoclinic ($m$-ZrO$_2$), tetragonal ($t$-ZrO$_2$), and cubic ($c$-ZrO$_2$) depending on temperature. $m$-ZrO$_2$ is stable below 1170 °C, $t$-ZrO$_2$ is stable between 1170 and 2370 °C, and $c$-ZrO$_2$ is stable above 2370 °C until the melting temperature of pure zirconia which is 2680 °C [21]. The diffusionless, $t$-ZrO$_2$ → $m$-ZrO$_2$ transformation results in 3-5% volume increase upon cooling. Under physical constrains, increase in volume will exceed the elastic limit of the material, resulting into loss of physical integrity and cracking which may ultimately lead to catastrophic failure.

To make zirconia as a suitable material for TBC top-coat use, the $t$-ZrO$_2$ → $m$-ZrO$_2$ transformation must be suppressed. This is done by use of stabilizing agents such as CaO, MgO, ScO$_3$, and Y$_2$O$_3$ [22, 23]. From the phase diagram (Figure 1.2) of the ZrO$_2$ rich side of a Y$_2$O$_3$-ZrO$_2$ system, it can be noticed that no tetragonal phase is present at room temperature [24]. Typically, 7-8 wt.% (~4 mol%) Y$_2$O$_3$ additions to stabilize ZrO$_2$ have been found to give the best lifetime performance [1, 3, 20]. If a mixture of this composition is cooled rapidly from 2200-2500 °C to room temperature, a metastable tetragonal phase called as $t'$ is formed instead of equilibrium mixture of $m$-ZrO$_2$ + $c$-ZrO$_2$ phases as shown by the phase diagram [1, 24]. The $t'$-ZrO$_2$ phase is resistant to the
detrimental $t$-ZrO$_2 \rightarrow m$-ZrO$_2$ transformation and is therefore desirable. Typical routes of processing TBC top-coats give required high cooling rates (e.g. air-plasma-spray (APS) process produces cooling rate of $10^7$ S$^{-1}$ [25]). This results in complete formation of $t'$-ZrO$_2$ phase.

Bhaduri et al. [26] studied the phase stability of a plasma-sprayed 7 wt.% YSZ (7YSZ) coating using Cu-K$_\alpha$ X-Ray Diffraction (XRD). The amount of $t'$-ZrO$_2$ and $t$-ZrO$_2$ present in the coatings was calculated from specimens heat-treated at 1200°C for 100-hr, and 1250°C for 25h, which were found to have 100% $t$-ZrO$_2$ in as-sprayed condition. Formation of $t$-ZrO$_2$ and c-ZrO$_2$ from $t'$-ZrO$_2$ followed the compositions predicted by the equilibrium phase diagram. Studies with different Y$_2$O$_3$ percentages and different temperatures performed by other researchers have confirmed these results [27, 28]. Good chemical homogeneity and size uniformity of starting powder and, extremely high cooling rate have been found to increase the $t'$-ZrO$_2$ phase stability up to 1700 °C [1].

Zirconates other than YSZ were also studied for TBC applications. La$_2$Zr$_2$O$_7$ found good potential for the use due to its low thermal conductivity and low elastic modulus [29]. Rare earth zirconates such as Gd$_2$Zr$_2$O$_7$, Gd$_{2.58}$Zr$_{1.57}$O$_7$ and Nd$_2$Zr$_2$O$_7$ were shown to possess~30 % lower thermal conductivities than that of 7YSZ [30]. Attractive thermo-mechanical properties of these materials make them suitable candidates for future use in the TBCs.
1.3 Processing of TBC Top-Coats

Although various methods are available for depositing overlay metallic and ceramic coatings on metal substrates, few important and most commonly used ones are mentioned in the following text.

1.3.1 Electron-Beam Physical Vapor Deposition (EB-PVD)

In this widely used method, film growth is obtained by condensation of a vapor on the substrate. The vapor can be produced by heating the consumable, enough to obtain evaporation by focused high-energy electron beam. The vapor is then transported to the substrate. EB-PVD method, in general, is semi-line-of-sight, and produces a surface that replicates the original one (an initially smooth surface will result in a smooth coating and vice versa) [31, 32]. The schematic of the EB-PVD process is shown in Figure 1.3.

Microstructural features of standard, thin EB-PVD top-coats have been characterized and well-documented in literature [1, 3, 33, 34]. Figure 1.1 shows a typical EBPVD TBC cross-section. The top-coat possesses: (i) thin (<2 μm) dense layer of polycrystalline YSZ with equiaxed grains at the metal/ceramic interface to provide good chemical bonding; (ii) columns of material (2 to 10 μm diameter) above the thin dense film consisting the remainder of the coating; (iii) nanometer-scale porosity within the columnar grains; and (iv) channels separating the columnar grains, normal to the metal/ceramic interface.
Due to columnar structure, these TBCs possess “strain tolerance”, i.e. high resistance to spalling under thermal cycling due to their disconnected columns [3, 33]. The porosity and the cracks help reduce the thermal conductivity (∼1.5 to 2 W.m⁻¹.K⁻¹) [1, 34]. Tailoring the structure of the deposited coating, using modifications in process variations, is a way to obtain TBCs with zig-zag microstructure, which offers further reduction in thermal conductivity while retaining strain tolerance [35]. These coatings also result in smoother (more aerodynamic) surfaces [36]. It is an established result that EB-PVD TBCs offer vastly longer lives in jet engine operating conditions, where maximum thermal cycling is expected, than TBCs processed by other routes [31]. Thus these have found applications in turbine blades and vanes in aircraft engines [1, 3]. Even though EB-PVD TBCs are more durable than APS TBCs; they are more expensive than APS TBCs due to low evaporated material deposition efficiency and low deposition rates [36].

1.3.2 Thermal Spraying

Thermal spraying consists of melting a ceramic/metal powder and projects it as molten particles onto the substrate. Upon impact with the substrate, the molten particle flattens and solidifies very rapidly. The adhesion is primarily mechanical. Typically, included porosity and oxide content are present in the as-sprayed metallic coatings. There are various types of thermal spraying methods; some commonly used in TBC deposition (for top-coat and bond-coat) are briefly described in this section.
1.3.2.1 Flame Spraying

This method uses combination of fuel gases and oxygen to generate temperatures close to 2750 °C. Acetylene, propane, hydrogen and natural gas are commonly used fuels to produce flames, to melt wires or powder of the material and propel them during coating deposition [37]. Typical particle velocity is about 40 m.s\(^{-1}\) and deposition rate is 1 to 10 kg.h\(^{-1}\) [24]. Porosity in the as-sprayed coating is usually 10-15%.

1.3.2.2 High Velocity Oxy-fuel Spraying (HVOF)

In this method, specially designed torch allows the compressed flame to expand freely upon exit from the nozzle [38]. This results in very high flame gas speeds. Benefits of using the HVOF process are associated with higher density of the coating compared to flame spraying, good bond-strength with the substrate and compressive residual stresses in the coating compared to tensile residual stresses in plasma-sprayed coatings [39]. However, the process cannot be applied to refractory ceramic materials due to low temperatures of the combustion flame [38].

1.3.2.3 Plasma Spraying

1.3.2.3.1 Air Plasma-Spray

Traditional plasma spray method is also known as air plasma-spray (APS) process since it is carried out in open atmosphere. Here the plasma plume is formed by the ionization of a gas mixture consisting mostly of an inert gas such as nitrogen or argon and helium or hydrogen. The ionized gas plasma not only melts but also propels the powder
of the coating material. The heat content and velocity of plasma jet is influenced by parameters such as nozzle type, arc current, mixture ratio of gases and gas flow rate [37]. Typically, temperature of the plasma can exceed 16,000 °C, while the substrate temperature will be between 50-150 °C [24]. Very high particle velocity (200-300 m.s⁻¹) in this process can result into 90-95% dense coatings with good deposition rates (1-5 kg.h⁻¹). Figure 1.4 shows schematic of a typical APS process.

APS deposition is advantageous because no vacuum is required, and the coating source is not fixed as it is in the EB-PVD process. This makes the orientation and manipulation of the part less critical [3]. Deposition rates for plasma sprayed coatings are very high compared to EB-PVD coatings with much lower cost involved. Additionally, typical, 15 to 25% porosity in APS TBCs provide for both low elastic modulus and low thermal conductivity [3]. Due to high deposition rates (> 4 kg.h⁻¹), better deposition efficiencies and lower cost compared to EB-PVD method, APS process is useful for mass production, especially for thicker coatings (>50 µm) [38]. Also, the APS process is capable of depositing coatings with continuously varying composition [38].

It is well-known that in APS coatings, lamellae of material are present as a result of the collision of molten powders with the substrate or with previously deposited lamellae. A number of defects including “splat boundaries”, large scale and small scale porosity between lamellae, micro-cracks and un-melted particles can be present depending on plasma-spray process parameters. Non-bonded areas may also be formed due to oxidation or entrapped air [40]. Figure 1.5 shows microstructure of the cross-
section of a typical APS top-coat specimen. The macro-cracks and other microstructural defects can be predominantly seen oriented along the metal/ceramic interface (Figure 1.5B).

Preparation of the substrate (cleaning, roughening etc.) is essential to ensure good interface between coating and substrate. However, the undulating nature of the metal/ceramic interface, which is required for better interlocking adhesion, produces out-of-plane stresses responsible for in-service failure of APS TBCs [3, 20]. Many plasma spraying parameters can affect the resulting coating microstructure and properties. These include temperature distribution in the plasma, gas and powder feed rates, spraying distance, spraying angle and characteristics of the powder feedstock. Important feedstock parameters include location of powder input into the plasma plume, composition and particle size distribution.

Low pressure plasma spraying (LPPS) and vacuum plasma spray (VPS) processes are variants of the conventional APS process. Contrary to atmospheric plasma spraying; the low-pressure plasma spraying process is performed in a vacuum chamber at a pressure of approx. 4-8 kPa [38]. Component and torch are moved with special manipulators capable of being exposed to the very fine metal dusts and high operating temperatures. The vacuum reduces slowing and cooling of the particles by air and avoids oxidation during spraying. Also density obtained by this route is much greater than the usual methods [41]. MCrAlY coatings deposited by LPPS process contain high density, good bond-strength and minimal internal oxidation [41]. In addition to deposition of MCrAlY bond-coats, intermetallic and composite coatings of Ni$_3$Al and MoSiO$_2$
deposited by VPS comprise superior mechanical properties compared to their APS counterparts [38].

### 1.3.2.3.2 Solution Precursor Plasma-Spray

Recently, a new plasma-based coatings deposition method — solution precursor plasma spray (SPPS) — has been developed and used to deposit highly durable TBCs [42, 43]. In the SPPS process, an aqueous chemical precursor feedstock that results in coating of desired chemistry is injected into the plasma jet. This is in contrast to the APS process, where ceramic powder is used as the feedstock [44, 45].

Figure 1.6 shows schematic of SPPS process. Plasma torch with the plasma power of 30-45 KW is typically used for the SPPS TBC deposition [46, 47]. Ar and H₂ are used as primary and secondary plasma gases. The liquid precursor feed delivery system that consists of a precursor storage tank and regulated nitrogen, which serves as solution precursor atomizing gas. It drives solution precursor through a hose to a gas atomizing nozzle mounted at 90° from the gun axis where aqueous solution of Zr and Y salts is injected into the plasma plume [46]. As the solution product travels along the axis of plasma, it undergoes variety of transformations (explained later) and deposits on substrate as solid solution of 93 wt.% ZrO₂ and 7 wt.% Y₂O₃ (7YSZ) [43].

Microstructure of an as-deposited thin SPPS coating is shown in Figure 1.7. It typically consists of the following features [5]: (i) lack of macro-splat boundaries found in conventional APS coatings, (ii) 3-D interpenetrating and uniformly distributed pores and, (iii) through-thickness vertical cracks which are uniformly spaced in the coating.
The through thickness vertical cracks in TBCs can provide strain-tolerance during thermo-mechanical cycling of the TBCs [3, 48, 49]. The immersion density of as-sprayed coatings was found to be 4762 Mg.m\(^{-3}\) [5].

As-deposited coating is formed by non-transformable tetragonal phase (\(t'\)) as identified by XRD [50]. No changes in the phase were identified after thermal cycling at 1121 °C [50]. In addition, appreciable sintering of the ceramic particles was found to take place at that temperature.

Based on the experimental results, following deposition mechanism was suggested for SPPS coatings formation [43]. Rapid evaporation and subsequent break-up of the atomized precursor are followed by precipitation/ gelation and pyrolysis. The precursor pyrolysis may take place during its flight in the plasma or at later stages. Xie et al. [51] further elaborated the deposition mechanisms based on single scan SPPS process experiments. Figure 1.8 shows a schematic of SPPS deposition process with division of plasma jet in three distinct regions. The central region (region III) is the hottest zone while the outer peripheral region (region I) of plasma jet is the coldest. The precursor droplets traveling inside region III are shown to undergo melting and solidification and give rise to splat morphology upon deposition (Figure 1.8E). On the contrary, the region I is shown to carry unpyroliized precursor to the substrate and results in the formation of coating flakes and irregular agglomerates as shown in Figure 1.8B. The central region (region II) with intermediate temperature has been characterized by mixture of both types of the above microstructures along with spherical ceramic particles primarily formed by melting and solidification of the pyrolized precursor before reaching the substrate.
In this context, penetration of the precursor droplets in different zones of plasma is crucial in the determination of coating microstructure. For this reason, momentum of droplets and plasma dynamics become important variables in the SPPS process. Both the factors can be controlled by various processing parameters including liquid feed rate, atomizing gas pressure and Ar gas flow rate [52]. This approach changes not only amounts of different microstructural constituents (such as flakes, molten particles, etc.) but also the distribution of amount of unpyrolized precursor during each pass. In particular, the later factor helps to control amount and distribution of porosity in the SPPS coatings with relative ease.

Factors behind formation of through-thickness vertical cracks in the SPPS coatings were studied by Xie et al. [53]. This was done by depositing the SPPS coatings on variety of substrates with varying coefficient of thermal expansion (CTE) mismatch. Contributions from CTE mismatch between coating and substrate and, transient cooling of the coating during spraying were shown to play a less important role in vertical crack formation in coating. Pyrolysis of the precursor deposited on the coating was identified as a major force behind it. Constrained volume shrinkage can result into in-plane tensile residual stresses in the top-coat as a result of the pyrolysis of already deposited precursor [53, 54]. Heat of the subsequent passes or thermal cycling can carry out the pyrolysis process. Pyrolysis of unpyrolized precursor used in the experiments was shown to take place when it was subjected to 350 °C and was thought to result in 2-3% volumetric shrinkage. Associated in-plane tensile stresses can be as high as 40 GPa which is much
higher than tensile strength of plasma-sprayed 7-YSZ (25 MPa [55]) and will lead to vertical cracks in TBC.

Thermal cyclic durability of SPPS coatings was determined by using 1-hr thermal cyclic testing at 1121 °C [46]. APS and EB-PVD coatings deposited on the same type of substrate were subjected to thermal cycling to compare their durability with SPPS coatings [46]. Average spallation life of SPPS coatings has been found to be 2.5 times greater than that of the APS coatings and 1.5 times greater than that of the EB-PVD coatings. Additional advantage of the SPPS process stems from the low processing costs. Cost involved in SPPS process is much less than that for the EB-PVD process and comparable to that of the APS process [46].

1.4 Thermal Conductivity of TBC Top-Coats

As the most important function of a TBC is to provide better thermal insulation to the underlying metallic components; the role of thermal conductivity of top-coat materials is vital in the heat transfer process. The first part of this section reviews basic principles of the thermal conductivity of porous ceramics. It is followed by review of thermal conductivities of plasma-sprayed and EB-PVD deposited ceramics. The section ends with brief history of modeling work done for TBC top-coats.

1.4.1 Theory of Thermal Conductivity of TBCs

The theory of heat conduction by lattice waves (elastic or ultrasonic waves with their spectrum broadening to very high frequencies) in solids can be used to understand how the conductivity is influenced by lattice defects, grain boundaries and extended
imperfections [56-58]. At high temperatures, the electromagnetic radiation within the solid should also be considered. Thermal conductivity by mobile carriers (waves or particles) can be expressed in the general form [56]

\[ k = \frac{1}{3} C v l \]  

(1.1)

where \( C \) is their specific heat per unit volume, \( v \) is their speed and \( l \) their mean free path. If the heat carriers are the waves ranging over a spectrum of frequencies \( f \), the relationship can be expressed as follows [56],

\[ k = \frac{1}{3} \int_0^{f_m} C(f) v l(f) df \]  

(1.2)

where \( C(f) df \) is the contribution to the specific heat per unit volume from the waves in the frequency interval \( df \), \( v \) is the group velocity of the waves and \( l(f) \) their attenuation length, usually a function of frequency. Also \( f_m \) denotes an effective upper limit to the spectrum because either \( v \) or \( l \) become very small for \( f > f_m \).

In real solids lattice defects and grain boundaries are present. They cause energy exchange between lattice waves to obtain thermal equilibrium [57]. Intrinsic thermal conductivity of a solid is reduced by weak binding, large atomic masses and structural complexity. Lattice imperfections further reduce effective attenuation length. In this regard, point defects scatter as the fourth power of frequency whereas grain boundaries scatter independent of frequency. Thus, the overall phonon thermal conductivity \( (k_p) \) can be expressed as [56]
\[ k_{p} = k_{i} - \delta k_{B} - \delta k_{p} \]  

(1.3)

where \( k_{i} \) is intrinsic thermal conductivity \( \delta k_{B} \) and, \( \delta k_{p} \) are the reductions due to the boundaries and point defects. \( k_{i} = \frac{\Psi}{T} \) where \( \Psi \) is a constant and \( T \) is absolute temperature.

At high temperatures, a significant portion of heat is transferred by radiation (\( i.e. \) by phonons). However, radiation is effective only in a narrow window of frequency. Below the absorption edge frequency, \( f_{A} \), radiation is not transmitted. Similarly, above a very high frequency, \( f_{O} \), radiation is strongly scattered [59].

### 1.4.2 Thermal Conductivity Values of YSZ

Laser-flash technique has emerged as the most popular method for thermal diffusivity (and so, thermal conductivity) of TBC top-coat materials [60-62]. The thermal conductivity of fully dense 7YSZ material was measured \( \sim 2.3 \ \text{Wm}^{-1}\text{K}^{-1} \) at 1000 °C [59]. This relatively low value of conductivity was attributed to its high concentration of point defects (oxygen vacancies and substitutional solute atoms), which scatter heat-conducting phonons.

In a typical APS TBC, the orientation of the cracks and pores normal to the heat flow reduces the thermal conductivity of the top-coat to 0.8 to 1.7 Wm\(^{-1}\)K\(^{-1}\) [62-65]. Effect of thermal cycling on thermal conductivity of 22MgO–ZrO\(_{2}\) coating was measured during the first, second and third thermal cycle [66]. Figure 1.9 shows thermal conductivity for APS coatings of varying heat-treatment (thermal cycles) in the temperature range of 400-800 °C [66]. Thermal conductivity was found to increase for
all measurement temperatures (in the range of 200-1200 °C) with thermal cycling at a decreasing rate. Reduction of the crack-like micro-porosity and increase in inter-splat contact has been observed due to the densification processes, typically caused by sintering. Additionally, the absence of the characteristic $1/T$ dependence for zirconia ceramics was ascribed to the fact that they contain a very high concentration of point defects and that the defects cause phonon scattering [2].

The porosity and the cracks also help reduce the thermal conductivity of EB-PVD TBCs to 1.5-2 Wm$^{-1}$K$^{-1}$ from higher values of fully dense material [58, 67]. This reduction in thermal conductivity is lesser as compared to APS TBCs, because the channels are parallel to the direction of heat flow.

Effective thermal conductivity of the TBC top-coats has been expressed in terms of amount of porosity and morphology of the process by using various analytical and numerical models. McPherson [68] proposed a model for thermal conductivity of APS coatings based on analogy between electrical resistance of metallic contacts and the heat flux. Further improvements in the APS thermal conductivity modeling were proposed by Golosny and co-workers [69], who developed analytical (Two Flux Regions) and numerical (finite difference) models, with and without radiative components for APS coatings. A recent study demonstrates the effect of microstructural parameters on the thermal conductivity of EB-PVD coatings by using non-interacting approximations [34].
1.5  Mechanical Properties

In order to obtain accurate lifetime expectancies and performance of the coatings system; it is necessary to have a reliable understanding of the mechanical properties of various TBC components. Typically these include monotonic and cyclic constitutive relationships, strength, elastic modulus, metal-ceramic interface bond-strengths, fracture toughness and directionality of the materials under various testing conditions. This section summarizes some key work in the area.

1.5.1  Stress-Strain Relationship of a Free-Standing Ceramic Top-coat

1.5.1.1  Monotonic Loading

Elastic stress/strain relationship of the thermal barrier coating system, and particularly of the ceramic top-coat, is fundamental since the elasticity relates the thermal expansion in the thermal cycle to the thermal stresses. These thermal stresses induce driving force for cracking and spallation of the ceramic topcoat [2, 3, 20]. Rejda et al. [70] studied the inelastic constitutive behavior of free-standing 8YSZ material. Low carbon steel cylindrical shafts were sprayed and selectively etched out to obtain free standing specimens. The compressive strength of the specimen was measured to be about 500 MPa, while the tensile strength was found to be only 26 MPa. Because of the porosity and cracks in the top-coat, monotonic stress/strain behaviors of most of the TBC top-coats are non-linear and complex and, not completely understood. As-sprayed, compressive secant modulus of 7YSZ top-coat has been reported over the range of 10-50 GPa depending on the microstructure and testing method [71, 72]. The compressive
secant modulus values were found to be higher in in-plane direction (along the metal/ceramic interface) compared to the transverse direction [71]. Heat treatment at 1400 °C is found to increase the secant modulus from 50 GPa to 100 GPa in few hours [72]. This has been attributed to locking together of overlapping splats, via diffusion across inter-splat boundaries and healing of micro-cracks. In general, the modulus of the free standing coating was found to decrease with (i) increase in applied load and (ii) increase in porosity [73, 74].

The role of lamella size was found to have minimum effect on the compressive fracture properties of standalone plasma-sprayed alumina coatings [73]. It was concluded that this result was likely to be specific to compression loading, as the nucleation and propagation of cracks in plasma-sprayed materials was likely to be controlled by the submicron porosity that exists between lamellae and is independent of the lamella size.

1.5.1.2 Cyclic Loading/Unloading

Significant hysteresis between the loading and unloading portions of the curve was observed for free standing ceramic top-coats deposited using APS process [73, 75-77]. Figure 1.10 shows results for a 8YSZ specimen subjected to multiple loading-unloading cycles at 800 °C [77]. It can be seen that hysteresis still occurred after 50 cycles, but the loop width was considerably smaller as compared to the earlier cycles. This was believed to be caused by wear on the sliding surfaces in the microstructure, making it easier for sliding to occur and thus lowering the amount of energy dissipated through friction during a cycle.
1.5.2 Properties of Bond-Coat and TGO

The bond-coat material must be ductile enough to relieve tensile stresses developed in the TGO during heating part of thermal cycle at the topcoat/bond-coat interface. But too much ductility of the bond-coat will induce high compressive stresses in TGO increasing the stored elastic energy in it during cooling part of a thermal cycle [78]. Thus the optimum bond-coat material would be the one with intermediate ductility both at low and high temperature, and in this respect, MCrAlY coatings are superior than the aluminides, which tend to be highly brittle at low temperatures. In general, MCrAlY coatings have lower DBTT and higher ductility than the aluminides [79]. Typical room temperature elastic modulus values for MCrAlY bond-coat are found in the range of 190-215 GPa [80]. For the α-alumina TGO, reported room-temperature Young’s modulus values are in the range of 200-375 GPa [80, 81].

1.5.3 Fracture Toughness

Fracture toughness of top-coat is dependent on deposition approach and is strongly affected by mode-mixity. It is also a function of crack length. For short cracks the mode-I toughness can be quite low [20]. As the crack extends resistance curve behavior arises, particularly in mode-II, because of strong influence of crack face friction. For APS materials the mode-I toughness is reported in the range: \(0.1 \leq K_{TBC}^{I} \leq 10\) MPa.m\(^{-1/2}\) [65, 72]. For long cracks \((a \geq 1\text{mm})\) in mode-II, \(K_{TBC}^{II} = 2-5 \text{ MPa.m}^{-1/2}\) [68, 82].

Generally, fracture toughness of a TBC top-coat is found to be anisotropic. Wessel et al. [83] have determined the toughness values for free-standing YSZ specimens using a
miniaturized 4-point loading device. They found that the crack path and fracture toughness have a strong dependence on structure of plasma sprayed TBCs. Segmentation was observed to follow pre-existing intra-splat cracks but was frequently deflected by interlaminar cracks, whereas opposite was found to be true for delamination. Due to splat morphology, the deflection segments were significantly longer in the case of segmentation, resulting in more pronounced R-curve behavior based on wake of controlled crack bridging (the values varied between 0.2 and 1.4 MPa.m$^{1/2}$ with corresponding variation in crack length). On the other hand, a constant value of toughness ($\sim$ 1.5 MPa.m$^{1/2}$) was observed in delamination direction. Using the micro-indenter technique the fracture toughness of the TGO is determined to be $\sim$1 MPa.m$^{1/2}$ [81].

Broad toughness ranges have been sited for BC/ceramic interface. This variability arises due to interfacial contamination or segregants. Some previous work [20, 84] has shown typical APS top-coat/bond-coat interfacial toughness to be $\sim$10 J.m$^{-2}$ for mode-I type of loading conditions. Fracture toughness of the top-coat/bond-coat interface under mode-II type of loading conditions has also been determined for EB-PVD coatings by various techniques. The wedge impression test results showed it to be $\sim$60 J.m$^{-2}$ when measured by using wedge impression test [85] and, was $\sim$70 J.m$^{-2}$ when measured by using barb-test method [86]. No data on fracture toughness values of APS coatings under mode-II loading has been found.
1.6  Failure of Plasma-Sprayed TBCs

Thermo-mechanical loading and environmental deterioration during engine operations lead to failure of the spallation of the TBCs. EB-PVD and APS TBC systems fail under different failure modes depending on the engine operating environment [3]. For these reasons, TBC failure mechanisms are not very clear till date. In general, fracture responsible for failure takes place in or close to the interface between the top-coat and the bond-coat [3, 20, 87, 88]. Various specific sources contributing to generation of failure of plasma-sprayed TBCs have been identified previously and are summarized in the following paragraphs.

1.6.1  Factors Contributing Towards TBC Failure

1.6.1.1  Stresses Caused by Mismatch in Thermo-Physical Properties

Different constituents of a TBC system have different thermo-physical properties. Due to this mismatch, cooling from high temperatures (relatively stress-free state) to room temperatures results in very high stresses. For temperature difference of $\Delta T$, the misfit stresses in top-coat with elastic modulus $E_{TBC}$ are given by [89]

$$\sigma = E_{TBC} \Delta \alpha_{TBC} \Delta T / (1 - \nu_{TBC})$$

(1.4)

where $\nu_{TBC}$ is Poisson’s ratio of top-coat, and $\Delta \alpha_{TBC}$ is the difference in CTE values of 7 YSZ top-coat and bond-coat, which are $10 \times 10^{-6} \, ^oC^{-1}$ and $15.2 \times 10^{-6} \, ^oC^{-1}$, respectively [90].
In case of rapid changes in temperatures, transient stresses are built up due to a temperature gradient in the coating. This is more prominent for a thick zirconia layer, which experiences thermal shock conditions. After several cycles, stress induced propagation of cracks may result in ultimate spallation of top-coat [16].

1.6.1.2 Formation and Development of TGO

Although alumina scale is needed for substrate protection, its growth results in a constrained volume expansion that leads to compressive “growth” stresses (~0.5-1 GPa) that persist at all temperatures [91]. Upon cooling, the thermal-expansion mismatch between the TGO and the bond-coat leads to very high “thermal” compressive residual stresses in the TGO that reach a maximum (3 to 6 GPa) at ambient temperature [3]. The strain energy in the TGO scales linearly with the TGO thickness and quadratically with the TGO stress, and drives fracture [20]. A critical limit of around 10 µm has been set for aero gas turbine coating working at 1000 °C; this limit is decreased at higher working temperatures [16].

TBC failure analysis should also consider the surface roughness at the top-coat/bond-coat interface. EB-PVD processed TBCs have a flat surface which allows oxide growth without generation of any stress. Curved geometry, however, will induce out-of-plane (σ_{yy}) stresses. Plasma-sprayed TBCs will introduce oxide growth stress due to the corrugated interface. The non-flat interface in combination with micro-cracks will favor an irregular oxidation at the interface, which further accelerates the cracking
process. These micro-cracks eventually coalesce into buckling or spallation cracks [3, 20].

1.6.1.3 Degradation of the Top-Coat

Following are the major sources of top-coat degradation:

1.6.1.3.1 Sintering of the Top-Coat

At very high temperatures sintering of the ceramic microstructure occurs. The Young’s modulus increases, which gives rise to a less strain compliant coating. This phenomenon becomes apparent for plasma sprayed TBCs at 1200 °C and higher [72]. The increase in Young’s modulus is expected to have negative effect on the life of the TBC due to increased top-coat stresses.

1.6.1.3.2 Erosion of the Top-Coat

TBCs, mostly EB-PVD TBCs, can be eroded severely by sand particles from operating environments and from loose particles from the combustor liners. The impact of particles can cause significant damage in the form of horizontal cracks in the coating and subsequent removal of the fractured sections [16]. If the sand particles melt into the coating, it can react and penetrate the coating to degrade it [2].

1.6.1.3.3 Chemical Degradation of the Top-Coat

This type of degradation is related to poor fuel grades. In contact with corrosive species such as molten V$_2$O$_3$, Na$_2$SiF and Na$_2$SO$_3$ [92], the zirconia is destabilized. This means that the equilibrium phase tetragonal zirconia is formed, which is in turn
transformed into monoclinic zirconia upon cooling, causing detrimental volumetric stresses.

1.6.1.3.4 Interface Degradation due to Non-Alumina Oxide Formation

When Al concentration in the bond-coat falls below certain critical level; alumina is no longer the thermodynamically preferred phase and other oxides, notably spinels, form [93]. It has been shown that these Ni, Co and Cr rich oxide/spinels are formed in the vicinity of the TGO region [10, 13]. These spinels show poorer mechanical properties than alumina. Formation of these oxides is associated with an increase in volume that can be disruptive and possibly have lower fracture energies [2]. Thus, formation of non-alumina oxides is speculated to result in premature failure of the TBCs.

1.6.2 Stress Analysis and Fracture Mechanics

The stresses having greatest relevance to the coating delamination are those normal to the interface, $\sigma_{yy}$, as they prescribe the delamination energy release rate [20]. From numerical analysis of the TBC systems, the stresses above the bond-coat apex regions were found to be tensile while others were compressive (Figure 1.11A) during very early stages of thermal cycling by some researchers [94-96]. But with eventual thickening of TGO, the stresses in apex region become compressive and in the lobes of the asperity they become tensile (Figure 1.11B). The magnitude of the interface stresses increase as the system cycles because of the displacements caused by the thickening of the TGO [89]. With further increase in TGO thickness in the small region around the apex, the stress is compressive. Elsewhere, the TBC experiences a relatively uniform
tension. From parametric studies performed using finite element method (FEM), it has been found that higher stresses arise as the modulus of the TBC and the high temperature yield strength of the bond-coat increase [89].

The observed stress patterns have been linked to crack-propagation and fracture in the APS TBCs. The changes in stress with cycling have been related to an increase in the energy release rate for cracks that originate and grow within the tensile zone between peaks in the interface oscillations. But once these cracks enter compressive zones present above the bond-coat asperities, these will experience “slow growth”. After penetration through the islands of compression above the peaks, cracks are subject to a minimum in the energy release rate, $G_{\text{min}}$. Abrupt failure occurs when $G_{\text{min}}$ exceeds the fracture toughness of the TBC. Based on the results of numerical analysis it has been shown that the value of $G_{\text{min}}$ increases linearly with the number of thermal cycles and thus reaches the critical value to cause the abrupt failure of the TBC.

The SPPS TBCs fail in a manner similar to APS coatings. Thin SPPS coatings (250 µm thick) when subjected to thermal cycling, developed small cracks at metal/ceramic interface [52]. These cracks were observed to grow eventually. When the delamination zone was large enough, large scale buckling failure driven by stored strain energy in the coating was shown to occur [52]. Figure 1.12 shows low magnification image of such a buckled sample.
Figure 1.1: Cross-sectional image of an electron-beam physical-vapor deposited (EB-PVD) TBC showing the temperature reduction provided by the TBC, schematically [3]. The figure also shows photograph of a gas turbine engine blade.
**Figure 1.2:** Phase diagram of the ZrO$_2$ rich side of a Y$_2$O$_3$-ZrO$_2$ [24]

**Figure 1.3:** Schematic of the EB-PVD process. The part to be coated is rotated in the vapor coming from the ingot target [1].
Figure 1.4: Schematic of the air-plasma process [1]

Figure 1.5: Typical microstructure of APS coating showing (A) large pores from faulty splat stacking and, (B) inter-splat micro-cracking [77].
Figure 1.6: Schematic of SPPS process [41]

Figure 1.7: SEM micrograph of a SPPS coating. Through-thickness vertical cracks (shown by arrows) and uniformly distributed porosity can be observed from image. Higher magnification inset in the upper right-hand side corner shows lack of macro-splat boundaries [51].
Figure 1.8: (A) Schematic of division of plasma plume in three different temperature regions; (B), (C) and (D) and, (E) show micrographs of coating resulting from precursor from regions I, II and III, respectively [51].
Figure 1.9: Thermal conductivity of 8YSZ top-coat measured after first, second and third thermal cycle. [66]

Figure 1.10: Cyclic loading-unloading of a 8YSZ free-standing specimen at 800 °C [77]
Figure 1.11: Residual stress distribution in top-coat along the interface (A) without TGO at the interface and, (B) with TGO at the interface [94].

Figure 1.12: Micrograph showing bucking of a thin SPPS coating; (A) top-view, (B) cross-section [97]
CHAPTER 2

THICK TBCs: NEED AND OBJECTIVES

For the next generation of combustion engines used for aerospace/marine applications and in energy production, higher combustion temperatures (>1300 °C) are desirable. Increasing the thermal resistance of the TBC top-coat would facilitate increase of the inlet temperatures of the engines. This can be approached three ways [98]: (i) lowering the thermal conductivity of the coating material by compositional modification (e.g. increasing the point defect concentration of the top-coat ceramic); (ii) lowering the overall thermal conductivity by increasing the porosity of the coating and (iii) increasing the thickness of the coating. The first approach has been explored previously and choice of materials is limited by their mechanical properties and/or cost (section 1.4.2). Also, the amount of pore fraction in a top-coat is restricted by factors such as mechanical integrity and environmental protection abilities of the TBC. In this context, increasing top-coat thickness offers direct increase in the thermal resistance without affecting its mechanical properties.
2.1 Benefits of Using Thick TBCs

Current state-of-art plasma sprayed TBCs (top-coat thickness of 0.2-0.5 mm) permit a temperature of about 900-950 °C for the inner air-cooled combustion chamber walls. A simple 1-D heat transfer analysis performed under equilibrium conditions can demonstrate the use of thicker TBCs, effectively. Such an analysis has been carried out for typical gas turbine engine operating conditions given in literature [99].

Figure 2.1 shows the relationship between reductions in metal/ceramic interface temperatures and top-coat thicknesses for three different gas turbine operating temperatures. Evidently, thick (>1.5 mm thick) TBCs offer much more temperature reductions in comparison with current state-of-art TBCs (thickness <0.6 mm).

Benefits associated with application of a thicker top-coat are as follows: (i) it allows increase in operating temperatures for gas turbine engines, which ultimately helps to improve its efficiency and reduce the level of toxic waste; (ii) for the same operating temperatures, thicker top-coat allows less stringent cooling requirements compared to their thinner counterparts, which again results in increased efficiency; (iii) due to higher thermal resistance, more reduction in the interface temperature is achieved by using thicker top-coats. This leads to reduced substrate-oxidation and creep of the bond-coat and superalloy-substrate and, thus results in improved component lifetime performance.

2.2 Applications of Thick TBCs

Static components, such as combustor walls, of a gas turbine engine can be effectively coated with thick TBCs. Additionally, fuel cost reductions are expected in
diesel engines resulted by the use of thick TBCs [100, 101]. A model has predicted that reduced heat rejection from cylinder would result cost reduction of 2% for a turbo-charged engine and 3% for a turbo-compound engine [100]. In these cases, the insulation of piston and cylinder head are typical projected applications of thick TBCs.

### 2.3 Limitations on Usage of the Thick TBCs

One of the major hurdles in the development and application of thick TBCs for engine components is their reduced lifetime due to spallation under typical gas-turbine engine operating conditions. This is caused by faster degradation of the thick TBC due to higher volume under stresses [70]. In addition to thermal expansion mismatch stresses, a thicker coating possesses higher internal stresses due to higher temperature gradients. Micro-cracks in APS coatings do not alleviate the mechanical and thermal stresses sufficiently, especially when the coating thickness is more than 750 µm [102]. Therefore, thick APS TBCs either spall during the deposition process or result in premature spallation during their thermal cycling [103, 104]. Although EB-PVD TBCs offer “strain-tolerant” microstructure compared to APS TBCs, the process is very expensive for deposition of ultra-thick TBCs.

In order to prevent premature spallation and improve the thermo-mechanical life of the thick TBCs, graded ceramic coatings have been suggested [105]. However, the approach is quite complex and costly. The graded TBCs face the major disadvantage from excessive oxidation of bond-coat material within top-cot layer. Formation of $\gamma$-Al$_2$O$_3$ and its subsequent conversion to $\alpha$-Al$_2$O$_3$ results in 8% volume decrease and
associated tensile residual stresses within graded layers [106]. In fact, careful fracture mechanics analysis has shown that graded interlayer does not necessarily lead to reduction in the stress intensity factor [107]. Additionally, the overall thermal conductivity of the top-coat is increased due to inclusion of higher thermal conductivity material in the graded layer.

Delamination cracks within ceramic layer can be arrested when segmentation is present and failure of coating is effectively delayed even when flaking of certain regions of coating takes place [102, 108]. Also through-thickness cracks in top-coat can result in lower elastic modulus of the coatings and less stress built-up in the top-coat/bond-coat interface regions [3]. In this context, the new SPPS method (described in section 1.3.2) provides a desired microstructure of the top-coat. Distributed porosity and through-thickness vertical cracks in the SPPS coatings provide required “strain-tolerance” [42, 52]. Although the SPPS process had been successfully used to deposit highly durable thin TBCs, its applications for the thick TBCs were not explored.

2.4 Objectives of the Undertaken Research

The main objective of the current work was to explore the SPPS process for the deposition of thick TBCs. Following tasks were set to study various aspects of the thick TBC development:

(i) To deposit thick TBCs using SPPS process

Due to aforementioned benefits associated with the SPPS process, it was proposed to deposit the ultra-thick (~4 mm thick) TBCs using this process. The microstructures
and performance of these TBCs was then to be studied and compared with its APS counterpart.

(ii) To determine the mechanical properties of the thick TBCs

In section 1.6 we saw how the mechanical properties of the top-coat play an important role in the durability of the TBC. To estimate the thick TBC durability and to understand its failure mechanisms it was proposed to study the compressive constitutive and indentation fracture toughness behaviors of the free-standing APS and SPPS coatings. Additionally, due to very high thicknesses of these coatings, it was expected that mode-II interfacial loading would involve in the coating delamination. Therefore, direct toughness measurement under mode-II loading was proposed to be studied for SPPS and APS TBCs using barb-pull test.

(iii) To elucidate failure mechanisms of the thick TBCs

It was expected that the failure mechanisms of the thick TBCs would be significantly different compared to their thinner counterparts. Therefore, detailed experimental investigation along with fracture mechanics analysis was proposed. The proposed experimental study included systematic characterization of interfacial damage and TGO growth as a function of thermal cycling.

(iv) To decrease thermal conductivity of the SPPS coatings by processing engineered top-coats

As pointed out earlier in section 1.4, thermal conductivity of the top-coat can be reduced by microstructural modification. In this regard, disk-shape porosity oriented in
the direction perpendicular to the heat-flux was expected to offer maximum resistance to its flow. Therefore, it was proposed to modify the SPPS process to obtain the desired TBC microstructures. The effects of the modified structure on the thermal conductivity were then to be studied by using analytical and numerical modeling.
Figure 2.1: Reductions in the bond-coat/top-coat interface temperature as a function of engine operating temperature. Note the effect of three different top-coat thicknesses on the temperature reductions.
CHAPTER 3

PROCESSING, MICROSTRUCTURES AND MECHANICAL PROPERTIES OF THICK TBCS

3.1 Introduction

As mentioned in Chapter 2, unique microstructural features and associated superior mechanical properties of the SPPS TBCs were thought to be suitable for the deposition of thick TBCs. However, this potential process was not explored for the deposition of TBCs of thickness >1 mm. Additionally, the mechanical properties of SPPS coatings have not been characterized in any detail as yet.

In this study we demonstrate, for the first time, the feasibility of depositing well-adherent 7YSZ TBCs of thickness ~4 mm on bond-coated superalloy substrates using the SPPS method. Microstructural features of these thick SPPS TBCs are characterized and compared to the APS TBCs of the same thickness. The large thickness of the SPPS coatings also allowed us to characterize the mechanical properties of the ceramic top-coat in some detail. To that end, we have characterized and compared the indentation-toughness and uniaxial-compression properties of the SPPS TBCs, along with the
reference APS TBCs. Additionally, direct measurements of interfacial fracture toughness of SPPS and APS TBCs under mode-II type of loading have been performed using barb-test method. We have also determined the thermal-cycling durability performance of these ultra-thick TBCs.

3.2 Experimental

3.2.1 Coatings Preparation

We will now look into the details of materials and methods used to fabricate APS and SPPS coatings in this study.

3.2.1.1 Substrate Materials

Two different types of substrate materials, austenitic stainless steel (AISI 304 steel) and bond-coated, polycrystalline Ni-base superalloy were used for the experiments in this dissertation. Bond-coated superalloy substrates were provided by industrial partners. Bond-coat material used was air plasma-sprayed Ni20Cr10Al11Y alloy. Substrate geometries and dimensions will be discussed later in context of specific experiments.
3.2.1.2 Top-Coat Materials

3.2.1.2.1 Solution Precursor

The precursor used here is an aqueous solution containing zirconium and yttrium salts, to obtain a solid solution of 93 wt.% ZrO$_2$ and 7 wt.% Y$_2$O$_3$ in the SPPS coatings. The precursor was provided by Inframat Corp. (Farmington, CT).

3.2.1.2.2 Powder

The APS coatings were deposited using (ZrO$_2$-7 wt.% Y$_2$O$_3$) powder (Metco 204NS, 104 mesh).

3.2.1.3 Substrate Surface Preparation and Characterization

One of the surfaces of stainless steel substrate was roughened by grit blasting with 30-35 mesh alumina grit followed by cleaning using acetone and deionized water. As mentioned in Chapter 1, the substrate surface roughness is a critical parameter for coating performance. Therefore, the bond-coat surface roughness and surface features have been carefully examined using the scanning white-light interferometer (Zygo, NewView 5000) and the scanning electron microscope (ESEM 2020, Philips Electron Optics, Eindhoven, The Netherlands; DSM 982, Zeiss DSM, Göttingen, Germany) before the thermal spraying.

3.2.1.4 Processing

The SPPS and APS coatings were deposited using the direct current (dc) 9MB plasma torch (Sulzer Metco, Westbury, NY), which was attached to a 6-axis robotic arm.
Cleaned substrates were preheated by using heat of plasma (preheating temperature \(\sim 200\ \degree C\)). The preheating temperature is achieved by twenty “dry” passes of plasma gun. In SPPS process, precursor is injected into plasma jet (Figure 1.6). Specially designed equipment is used for liquid feed delivery. All specimens were deposited by Inframat Corp. (Farmington, CT).

For the present study, three different sets of APS and SPPS coatings were deposited and prepared. The brief description is as follows:

(i) For microstructural evaluation and thermal cycling

Bond-coated superalloy substrates (disks: diameter 25.4 mm, total thickness \(\sim 5.4\) mm, bond-coat layer thickness \(\sim 0.15\) mm) obtained from a commercial source were deposited with coating thickness of 4 mm.

(ii) For fracture toughness and compression testing

Grit-blasted, plasma-preheated stainless steel coupons, which were either disks (diameter 25.4 mm, thickness 4 mm) or plates (50×70×4 mm\(^3\)) deposited with coatings of thickness \(\sim 3.4\) mm. In order to obtain fully free-standing coatings, the as-sprayed SPPS and APS specimens were dipped in a 40% HNO\(_3\) solution for 2 hrs, where the acid selectively attacked the partially-attached metal/ceramic interfaces. The free-standing coatings were cleaned thoroughly and dried before further preparation. In order to study the effects of heat-treatment on the mechanical properties, some of the free-standing SPPS coatings were heat-treated at 1100 °C for 2 hrs in air using a box furnace (Thermolyne, Dubuque, IA).
(iii) For interfacial shear mechanical properties measurement

Figure 3.1A shows schematic of the barb test specimen. 304 stainless steel substrates were machined to the final size of (50×6×3 mm³) with a hole of diameter 3.2 mm as shown in the schematic. The substrates were partly coated with Ni4.5Al powder (Metco 450NS) using the APS process. The final thickness of the NiAl bond-coat layer was ~12 µm. A layer of top-coat of 250-300 µm thickness was deposited on the bond-coat layer using either SPPS or APS process.

Only one surface (circular or rectangular) of each specimen was coated. It should also be noted that most of the >3 mm thick APS coatings were found to be detached partially from the substrates during deposition.

The densities of the free-standing SPPS and APS coatings were measured using the Archimedes principle, with deionized water as the immersion medium.

3.2.2 Thermal Cycling

Thermal cycling testing of the 4 mm thick APS and SPPS TBCs on bond-coated superalloy substrates was carried out using an automated thermal cycling furnace (CM Inc., Bloomfield, N.J.). The thermal cycle consisted of a 5-minute heat-up from room temperature to 1121 °C, a 45-minute hold at that temperature, followed by a 10-min forced-air quench to room temperature. A sample was considered to have failed when the coating was completely detached from the substrate. A total of 4 SPPS TBC specimens were tested. Only one reference 4 mm thickness APS TBC specimen could be tested because most APS coatings were found to be partially detached from the substrate.
during deposition. Partial detachment of thick APS TBCs during deposition has been observed by others (see e.g. [17]).

3.2.3 Mechanical Testing

3.2.3.1 Fracture Toughness Measurements

Cross-sections of the SPPS and the APS coatings were polished to a 1 µm finish using routine ceramics polishing techniques. These polished cross-sections were indented using Vickers diamond pyramid with a contact load \(P\) of 49 N (5 indentations per material). Care was taken to align the diagonals of the square Vickers impression as shown in Figure 3.2. Radial cracks, emanating from the indentation corners, running parallel to the deposition surface are referred to as “in-plane,” while those perpendicular to that surface are referred to as “out-of-plane.” The sizes of the hardness impressions \(a\) and sizes of the in-plane and out-of-plane cracks \(c\) were measured using a scanning electron microscope or SEM (ESEM 2020, Philips Electron Optics, The Netherlands). The hardness \(H\) was determined using the equation: \(H = P/2a^2\) [109]. The formulation due to Lawn and co-workers [109] was used to determine the in-plane and the out-of-plane toughness values: \(K_{IC} = 0.016(E/H)^{0.5}Pc^{-1.5}\). The elastic-modulus \(E\) was measured using uniaxial compression testing.

3.2.3.2 Compression Testing

The free-standing SPPS and APS coatings were carefully diced into cubes (3.3 mm\(^3\)) using a precision saw (Isomet 1000, Buehler, Lake Bluff, IL) equipped with
diamond wafering blade, and all surfaces were polished to a 1 μm finish. The cube specimens were then tested in uniaxial compression using a screw-driven mechanical testing machine (Model 5869, Instron Corp., Canton, MA), in two different orientations — in-plane and out-of-plane — as shown schematically in Figure 3.3B. For compression testing, the cube specimens were sandwiched between two highly polished tungsten carbide platens (Figure 3.3A). Full articulation of the platens, and appropriate positioning fixtures assured alignment of the specimens with the loading axis. The load was measured using a calibrated load cell, and the platen displacement was measured using precision extensometers mounted between the platens. The contact between the specimen and the platens was lubricated with grease. The specimens were tested either in load control (20 N.s⁻¹) mode or displacement control (0.001 mm.s⁻¹) mode.

Three types of uniaxial-compression tests were conducted. In the first type of test, the specimens were loaded in displacement-control until failure occurred. This test allowed us to evaluate the compressive elastic moduli and the average ultimate compression strengths of the SPPS and the APS coatings. At least 4 specimens were tested per material and orientation. In the second type of test, the specimens were loaded in load-control up to a peak load of 300 N, and they were fully unloaded, which constituted the first cycle. The same specimens were then subjected to a second cycle and a third cycle where the peak loads were 600 N and 1000 N, respectively. The latter tests allowed us to study the mechanical hysteresis in the SPPS and the APS coatings. Finally, the effects of constant-stress-amplitude cycling were also investigated. The
SPPS specimens were compressively loaded in the in-plane direction up to a peak load of 2000 N and then were fully unloaded. The cycle was repeated 10 times.

3.2.3.3 Barb-Pull Test

Purpose of the barb-pull test is to measure mode-II fracture toughness of a coating. Barb test specimens deposited by APS and SPPS processes as described in section 3.2.1.4 were milled (Lagun FTV-2SE vertical milling machine) and polished using SiC paper (grit 1000) to obtain final dimensions of top-coat as shown in Figure 3.1A. Sides of the specimen were also carefully polished to remove excess deposits. Finally non-coated sides of two such substrates were glued to each other by using an epoxy adhesive to obtain a barb specimen. Four APS and two SPPS specimens were tested.

Figure 3.1B shows schematic of barb-test fixture. This fixture was slightly modified than that used by Kagawa et al. [86]. Hydraulic testing machine (Model 1322, Instron Corp., Dayton, OH) was used to apply tensile loads. While the bottom part of the test fixture was rigidly attached to the machine, the upper part was attached through universal joint to ensure alignment during testing. Knife edges, made of high speed tool steel, were adjusted to brush against the bond-coat surface of the specimen. They were then locked by clamps provided in the bottom part of the test fixture. This ensures proper contact with specimen surface throughout the test. Tensile loads were then applied in displacement controlled manner. The displacement rate was ~0.0016 mm.s⁻¹. Ceramic coating part of the specimen was projected to bear applied load over its entire cross-
section uniformly. The load vs. displacement curve was then recorded for each of the specimens.

3.2.4 Characterization

Cross-sections of as-sprayed and thermally-cycled specimens were obtained by cutting them with a low speed diamond saw (Buehler Isomet-1000). Thermally cycled and spalled TBC specimens were epoxy mounted prior to sectioning, in order to avoid artifacts at the failure locations. Sectioned samples were again mounted in epoxy to obtain specimens of cylindrical geometry. Mounted specimens were polished using SiC polishing papers (grit 60, 320, 800, 1000 and 1200, in that order). Subsequently the samples were subjected to abrasive polishing (diamond spray with 9, 6, 3 and 1 µm, in that order). The load used for semi-automatic polishing was 5 lbs with wheel speed of 100-200 rpm.

Low magnification (up to 800X) microstructural features of specimens were revealed by using an optical microscope (Olympus-PME3, Center Valley, PA). Environmental scanning electron microscope (Philips XL 30 ESEM) was used to obtain higher magnification microstructural imaging and elemental analysis. The ESEM was equipped with field emission electron source and energy dispersive spectrometer (EDS). Specimens characterized using ESEM observations were coated with very thin layer of Au-Pd or carbon to increase the electrical conductivity of the surface.
3.3 Results and Discussion

3.3.1 Substrate Roughness

Substrates with relatively high bond-coat surface roughness were selected in this study (Table 3.1). This was prompted by the requirement of good adhesion of top-coat to substrates in thick TBCs. Figure 3.4 shows typical surface profile of the bond-coat chosen for this study.

3.3.2 Microstructures

Figure 3.5A shows cross-sectional SEM micrographs of a thick SPPS coating at low and high magnifications, respectively. These thick SPPS coatings are characterized by branched vertical cracks; this is in contrast with thin SPPS coatings (250-300 μm), where unbranched vertical cracks are observed [43, 110, 111]. The vertical cracks are a representation of separated columns running perpendicular to the substrate/coating interface. The separated vertical columns appear as “mudflat” pattern from the top, as seen in the top-view optical micrograph in Figure 3.6. As the coating becomes thicker, columns with larger diameters become more stable, which manifests itself as branched vertical cracks in the cross-section view.

The higher magnification SEM micrograph of SPPS coating cross-section (Figure 3.5A) shows a lack of horizontal “splat” boundaries/cracks. Such horizontal “splat” boundaries/cracks are always present in APS coatings, as seen in the cross-sectional SEM micrograph of the free-standing APS coating (Figure 3.5B), and they can be up to 100 μm long. Long vertical cracks were not present in the APS coatings.
The densities of the SPPS and the APS coatings were determined to be 4.73 Mg.m\(^{-3}\) and 5.16 Mg.m\(^{-3}\), respectively. Assuming that fully-dense 7YSZ has a density of 6.07 Mg.m\(^{-3}\), the porosity in the SPPS coating is \(\sim 22\%\), and that in APS coating is \(\sim 15\%\). It is important to note that the porosity of the SPPS coatings can be tailored between 5% to 40% by adjusting the processing conditions. Figure 3.5A shows that the porosity in the SPPS coating is isotropic and randomly distributed. In contrast, the pores in the APS coating (Figure 3.5B) are sheet-like and aligned along the substrate/coating interface.

The microstructures of APS ceramic coatings have been studied extensively, and the mechanisms by which they arise have been documented in the literature [44, 45]. In the case of SPPS coatings, an understanding of their deposition mechanisms is beginning to emerge [43, 110-112]. It has been shown that the SPPS coatings form by fundamentally different mechanisms relative to the APS coatings, which result in the isotropic porosity and the lack of “splat” boundaries/cracks in the SPPS coatings. It has also been shown that the formation of the vertical cracks in SPPS coatings is due to a combined effect of thermal-expansion-mismatch stresses and stresses arising from the pyrolysis of remnant precursor embedded within the coating during the deposition process [113].

### 3.3.3 Hardness and Fracture Toughness

Figure 3.7A and B show SEM micrographs of Vickers indentation sites in SPPS and APS coatings, respectively. At the same magnification, the hardness impression in the SPPS coating is seen to be smaller than the one in the APS coating. The average
hardness values of the SPPS and the APS coatings were determined to be 5.4 GPa (range 6.2-4.1 GPa) and 3.9 GPa (range 4 to 3.6 GPa), respectively. It is not clear why the hardness of the SPPS coatings is higher than that of the APS coating, despite the higher porosity in the SPPS coatings.

The in-plane crack in the SPPS coatings (Figure 3.7A) appears to be significantly shorter than that in the APS coating (Figure 3.7B). The in-plane crack in the APS coating appears to follow the “splat” boundaries (Figure 3.7C). This behavior is similar to what has been observed in other studies on crack-propagation in APS coatings using micro-mechanical testing devices (not indentation) [114]. The in-plane elastic moduli for SPPS and APS coatings estimated from the compression tests (section 3.3.4) were used in calculating the indentation-toughness values reported in Figure 3.8. It can be seen clearly that the in-plane indentation toughness of SPPS coatings in mode-I is over five times that of APS coatings. This is particularly important because the plane parallel to the metal/ceramic interface (in-plane) within the ceramic top-coat is the primary location of spallation failure in plasma-sprayed TBCs [65, 80]. The lower in-plane toughness in the APS coatings can be attributed to the presence of weak, long “splat” boundaries and cracks in that orientation. Although “splat” boundaries exist in SPPS coatings, they are 50 to 100 times smaller than those found in APS coatings [111]. This is due to the fundamentally different deposition mechanisms in SPPS that result in “ultra-fine splats” that are 1 to 5 µm in diameter, compared to the “splats” in APS coatings that are ~100 µm in diameter [111].
The in-plane and the out-of-plane cracks in the SPPS coating appear to be similar in length in Figure 3.7A. Thus, the toughness of the SPPS coating is isotropic within 30% (Figure 3.8). This is expected considering the random nature of the SPPS coating microstructure. In the case of the APS coatings, well-defined out-of-plane cracks could not be found, precluding estimation of the indentation toughness APS in the out-of-plane orientation. Out-of-plane cracks in APS are likely to be heavily bridged by the “splats” that run perpendicular to the cracks, resulting in crack arrest. Thus, the highly textured microstructures in APS coatings result in the extremely pronounced toughness anisotropy. Such anisotropy in the indentation toughness of APS ceramic coatings has been reported by others (see e.g. [115, 116]).

In a recent study, Choi et al. [117] measured the toughness, using conventional methods (single-edge V-notch beam SEVNB and double cantilever beam DCB), of free-standing 8YSZ APS coatings in the in-plane and out-of-plane orientations. They found that the toughness to be isotropic. This apparent discrepancy can be explained based on the rising $R$-curve behavior — initial increase in toughness with crack length followed by a toughness plateau [109] — observed in APS TBCs due to crack-bridging [114]. Generally, the indentation test samples the short-crack region of the $R$-curve, while the conventional toughness tests (DCB) sample the long-crack plateau region [109]. Due to the heterogeneous nature of the APS coatings, it appears that the $R$-curve for the cracks in the in-plane orientation rises slowly with the crack size, resulting in a low toughness value in the indentation test but a high plateau toughness. In contrast, the $R$-curve in the out-of-plane orientation is expected to rise steeply with crack size due to crack-bridging.
by “splats”, making it difficult to measure the short-crack toughness using indentation. Since micro-mechanisms of APS TBC failure are largely controlled by local, or short-crack, toughness [65, 80], the in-plane indentation toughness is the most relevant toughness in the context of TBC failure. Although the ultimate spallation-failure of APS TBCs is a long-crack phenomenon, it is the result of a complex link-up of multiple short-cracks [5, 6], which is quite different from the propagation of single, dominant long-cracks used in conventional toughness tests.

Since the Vickers indentation-toughness test involves large local deformations at the microstructural level, the in-plane elastic modulus is considered to be the most relevant in the toughness calculations [118].

### 3.3.4 Compression Behavior

Figure 3.9 shows typical compression stress-strain responses of SPPS and APS coatings tested in in-plane and out-of-plane orientations. The in-plane stress-strain curves for both materials are characterized by non-linear deformation behavior, followed by linear behavior prior to failure. The hysteresis observed in the stress-strain behavior at low stresses (Figure 3.10A and B; Table 3.2) further confirms the permanent deformation in the SPPS and the APS coatings during uniaxial compression. The hysteresis in both coatings is characterized by an increase in the secant elastic modulus with successive load/unload cycles (Table 3.2). The non-linear compression (uniaxial) behavior in APS coatings has been observed by others [117, 119-121], and it has been attributed to the sliding of microcracks in the coating. With increasing compressive stress, microcracks
close-up, resulting in elasticity, characterized by a linear stress-strain response. This is followed by the failure of the coating. In the case of the SPPS coatings, the non-linear response can be attributed to cracking and sliding at the pores, followed by compaction; this has also been observed by others in porous ceramics [74, 122]. The more pronounced deformation (strain) in the SPPS coating could be due to the higher porosity in the SPPS coating compared to the APS coating.

The in-plane ultimate compressive strengths and the elastic moduli for SPPS and APS coatings are reported in Table 3.3. The linear portions of the stress-strain curves were used to estimate the elastic moduli. The compressive strengths and the elastic moduli for the two coatings are observed to be comparable. This is probably because the high-stress behavior is dominated by the compacted material in both cases, where the microstructural differences are less likely to have an effect. The difference in the microstructures is manifested in the low-stress behavior, where more pronounced deformation is observed in the SPPS coating.

The compression stress-strain behavior for APS coatings in the two orientations is quite similar, with the ultimate compressive strength in the out-of-plane orientation being somewhat lower. In contrast, the SPPS coating is significantly more compliant and weaker in the out-of-plane orientation. This can be attributed to the vertical cracks in the SPPS coatings, which are likely to dominate the compression behavior at the macro scale — easy sliding and failure is likely to occur along these vertical cracks in the out-of-plane orientation.
Typical stress-strain behavior for the SPPS specimens subjected to constant-amplitude multiple-stress cycling in the in-plane orientation is shown in Figure 3.11. Total strain was found to be increasing with successive load/unload cycle. This is attributed to “looseness” of the structure of thick SPPS coating. However, due to subsequent compaction of the specimen, this increase in the total strain value was found to be decreasing during each successive loading cycle. The phenomenon of increase in total strain during each additional loading cycle of the same peak stress is absent for the APS coatings. Here each stress cycle has common point maxima for the stress/strain curves. For the SPPS specimens tested in the in-plane direction average values of secant modulus for the first and the tenth loading cycles have been found to be 10.5 GPa and 16 GPa, respectively.

Upon heat-treatment, the SPPS coatings become stiffer and stronger in both the in-plane and out-of-plane orientations (Table 3.3). This is most likely due to the heat-treatment-induced complete pyrolysis of the unpyrolyzed material that is ubiquitously present in the as-sprayed SPPS coatings [111].

Figure 3.5A shows that most parts of the macro-cracks in free-standing SPPS coatings are aligned along the out-of-plane loading direction. Under compressive applied loads in that direction, these cracks remain unclosed and grow along the loading direction. When the applied load value approaches materials ultimate strength, axial splitting occurs along these pre-existing cracks. Slicing of the specimens along the out-of-plane loading direction is a clear evidence of this mechanism (Figure 3.12A). On the other hand, failure of the specimens subjected to the in-plane loading direction was
characterized by shear faulting (Figure 3.12B). From experimental observations, it can be inferred that the proportion of through thickness cracks, which are inclined to the loading direction, play an important role in determining the failure mode. A possible explanation for shear faulting is similar to that observed for brittle failure of ice [123]. Here the pre-existing cracks inclined to loading direction can form a wing-crack pattern under the applied load, which ultimately join together to form debris of material along the 45° direction resulting in fracture.

For APS specimens loaded in the out-of-plane direction, shear faulting mechanism was found to be operative. Micro-porosities and micro-cracks along horizontal splat boundaries provide an easy path for failure propagation in the in-plane loading direction and thus axial splitting mechanism was observed for this case of loading. A further study of detailed microstructural changes including micro-crack initiation and propagation under applied load is necessary to enhance the understanding of failure mechanisms for plasma-sprayed coatings.

3.3.5 Interfacial Fracture Toughness under Mode-II Loading

Figure 3.13 shows typical load-displacement curves for APS and SPPS barb specimens subjected to the test. For the APS specimen, load increases with the displacement of the machine heads almost linearly. Maximum load ($P_{\text{max}}$) corresponds to load required to delaminate the coating from the substrate. Once the $P_{\text{max}}$ is reached; the load drops off suddenly but not to the zero value. This suggests that the coating is not completely separated from the substrate at that instant of time. Results for APS
specimens are similar to that of the EB-PVD specimens where these intermittent drops in the load values were correlated with incremental increase in the interfacial cracks [86].

For the SPPS specimen, it can be observed that load increases very rapidly with displacement (Figure 3.13). Once the load reaches its peak value; it drops suddenly to zero. From visual observations during the test, it appears that as soon as \( P_{\text{max}} \) is reached the coating delaminates instantaneously. This indicates that delamination-crack growth for the SPPS coatings is very rapid. Also the \( P_{\text{max}} \) value for SPPS specimens were found to be consistently lower that those for the APS specimens.

Based on formulation by Hutchinson et al. [86, 124], strain energy release rate of the top-coat/substrate interface is given by:

\[
G_i \approx \frac{P_{\text{max}}^2}{4} \left( \frac{1}{E_{\text{sub}}h_{\text{sub}}w_{\text{sub}}^3} + \frac{1}{E_{\text{tbc}}h_{\text{tbc}}w_{\text{tbc}}^3} \right)
\]  

(3.1)

\( E_{\text{tbc}} \) and \( E_{\text{sub}} \) values were taken from section 3.3.4. Room temperature Young’s modulus value of stainless steel (AISI 304) substrate was taken as 200 GPa. Measured values of top-coat and substrate thickness (\( h_{\text{tbc}} \) and \( h_{\text{sub}} \)) and, width (\( w_{\text{tbc}} \) and \( w_{\text{sub}} \)) were used in Equation 3.1. The equation is based on the assumptions that entire elastically stored energy in the specimen is utilized in creation of new surface due to crack formation and the applied load is in pure mode-II.

Figure 3.14 shows average critical strain energy release rate values (\( G_c \)) for APS and SPPS coatings along with scatter in the data. It is clear that the average \( G_c \) value and so the interfacial fracture toughness under mode-II loading of APS coatings is much higher than that of the SPPS coatings for given conditions. The average \( G_c \) value of
SPPS coatings is comparable to that of the EB-PVD coatings, which was reported to be 60-90 J.m\(^{-2}\) [86]. It should be noted that \(G_c\) values for EB-PVD TBCs were obtained in the presence of TGO. In current studies, no TGO was present at the interface.

Fracture occurs along the bond-coat/top-coat interface in both, APS and SPPS specimens (Figure 3.15). Fracture surface of the APS specimen shows frictional wear tracks present on the bond-coat side of the specimen. It appears that the wear tracks are caused by macroscopically large, hard splats in APS coating. This leads to higher frictional dissipation and thus higher effective “crack-shielding”. Previously, crack face friction along with the interface roughness has been found to increase apparent mode-II fracture toughness of bi-layer materials [125]. On the contrary, no such wear tracks were found to be present in SPPS specimens. Thus primary contribution to the mode-II fracture toughness of SPPS coatings appears to come from material separation.

### 3.3.6 Thermal Cycling

Figure 3.16 shows the relative thermal cycling lives of APS and SPPS TBCs. While the APS coatings of ~4 mm thickness spalled either spontaneously or prematurely (40 cycles), the average thermal cycling durability of SPPS TBCs of the same thickness was found to be 820 cycles. This dramatically improved durability in the SPPS TBCs is clearly evident from these results. This improved durability is correlated with unique microstructural features and associated mechanical properties of the SPPS TBCs and discussed in the Chapter 4.
### Table 3.1: Bond-coat surface roughness

<table>
<thead>
<tr>
<th>Sample Location #</th>
<th>PV (μm)</th>
<th>RMS(μm)</th>
<th>Ra(μm)</th>
<th>Size X (μm)</th>
<th>Size Y (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>103</td>
<td>17</td>
<td>13</td>
<td>0.72</td>
<td>0.54</td>
</tr>
<tr>
<td>2</td>
<td>102</td>
<td>14</td>
<td>11</td>
<td>0.72</td>
<td>0.54</td>
</tr>
<tr>
<td>3</td>
<td>94</td>
<td>14</td>
<td>11</td>
<td>0.72</td>
<td>0.54</td>
</tr>
<tr>
<td>AVG</td>
<td>100</td>
<td>15</td>
<td>12</td>
<td>0.72</td>
<td>0.54</td>
</tr>
</tbody>
</table>

### Table 3.2: Maximum stress and elastic modulus for repeated compressive loading/unloading of SPPS and APS coatings.

<table>
<thead>
<tr>
<th>Coating/Orientation</th>
<th>Cycle Number</th>
<th>Max. Stress (MPa)</th>
<th>Secant Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPPS/In-Plane</td>
<td>1</td>
<td>27</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>55</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>93</td>
<td>13.6</td>
</tr>
<tr>
<td>APS/In-Plane</td>
<td>1</td>
<td>32</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>68</td>
<td>13.4</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>110</td>
<td>17.3</td>
</tr>
</tbody>
</table>

**Table 3.2:** Maximum stress and elastic modulus for repeated compressive loading/unloading of SPPS and APS coatings.
<table>
<thead>
<tr>
<th>Coating</th>
<th>Orientation</th>
<th>Ave. El. Mod. (Range) GPa</th>
<th>Ave. Comp. St. (Range) MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPPS</td>
<td>In-Plane</td>
<td>49 (77-44)</td>
<td>540 (722-301)</td>
</tr>
<tr>
<td></td>
<td>Out-of-Plane</td>
<td>22 (30-9)</td>
<td>258 (306-190)</td>
</tr>
<tr>
<td>SPPS (Heat-Treated)</td>
<td>In-Plane</td>
<td>100 (122-71)</td>
<td>629 (697-504)</td>
</tr>
<tr>
<td></td>
<td>Out-of-Plane</td>
<td>67 (75-58)</td>
<td>368 (424-306)</td>
</tr>
<tr>
<td>APS</td>
<td>In-Plane</td>
<td>40 (47-35)</td>
<td>578 (648-423)</td>
</tr>
<tr>
<td></td>
<td>Out-of-Plane</td>
<td>38 (41-32)</td>
<td>476 (591-335)</td>
</tr>
</tbody>
</table>

**Table 3.3:** Elastic modulus and compressive strength of SPPS and APS coatings
Figure 3.1: Schematics of (A) a Barb-pull test specimen along with its dimensions and (B) the Barb-pull test set-up.
**Figure 3.2:** Schematic illustration showing in-plane and out-of-plane orientations for indentation test

**Figure 3.3:** Schematic illustration showing: (A) uniaxial compression test set-up; (B) in-plane and out-of-plane orientations for the uniaxial compression test
Figure 3.4: Typical surface profile of the bond-coat obtained by using optical interferometer
Figure 3.5: (A) Cross-sectional SEM micrograph of a SPPS coating at low and high magnifications. Arrow indicates a vertical crack in the high-magnification micrograph. (B) Cross-sectional SEM micrograph of APS coating showing “splat” boundaries (arrows)
**Figure 3.6:** Top-view optical micrograph of a SPPS coating showing the “mud-flat” pattern
Figure 3.7: SEM micrographs of Vickers indentation (49 N load) sites in: (A) SPPS coating and (B) APS coating. Arrows indicate in-plane and out-of-plane cracks. (C) High-magnification SEM micrograph showing the in-plane indentation crack following a “splat” boundary in the APS coating.
Figure 3.8: Indentation toughness of the SPPS and APS coatings. The histogram represents the average readings from 5 indentations, and the error bars represent the data range. The toughness in the out-of-plane orientation in the APS coating could not be estimated because well-defined cracks did not form in that coating.
Figure 3.9: Typical uniaxial-compression stress-strain curves for SPPS and APS coatings in in-plane and out-of-plane orientations.
Figure 3.10: Typical uniaxial-compression stress-strain curves during 3 cycles of loading-unloading with successively increasing loads: (A) SPPS coating and (B) APS coating. The loading and unloading parts of the curves are marked in (A).
Figure 3.11: Loading/unloading curves obtained during the first and the tenth cycle for a SPPS specimen. They have been offset for clarity.

Figure 3.12: Optical micrographs of: (A) fracture surface of a SPPS coating that has undergone vertical splitting under applied out-of-plane loading and; (B) shear faulting in a SPPS coating under in-plane compressive loading
**Figure 3.13:** Load-displacement curves for APS and SPPS specimens subjected to bar-pull test.

**Figure 3.14:** Strain energy release rate of the SPPS and APS coatings. The histogram represents the average values, and the error bars represent the data range.
Figure 3.15: SEM micrograph of the fracture surface of the bond-coat side exposed due to top-coat delamination for (A) SPPS Barb specimen shows fracture propagation along the bond-coat/top-coat interface with bond-coat surface profile visible; (B) APS Barb specimen shows presence of wear tracks are along the block arrow. The fracture in APS specimens also occurs along the top-coat/bond-coat interface.
Figure 3.16: Thermal cycling durability of APS and SPPS ultra-thick TBCs (~4 mm thickness) on bond-coated superalloy substrates. Only 1 APS TBC specimen could be tested. The SPPS histogram represents the average of 4 specimens, and the error bars represent the data range.
CHAPTER 4

FAILURE OF THICK PLASMA-SPRAYED TBCS: ANALYSIS AND CHARACTERIZATION

4.1 Introduction

In the previous chapter, the SPPS process has been shown to improve the thermal cyclic performance of ultra-thick (4 mm thick) TBCs, dramatically, compared to their APS coated counterparts. In this chapter, we have analyzed failures of the ultra-thick TBCs by using fracture mechanics principles. Based on the TBC failure mechanisms, improved thermal cyclic life of SPPS TBC has been justified.

On the fundamental level, the TGO developed at the interface of top-coat and substrate plays a major role in TBC failure [3, 126, 127]. While the formation of the TGO is unavoidable, the ideal bond-coat is engineered to ensure that the TGO forms as $\alpha$-Al$_2$O$_3$ due to its desired metallurgical and mechanical properties. However, experimental evidence has shown the presence of non-$\alpha$-Al$_2$O$_3$ oxides and spinels; also known as mixed oxides, at the TGO [11, 15, 65, 128, 129]. The mixed oxides grow at very high rates compared to the pure $\alpha$-Al$_2$O$_3$ and result in higher TGO thickness. This
can be attributed to their “non-protective nature” associated with very high porosity and higher ion transport rates compared to alumina. Also the mixed oxides form and grow very non-uniformly at the interface. This spatial variation in TGO growth rates across the bond coat surface will tend to develop out-of-plane tensile stresses in the vicinity of the TGO/top-coat interface [130]. Additionally, mechanical properties of these mixed oxides and mixed oxide/alumina are inferior to pure $\alpha$-Al$_2$O$_3$ TGO [3]. All these factors are expected to enhance TBC spallation. For these reasons formation of the mixed oxides is highly undesirable and referred to as the chemical failure of the TBC.

Therefore, adequate knowledge of TGO growth kinetics and phase distribution in TGO is necessary in order to understand TBC failure mechanisms. Although transmission electron microscopic (TEM) studies were performed on early stages of high-temperature-oxidation of bare bond-coat alloys and EB-PVD TBCs [131-134], TGO growth in plasma-sprayed TBCs remained relatively unexplored. Till date, no detailed characterization studies were available for the SPPS TBCs. Additionally, effects of long term thermal cycling on the TGO growth in plasma-sprayed TBCs, especially thick TBCs, were unknown.

In this context, interrupted thermal cycling experiments have been performed on 1.5 mm thick APS and SPPS coatings deposited on bond-coated superalloy substrates. Interface degradation along with TGO growth kinetics is studied from cross-sectional examination of these specimens. Detailed TEM studies of development and distribution of various TGO phases have been carried out for the APS and SPPS TBC specimens.
subjected to 1 and 140 thermal cycles. Based on the observations and previous studies, mechanisms of chemical failure of the TBC have been proposed.

4.2 Experimental

4.2.1 Processing

The SPPS and APS coatings were processed by the method described in section 3.2.1. Ten SPPS and 6 APS coatings of ~1.5 mm thickness were deposited on bond-coated superalloy substrate. The superalloy substrate specifications are given in section 3.2.1.1. All the coating deposition was carried out by Inframat Corporation (Farmington, CT).

4.2.2 Thermal Cycling

Thermal cycling tests of the APS and SPPS TBCs were carried out using an automated thermal cycling furnace (CM Inc., Bloomfield, NJ) as described in section 3.2.2. Three each of SPPS and APS TBC specimens were subjected to complete failure to determine thermal cyclic durability of the TBCs. The TBCs were also subjected to interrupted-thermal cycling to study their failure mechanisms. The SPPS TBC specimens were taken out of the thermal cycling furnace after 1, 10, 40, 140, 400 and 500 thermal cycles. The APS specimens were taken out of the furnace after 1 and 140 thermal cycles. One of the SPPS samples was also subjected to 105 hours of isothermal heating (equivalent to the peak hold temperature of 140 thermal cycles) at 1121 °C in order to make comparisons with thermally cycled specimen.
4.2.3 Characterization

Scintag XDS 2000 diffractometer (Cu-K$_\alpha$ radiation) x-ray diffractometer was used to identify phases present in top-coat and failed samples.

Cross-sections of coatings were cut and polished using routine metallographic techniques. The cross-sectional microstructures were observed in an optical microscope (Olympus-PME3, center Valley, PA) and a SEM (ESEM 2020, Philips Electron Optics, Eindhoven, The Netherlands; DSM 982, Zeiss DSM, Göttingen, Germany) equipped with energy dispersive x-ray spectroscopy (EDS). Specimens for TEM study were prepared by focused ion beam instrument (FIB), Strata DB235 (FEI Company, Hillsboro, OR). The samples were prepared according to the procedure described by Abolhassani et al. [135]. FEI Tecnai TF20 TEM/STEM equipped with X-twin objective lens pole-piece (spherical aberration coefficient Cs $\approx$1.3 mm), an atmospheric-thin-window energy dispersive x-ray spectroscopy system (EDS; EDAX, Mahwah, NJ), and an imaging filter (GIF 2000, Gatan Pleasanton, CA) with electron-energy-loss spectrometer (EELS, FEI Company, Hillsboro, OR) were used for the study. Simulation of diffraction patterns were produced using Stadelmann’s JEMS software package [136]. Quantitative image analysis was performed on the optical microscopic and SEM images (at least 25 micrographs per coating) using an image-analysis software (Clemex Vision, Clemex Technologies Inc., Longueil, Canada).
4.3 Fracture Mechanics Analysis of Thick TBC Failure

Elastically stored strain energy of a coating and the driving force for delamination (i.e. steady state strain energy release rate ($G_{ss}$)) increases with thickness of the coating. With the presence of free edges, where the coatings and the substrate ends at the same location, and sufficiently long interfacial crack is present, the steady state energy release rate can be given by [137]:

$$G_{ss} = \frac{\sigma_{TBC}^2 H_{TBC}}{2E_{TBC}}$$  \hspace{1cm} (4.1)

where $\sigma_{TBC}$ gives in-plane compressive stresses within TBC developed during cooling from high temperatures due to differences in coefficients of thermal expansion (CTE) of TBC ($\alpha_{TBC}$) and substrate ($\alpha_s$). $H_{TBC}$ denotes thickness and $E_{TBC}$ elastic modulus of the TBC. It should be noted that delamination is primarily driven by mode-II loading (shear) under such circumstances.

As pointed out previously in section 3.3.2, microstructure of a SPPS coating is dependent on its thickness. In order to capture the effect of top-coat microstructure on the residual stresses developed in a TBC precisely, microstructure-based numerical simulations using finite element analysis were carried out. Object oriented finite (OOF) element analysis is a relatively new finite-element based approach that combines data in the form of microstructures with fundamental material data (such as elastic modulus, thermal conductivity or CTE of the constitutive phases) as a basis for understanding behavior of complex materials [138]. Although the used version of OOF (a public
domain software [139]) is limited to two-dimensional microstructures, it has been used successfully in analyzing elastic modulus [140], thermal stresses [141, 142], thermal expansion [140], and thermal conductivities [143] of complex materials, including APS TBCs.

Optical and SEM micrographs of the APS and SPPS coatings were used as inputs for OOF. Figure 4.1A shows a typical micrograph of a thin APS coating used in the study. It was converted to a binary image containing ceramic phase and, porosity and “splat” boundary phase. Then, the images were mounted on a 5.4 mm thick substrate schematic to complete the TBC system for the simulation purpose (Figure 4.1B). This was followed by assigning intrinsic material properties to all the three TBC phases as given in Table 4.1. As the APS coatings did not show significant microstructural variation with thickness, only thin (0.2 mm thick) coatings were used to obtain simulated stresses. On the contrary, micrographs of coatings of three different thicknesses (0.2, 1.5 and 4 mm) were used for the stress simulation studies of the SPPS coatings. Thick SPPS coatings did not allow us to capture minuscule microstructural features while considering the entire TBC system. Therefore, the micrographs of SPPS coatings were converted into binary images in such a way that one phase was “material phase” consisting of ceramic material including internal porosity while the other phase consisted of branched vertical cracks (Figure 4.2). The elastic modulus value for the “material phase” was taken from the compression test experiments (section 3.3.4). The binary images were then meshed using an adaptive meshing procedure, which allowed the subdivision of the elements and movement of nodes to conform to the microstructure. This helps in minimizing the
energy functional parameter of the mesh, which can be further reduced by an “annealing” procedure at the conclusion of the meshing operation. After meshing the TBC micrographs effectively in OOF, pertinent boundary conditions were applied as explained by Hsueh and co-workers [90]. Finally, TBC system was equilibrated from its assumed stress-free temperature (1121 °C) under $\Delta T = -1100$ °C. Example of a meshed-micrograph along with the map of in-plane stress distribution for a thin APS coating is shown in Figure 4.1.

Results of the OOF analysis are summarized in Table 4.2. The 4 mm thick SPPS TBC top-coats developed very small residual stresses in the in-plane direction. This can be attributed to the “open” structure of these ultra-thick SPPS TBC top-coats resulted due to high-density branched vertical cracking (section 3.3.2). With the decrease in the thickness of SPPS TBCs, high-density branched vertical cracking becomes through-thickness cracks with reduced branching (compare Figure 4.3 with Figure 4.2). As expected, relatively higher in-plane residual stress is developed in the APS top-coat due to lack of “strain-tolerant” vertical cracks in it.

Using Equation (4.1), stress data from Table 4.1 and material parameters from Table 4.2, the calculated $G_{ss}$ values for APS and SPPS TBCs are plotted in Figure 4.4. It can be seen that due to higher in-plane stresses, $G_{ss}$ for APS coatings is much higher compared to the SPPS coatings of the same thicknesses. Also the $G_{ss}$ value for a 4 mm APS coating is higher than critical energy release rate under mode-II loading ($G_c$) (section 3.3.5). Thus delamination of an APS coating can be expected either in as-
sprayed conditions or during early thermal cycling. This confirms our experimental observation of low thermal cyclic life of the thick APS TBC.

From the barb-test measurements, the average $G_c$ value for as-sprayed SPPS coatings is $\sim 66 \, \text{J.m}^{-2}$ (section 3.3.5). Due to lack of sufficient mode-II energy release rate for a 4 mm thick SPPS TBC, crack propagation would occur under combined mode-I and mode-II loading conditions [144]. Tensile stresses normal to the interface required for mode-I type of loading are developed and modified as a function of thermal cycling and TGO growth in TBCs. Cross-section of 1.5 mm thick SPPS TBC subjected to 40 thermal cycles show that small regions of coating delaminate along the interface (Figure 4.5). The delaminations eventually grow with further thermal cycling to join with each other and complete spallation failure of the TBC occurs. However, due to very high mode-I fracture toughness of the SPPS TBCs (section 3.3.3), crack propagation is significantly delayed. Similar kind of failure phenomenon is expected for 4 mm thick SPPS TBCs. It should be noted that no single large-scale-delamination and associated buckling was observed for thick SPPS TBCs.

Due to primary role of mode-I type of loading in the failure of thick SPPS TBCs, the OOF analysis was also performed to study the effect of top-coat thickness on the out-of-plane interfacial stresses. For this purpose, schematics of TBC system with top-coat, TGO and bond-coat layers were used as the inputs for OOF (Figure 4.6). As it can be noticed, the interface oscillations were assumed to be a cosine wave function. Three different top-coat thickness values, 375 $\mu$m, 1125 $\mu$m and 2500 $\mu$m were used to simulate the thickness effect. Also the TGO thickness was varied systematically between 1-6 $\mu$m.
The TGO thickness was increased towards the bond-coat side assuming its inward growth. After following the procedure described earlier for OOF simulations, the microstructures were equilibrated under $\Delta T = -1100 \, ^\circ C$. However, as substrate is not included in the schematics used here, the distortion in the interface direction is assumed to be constrained by thermal strain of the substrate. This is a valid assumption because the substrate is thick and much stiffer than the composite of top-coat and bond-coat [90].

Effect of thermal cycling on the out-of-plane stresses ($\sigma_{yy}$) in the interface region was found very similar to previous studies as described in section 1.6.2. Figure 4.7 shows maximum $\sigma_{yy}$ stresses in the top-coat side at various interface regions, for different TGO and top-coat thicknesses. It can be seen that these stresses are almost independent of the top-coat thickness with and without the presence of the TGO. Thus contribution from mode-I type of loading to the crack propagation remains almost unchanged with increasing the top-coat thickness. This explains why thermal cyclic lives of thick SPPS TBCs are comparable to those of the thin TBCs studied in ref. [145].

A SEM image of the top side of substrate of a spalled, ultra-thick (4 mm thick) APS TBC is shown in Figure 4.8A. Only light phase (top-coat with porosity and cracks in it) can be observed. This indicates that failure in the 4 mm thick APS TBC occurs within the ceramic top-coat in the interfacial vicinity. On the contrary, for the SPPS coating failure path is seen to travel through both top-coat and TGO (Figure 4.8B). Both, light (top-coat) and dark (TGO) phases can be observed. This type of failure is similar to that of the thin SPPS and APS TBCs [89, 97, 146].
4.4 Results for Thermal Cycling of SPPS and APS TBCs

Figure 4.9 shows a comparison of thermal-cycling lives of SPPS TBCs and reference APS TBCs. The lifetime improvement by the use of 1.5 mm thick SPPS TBCs compared to the APS TBCs was insignificant.

4.4.1 Interrupted Thermal Cycling

We will now focus our attention to the microstructural development of the TGO and its chemical failure during thermal cycling of 1.5 mm thick APS and SPPS TBCs.

4.4.1.1 Interrupted Thermal Cycling of SPPS TBCs

Cross-sectional view of the as-sprayed coating shows good bonding between the top-coat and the bond-coat (Figure 4.10A). Also no oxide phase could be detected at the top-coat/bond-coat interface. SPPS specimen subjected to one thermal cycle cross-section shows presence of dark and grey phases of TGO (Figure 4.10B). Here the TGO layer appears to be non-uniform in thickness. With further thermal cycling thickness of both the TGO phases was observed to increase. Figure 4.10C-G show cross-sectional SEM images of SPPS TBC specimens subjected to 10, 40, 140, 400 and 735 thermal cycles, respectively. Fracture surface of a spalled TBC specimen (substrate side) was characterized using x-ray diffractometer. 7YSZ along with NiAl₂O₄, NiO, and α-Al₂O₃ were detected at the failure locations (Figure 4.11).

Combining the outcomes of the EDS spot analysis (not shown here) and x-ray diffraction patterns, the grey phase was identified to be a mixture of Ni and Cr-oxides
along with their spinels while the dark phase was identified as $\alpha$-Al$_2$O$_3$. For the samples thermally cycled for 400 cycles and more, a Y-rich phase was found in alumina columns.

Bond-coat layer of the specimens used in this study were deposited using APS process. Its microstructure, especially in surface/subsurface regions, is typically characterized by three main features: (i) bond-coat material with surface waviness (or roughness) and subsurface open porosity separating it from rest of the bond-coat (with effective diameter of 5-40 $\mu$m) referred to as “asperity regions” (shown by arrows in Figure 4.12A); (ii) surface splats/ small bond-coat regions (~1-5 $\mu$m thick) separated from remainder of the bond-coat by open porosity or thin alumina layer around them and referred to as “diffusionally isolated splats” (shown by arrows in Figure 4.12A); (iii) relatively plane bond-coat/top-coat interfaces other than “asperity regions” and “diffusionally-isolated splats” are referred to as “planar regions”. Typically, interface in the “planar regions” have almost complete access to remainder of the bond-coat due to the absence of continuous open-porosity and oxide inclusions. Regions of type (i) and (ii) together are referred to as “diffusion cells” as they are diffusionally isolated from the remainder of the bond-coat. Thin layer of alumina around the splats is a result of oxidation of metal during spraying operation.

Figure 4.13 shows the relationship between TGO thickness and thermal cycles for combined “asperity regions” and “diffusionally-isolated splats”. Figure 4.14 shows the similar relationship for “planar regions” of bond-coat/ top-coat interface. It can be observed that for combined “asperity regions” and “diffusionally-isolated splats” thickness of mixed-oxide scale and total TGO thickness are higher than those for the
“planar regions”. On the other hand, only $\alpha$-Al$_2$O$_3$ TGO thickness has been found to increase primarily with almost no change in mixed oxide scale thickness in “planar regions”. With having background of the TGO development on “macro-level”, we will now look into the finer details of various TGO phases and their distribution obtained by using TEM. The results are presented for the SPPS TBCs subjected to 1 and 140 thermal cycles.

4.4.1.1.1 SPPS Specimen Subjected to 1 Thermal Cycle

A low magnification high-angle annular dark field (HAADF) TEM image of cross-section of metal/ceramic interface of sample subjected to one thermal cycle is shown in Figure 4.15A. Based on contrast and morphology differences five different layers can be revealed in the micrograph. Figure 4.15B shows EDS elemental profiles corresponding to line A-B, drawn across the interface. We will now look into the details of these layers, individually.

Starting at ‘A’ along the line A-B, layer (layer #1) in the micrograph, identified as bond-coat layer, found to have grain size in the range of 0.5-2 µm. From EDS compositional analysis (Table 4.3), the aluminum in this region close to interface is seen to be depleted. The structure is expected to be similar to one described in previous studies on transient oxidation of NiCrAlY alloys at 1100 °C [132] and is not discussed here in further details.

Layer #2 next to layer #1 along the line A-B has unambiguously been determined as $\alpha$-Al$_2$O$_3$ layer with the aid of electron diffraction pattern (EDP) (Figure 4.16) and EDS
study (Figure 4.15B). The thickness of this irregularly thick layer is in the range of 0.1-0.5 µm. The size of the equiaxed alumina grains was 0.1-0.3 µm and in most of the areas only monolayer of alumina grains was observed. The average grain size in layer #1 is much bigger than the alumina grains and several orientation relationships (if any) could be found between layer #1 and layer #2. At very few locations, small pores and Ni-rich grains (grain-size <50 nm) associated with them were found. Additionally, grains of yttrium-aluminum garnet (Al₃Y₃O₁₂) were identified within the Al₂O₃ layer by using micro-diffraction patterns (Figure 4.17 and its inset). The garnet grain size was found to be 50-100 nm. The EDS standard-less analysis indicated that Al:Y element ratio was close to 2:1.2, which is very close to cation ratio in aluminum-yttrium garnet.

A coarse-grained layer (layer #3) of mixed oxides can be observed above the Al₂O₃ layer in Figure 4.15A. The thickness of this layer is ~ 0.2-0.5 µm. Pores were found to be uniformly spread in this layer with pore size varying between 0.05 and 0.5 µm. They were primarily found in intergranular regions and had equiaxed and tubular shapes.

ED together with EDS analysis demonstrated that the layer is primarily consisted of nickel aluminate spinel -NiAl₂O₄ having spinel (Fd₃m) crystal structure. However, fraction of Ni in the layer was found to increase in the direction away from alumina layer while fraction of Al was found to increase in the opposite direction (Figure 4.15B). Absence of a fixed chemical composition corresponding to the spinel stoichiometry can be contributed to presence of mixed oxides and spinels in the layer. This was confirmed by the presence of other Cr and Ni-rich phases in additional to the spinel phase.
One of the coarse \( \text{NiAl}_2\text{O}_4 \) grains together with corresponding selected area diffraction pattern (SADP) is shown in Figure 4.18. The lattice parameter determined from ED as \( a=0.82 \) nm. The lattice parameters of the \( \text{NiAl}_2\text{O}_4 \) compound is larger than from PDF#65-3102 (\( a=0.8046 \) nm). It is likely that \( \text{Al}^{+3} \) cation in the spinel might have been substituted by \( \text{Cr}^{+3} \) ions in this region. \( \text{NiO} \) is the second largest phase by area fraction in this layer. EELS maps of the region (Figure 4.19) revealed that the presence of the Ni-rich grains in this layer is predominantly in regions away from the \( \text{Al}_2\text{O}_3 \) layer. Almost all \( \text{NiO} \) grains (cubic, \( Fm\bar{3}m \) space group, \( a=0.4177 \) nm) were found to be surrounded by \( \text{NiAl}_2\text{O}_4 \) grains (Figure 4.20A). ED study (Figure 4.20B) shows the cube-on-cube orientation relationship between \( \text{NiO} \) and \( \text{NiAl}_2\text{O}_4 \) grains (\( [011]_{\text{NiO}} \parallel [011]_{\text{NiAl}_2\text{O}_4} \), \( [100]_{\text{NiO}} \parallel [100]_{\text{NiAl}_2\text{O}_4} \)). From this evidence conversion of \( \text{NiO} \) to \( \text{NiAl}_2\text{O}_4 \) can be surmised. Finally, it should be noted that the interface between layers #1 and #2 showed presence of some \( \gamma\)-\( \text{Al}_2\text{O}_3 \) grains adopting the spinel crystal structure (\( Fd\bar{3}m \) space group, \( a=0.7924 \) nm).

A thinner layer of fine grained mixed oxides with grain size \( \sim 0.05-0.1 \) \( \mu \)m (layer #4) was observed above the coarse \( \text{NiAl}_2\text{O}_4 \) phase layer (Figure 4.21). ED study together with EDS and EELS indicated that this layer primarily contained \( \text{NiAl}_2\text{O}_4 \) grains. Randomly spread few \( \text{NiO} \) and \( \text{Cr}_2\text{O}_3 \) grains were also identified. Due to small dimensions of grains mostly ring diffraction patterns were analyzed (Figure 4.21, inset). HAADF imaging together with EDS scan revealed small (<50 nm) spherical zirconia grains embedded in the layer (Figure 4.22).
In addition to $\gamma$-$\text{Al}_2\text{O}_3$, NiO and NiAl$_2$O$_4$, Cr-rich grains of two types were observed notably in layer #2 and layer #4. The first were Cr$_2$O$_3$ grains with $\sim$0.1 $\mu$m size having hexagonal ($R\overline{3}c$) structure with lattice parameters $a$=0.468 nm and $c$=1.28 nm (Figure 4.23A). The parameters are slightly (5%) smaller than these for the esckolaite ($a$=0.4958nm, $c$=1.3594 nm, see PDF #38-1479). EDS study showed the presence of 10 at.$\%$ Al in Cr$_2$O$_3$ grains which can substitute Cr$^{3+}$ ions and reduce the unit cell size. Second type of Cr-containing grains were those of chromium nickel spinel (NiCr$_2$O$_4$) with traces of Al, which adopted cubic structure ($Fd\overline{3}m$) with lattice parameters $a$=0.848 nm (Figure 4.23B). The size of unit cell has been found slightly larger than one determined by XRD (PDF #23-1271 $a$=0.8316 nm).

Finally, layer #5, the last layer along the line A-B, was found to be a primarily 7YSZ ceramic layer. Coarse YSZ grains with large open pores can be seen in the Figure 4.15A. ED study pointed that 7YSZ grains adopted tetragonal crystal structure with space group P4$_2$/nmc. The interface between layer #4 and layer #5 is not sharp. Figure 4.24 shows EELS map of this area. Ni-rich TGO grains were found to be penetrating the top-coat layer. The depth of penetration is limited to 1-1.5 $\mu$m. The Ni-rich phase was determined to be NiO from selected area electron diffraction (SAED) pattern (not shown here). As mentioned previously, globular grains of 7YSZ are also found to be present randomly in layer #4.
4.4.1.1.2  SPPS Specimen Subjected to 140 Thermal Cycles

Figure 4.25A shows a low magnification TEM image of sample subjected to 140 thermal cycles. Similar to the sample subjected to one thermal cycle, five distinct layers have been identified based on contrast and microstructural differences. Again, these five layers have been identified as bond-coat, alumina, coarse-mixed oxide/spinel, fine-mixed oxide/spinel, and 7YSZ top-coat, in that sequence. Typical EDS spot analysis results for these layers is given in Table 4.4. The bond-coat layer (layer #1) is found to have much smaller amount of Al (1-5 at.% compared to original ~ 20 at.% ) from the EDS data.

Layer next to the bond-coat is a layer of columnar grains of \( \alpha\)-Al\(_2\)O\(_3\) (layer #2) as determined by EDS and confirmed by ED pattern (Figure 4.25B). Its thickness was found to be 3.5-4 µm. Thickness of alumina is very uniform compared to the case of sample subjected to one thermal cycle. It was also found that alumina grains did not show any preferential growth direction. It appears that the orientation is decided by that of the bond-coat grain on which it grows. This can be observed from Figure 4.25A where different columns appear on different BC grains. The same image also shows that the interface between bond-coat and alumina layer is very intact. Further observations of the specimen revealed the presence of elongated porosity and a few Ni-rich regions (~9 at.% compared to 3-4 at.% in bulk grains) at the alumina grain boundaries (Figure 4.26). This amount is still much higher than the maximum solubility of Ni in \( \alpha\)-Al\(_2\)O\(_3\) (1 at.% ) [147] and is, possibly, due to non-equilibrium.
Next two layers (#3 and #4) have the same composition and different grain size distribution. Primarily, nickel-aluminate spinel (cubic, \(Fd\bar{3}m\)-space group) with grain size 0.05-0.2 \(\mu\text{m}\) was observed. The SAED of spinel grains (Figure 4.26) demonstrated that lattice parameter \(a = 0.82\ \text{nm}\). The Cr content in the grains determined by EDS was 6-7 at.\%. Negligible amount of Zr and Y (~1-2 at.\%) was in these grains. The spinel composition in the sample has been found to be more stable than that for the sample subjected to one thermal cycle: The changes of element concentration did not exceed 8 at.\%. The boundary between the two layers is artificial as the grain size is progressively decreasing towards top-coat side. Total thickness of the two layers is 1-1.5 \(\mu\text{m}\). The elongated pores have been found at the interface between the alumina and the spinel layer. Pore length was ~50-200 nm and thickness was in the range of 20-80 nm. No NiO has been identified near the pores or at the top of the spinel layer as it was found for the SPPS sample subjected to one thermal cycle. Small YSZ grains ~50 nm in size were embedded in the top part of the layer.

Finally, the topmost layer (layer #5) was primarily comprised of 7YSZ in the topcoat. At the interface, very fine 7YSZ grains were found to be surrounded by the matrix of Ni(Al,Cr)\(_2\)O\(_4\). Amount of ZrO\(_2\) in the layer was found to increase towards the top-coat side. The total thickness of zone of mixture of spinel and 7 YSZ was found ~1 \(\mu\text{m}\). Porosity, which is the characteristic of spinel and top-coat layers, was observed to be minimum in this zone. The top-coat was found to be pure tetragonal phase of 7YSZ.
4.4.1.3 **Damage Evolution Due to Thermal Cycling**

During early stages of thermal cycling, long cracks were seen to develop at the edges of the TBC specimen. They were formed at the interface inside the top-coat. Cracks in the regions away from the edges were primarily formed inside top-coat in the regions of concave bond-coat asperities (Figure 4.5). These in-plane cracks propagate and coalesce with thermal cycling. Development of crack pattern during thermal cycling has been shown in Figure 4.27. Lengths of cracks observed in various interface regions were measured on cross-sections of 6000-µm wide specimens. It can be observed that most of the cracking occurs inside the top-coat and through the TGO. Failed sample shows sudden increase in the proportion of TGO cracks suggesting that final failure is mostly dominated by crack propagation through the TGO.

4.4.1.2 **Interrupted Thermal Cycling of APS Coatings**

Formation, growth and distribution of various phases of TGO for APS coatings were found to be very similar to that of the SPPS coatings. Figure 4.28 shows the cross-sectional micrographs for 1.5 mm thick APS TBCs subjected to 1, 140 and 520 thermal cycles. Thicknesses of the dark and grey TGO layers at various thermal cycles are given in Figure 4.13 and Figure 4.14. Distribution of various TGO phases for the APS TBC specimen subjected to 1 thermal cycle is shown in Figure 4.29. It can be seen that the interface region is characterized by four distinct layers. The chemistry and morphology of these layers was found to be very similar to the interface layers of the SPPS TBC subjected to 1 thermal cycle described earlier.
4.4.2 Isothermal Heat-treatment of SPPS TBCs

The SPPS specimen subjected to 105-hr of isothermal heating at 1121 °C (equivalent to the peak temperature hold-time for 140 thermal cycles) showed thick mounds of non-\(\alpha\)-\(\text{Al}_2\text{O}_3\) oxides above alumina TGO as shown in Figure 4.10H. The mounds were always secluded from the remainder of the bond-coat by open porosity and were associated with “diffusionally isolated splats” of the bond-coat surface. In some cases, these mounds of mixed oxides were found to contain very high porosity. From the figure, it can also be noted that the layer of mounds did not follow the contour of the alumina TGO beneath it. This is contrary to the case “asperity regions” and “regular regions” where newly formed grey phase followed the contours of dark phase beneath it (e.g. refer to Figure 4.12A).

4.5 Discussion

Based on experimental evidence, numerical analysis (section 4.5.2.2) and relevant literature, following TGO growth mechanisms can be suggested for thick SPPS and APS TBCs subjected to thermal cycling at 1121 °C.

4.5.1 Early Oxidation

Very negligible amount of Al (with activity of Al, \(a_{\text{Al}}>10^{-17}\)) in the bond-coat is sufficient to form protective \(\alpha\)-\(\text{Al}_2\text{O}_3\) at the bond-coat/top-coat interface for the given temperature [15]. However, specimen subjected to only 1 thermal cycle showed presence of non-alumina oxides and spinel at the interface (Figure 4.15). This observation leads to the conclusion that kinetics of the oxidation dominates over the thermodynamics of the
thermodynamics of the process during the transient oxidation period. Rapid consumption of available oxygen and relatively small diffusion occurring in the bond-coat/top-coat interface region during first few minutes of high-temperature hold results into the formation of discontinuous spinel layer (NiAl$_2$O$_4$ and Ni(Cr,Al)$_2$O$_4$) along with islands of NiO and Cr$_2$O$_3$. This is very similar to the observations with bare NiCrAlY alloys subjected to high temperatures for a very short duration [131, 148]. As the high-temperature exposure continues, diffusion of Al towards the oxide/bond-coat interface becomes significant with time. Oxygen diffusion through mixed oxide layer results in selective oxidation of aluminum at the interface. Thus formation of alumina grains of $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ beneath spinel layer and mixed oxide layers starts to take place (Figure 4.16).

Formation of NiAl$_2$O$_4$ by solid state reaction between NiO and Al$_2$O$_3$ grains, adjacent to each other in the TGO, may also take place during transient oxidation period. Once the product phase (NiAl$_2$O$_4$) forms at the interface of reactant phases, with proper contact between phase boundaries, counterdiffusion of Al$^{3+}$ and Ni$^{2+}$ cations through the spinel is a well-known phenomenon [149-151]. Following reactions are expected to occur at 1121 °C [149]:

At spinel/alumina interface,

$$3\text{Ni}^{2+} + 4\text{Al}_2\text{O}_3 \rightarrow 3\text{NiAl}_2\text{O}_4 + 2\text{Al}^{3+}$$

Reaction 4.1

At spinel/NiO interface,

$$2\text{Al}^{3+} + 4\text{NiO} \rightarrow \text{NiAl}_2\text{O}_4 + 3\text{Ni}^{2+}$$

Reaction 4.2
In a specimen subjected to 1 thermal cycle, this reaction was observed to take place at multiple locations (Figure 4.20).

4.5.2 Oxidation During Later Stages

We will now look at the TGO growth occurring at later stages of thermal cycling. To understand the phenomenon better, we will discuss the oxidation behavior in different types of bond-coat/top-coat interface regions separately.

4.5.2.1 Planar Regions

In the “planar regions” of the bond-coat/top-coat interface, $\alpha$-Al$_2$O$_3$ appears to be the only oxide to grow beneath the mixed transient oxides once the steady state oxidation process is achieved. The spinel layer does not grow during continued thermal cycling and its thickness remains almost constant (~1.5 micron) till the TBC failure. Thus the $\alpha$-Al$_2$O$_3$ offers complete protection of the bond-coat and hinders outward diffusion of Ni and Cr effectively.

As observed earlier, initially nucleated Al$_2$O$_3$ grains have equiaxed shapes (Figure 4.16). This observation can be related to studies performed on other alloy systems developing alumina scales [152-154]. It has been proposed that during initial stages of oxidation, Al diffuses outwards at rapidly decreasing rate to form Al$_2$O$_3$. This is followed by recrystallization of the oxide at gas/scale interface resulting into equiaxed grains. The voids present at mixed oxide/alumina interface in the present study are thought to be a result of outward diffusion of cations from the substrate to the scale [155]. Further growth of alumina results in columnar grains. The columnar and coarse $\alpha$-Al$_2$O$_3$
grains in contact with bond-coat after relatively large thermal exposure (140 thermal cycles) and, very intact alumina/bond-coat interfaces (Figure 4.25) point toward the alumina growth by inward oxygen diffusion along grain boundaries [155]. However, some recent work has demonstrated that outward diffusion of Al along the $\alpha$-Al$_2$O$_3$ grain boundaries can partially contribute to the oxide growth [156]. Diffusion controlled growth of $\alpha$-Al$_2$O$_3$ is further demonstrated by its parabolic growth with parabolic growth constant $K_p=9-17\times10^{-17}$ m$^2$.s$^{-1}$ in “planar regions” (Figure 4.13). This value is very similar to that reported in literature [157].

4.5.2.2 Asperity Regions and Diffusionally-Isolated Splats

Contrary to the “planar regions”, thermal cycling resulted in thickening of mixed oxide layer above $\alpha$-Al$_2$O$_3$ layer for “asperity regions” and “diffusionally-isolated splats” of the bond-coat/top-coat interface (Figure 4.14). The experimental results of formation of NiO as the outermost layer in equilibrium with Ni-Cr aluminates and; Ni-Cr aluminates in equilibrium with $\alpha$-Al$_2$O$_3$ and Cr$_2$O$_3$ are shown to be thermodynamically feasible for the given bond-coat alloy composition [158]. Although diffusion of Ni and Cr through $\alpha$-Al$_2$O$_3$ has been proposed as a way to form spinel and Ni/Cr oxides above impervious $\alpha$-Al$_2$O$_3$ TGO [20], the diffusivity of Ni in $\alpha$-Al$_2$O$_3$ scales is reported to be a very small value in the temperature range concerned [151]. Therefore, discontinuities in $\alpha$-Al$_2$O$_3$ layer, in addition to the necessary thermodynamic conditions, are required to form mixed oxides above the $\alpha$-Al$_2$O$_3$ TGO.
For “asperity regions”, tensile stresses (both, $\sigma_{xx}$ and $\sigma_{yy}$) have been determined to be present in the TGO during first few thermal cycles (~10 cycles) [89]. As a result of this, through-thickness cracking of TGO can be expected [157, 159]. Figure 4.30 shows SEM micrograph of cross-section of a 1.5 mm thick SPPS specimen subjected to 40 thermal cycles. Through-thickness crack and corresponding Ni-rich mixed oxide (grey) phase passage (shown by an arrow) can be observed. Secondly, from the experimental observations, the “diffusively-isolated splats” never form continuous alumina layer around them (e.g. refer to Figure 4.10H). Thus, the requirement of discontinuous $\text{Al}_2\text{O}_3$ layer for the formation of mixed oxide above it is satisfied by different means for “asperity regions” and “diffusively-isolated splats”.

Under these circumstances, bare metal surface of bond-coat is exposed to oxygen at high temperatures. When enough Al supply for the formation of $\text{Al}_2\text{O}_3$ is not available at the interface, mixed oxides can form to heal the TGO. Typically, this occurs when concentration of Al in the center of metallic “asperity regions” and “diffusional splats” (jointly known as “diffusion cells”) falls below ~4-5 at.% [157] and is termed as chemical failure of the TBC. Feasibility of formation of such Al-depleted “diffusion cells” of different shapes and sizes can be verified by using numerical analysis done by using finite difference method (FDM).

4.5.2.2.1 Numerical Analysis

As mentioned earlier, “planar regions” of the bond-coat/top-coat interface form alumina according to the parabolic growth law (Figure 4.13). Al consumed to form
Al₂O₃ is taken away from the bond-coat cell. This necessitates Al flux to the interface due to reduction in its concentration at the interface. Equations based on balance of fluxes were used to obtain analytical solutions for interface Al concentrations and thus the time required for chemical failure of diffusion cells [159, 160]. However, value of the input parameters, such as diffusivity of Al ($D_{\text{Al}}$) and parabolic growth rate constant ($K_p$), used in the analytical solutions may change over a wide range depending on the original composition of the bond-coat and time.

In this context, a simple FDM model, which takes into account the changes in diffusivity and alumina growth rate, can be more realistic. Also the analytical models assume highly simplified geometries, such as rectangular “diffusion cell” with one dimensional flux, contrary to the experimental reality. One-dimensional and two-dimensional FDM, which can consider more complex geometries, offers more practical solutions. This model, which was originally proposed by Nesbitt and co-workers [130, 161] has been modified for the current case. Details of the model and analysis are given in Appendix A.

Now let us look at the case of a rectangular bond-coat “diffusion cell” from “diffusionally isolated region”. Figure A.1A in Appendix shows SEM image of a typical example of this type of bond-coat cell. A simplified schematic of such a cell can be represented as shown in Figure A.1A for the modeling purpose.

Figure 4.31 shows a graph of diffusion cell size versus number of thermal cycles at which the chemical failure may occur. For the cells of thickness less than 8 μm and length of 40 μm, chemical failure is seen to occur during the very first thermal cycle.
With further increase in cell size, chemical failure is predicted to be delayed. In this respect, thickness of the cell has more pronounced effect compared to the length of the cell. Similar calculations for cells of other shapes and sizes are presented in Appendix A.

The predictions of the model were verified using the experimental observations. “Diffusion cells” of various thicknesses of the SPPS TBCs subjected to 1 and 10 thermal cycles were verified for chemical failure. A cell was considered to have failed when the grey layer thickness around it was more than 1 μm thick. Figure 4.31 shows the predictions made for the case of rectangular cell and corresponding experimental evidence. The predictions seem to match the experimental data very well for the “diffusion cells” of thicknesses of up to 25 μm.

Chemical failure of a thin splat (thickness <5 μm) can also occur without thermal cycling. A SPPS specimen subjected to 105-hr heat-treatment at 1121 °C showed presence of mounds of Ni-rich mixed oxides present in some regions of interface but absence of growth of mixed oxides at most of the wavy interface asperity regions (Figure 4.10H). Thus mechanical failure of Al₂O₃ TGO induced by thermal-cycling is not essential for the formation of mixed oxides above the Al₂O₃ layer. However, it supplements the mixed oxide formation in the “asperity regions” as described earlier.

No matter what route it takes to cover alumina with Ni/ NiO, it slowly converts to NiAl₂O₄ spinel as given by Reaction 4.1. The amount of excessive mixed oxide in the “asperity regions” and at the “diffusionally isolated splats” compared to the “planar regions” can be obtained from Figure 4.13 and Figure 4.14. The results reveal that
growth rate of spinel is non-linear and is decreasing with time. This could be attributed to the reduced rate of Reaction 4.1 due to consumption of NiO during the reaction and increase in spinel layer thickness.

With further increase in thermal cycling time, some protection is offered to bond-coat material by mixed oxide and discontinuous alumina layer [162]. The α-Al₂O₃ layer in “asperity regions” becomes more and more dense and defect-(cracks and internal porosity) free with time. Although “diffusionally isolated splats” never form alumina layer around them, an impervious alumina layer can be formed on bond-coat surface beneath them. Additionally, yttrium-rich regions with peg-like shapes are developed along the boundaries of columnar alumina grains during later stages of the thermal cycling (>500 thermal cycles). It has been suggested that these pegs conduct oxygen rapidly along the alumina grain boundaries and also cause the cation transport inhibition in those regions [155]. With the excessive thermal cycling, mixed oxide formation could be expected to form beneath the α-Al₂O₃ TGO due to drop in Al amount below critical level [157]. This was not observed in the present study until the complete spallation of TBCs.

Meantime, NiO and NiAl₂O₄, which penetrates into top-coat porosities during early stages (Figure 4.24) would subsequently break-down the YSZ, and spheroidize YSZ particles resulting in mixed interface zones between top-coat and TGO (Figure 4.25).
### Table 4.1: Intrinsic properties of various TBC constituents [90]

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s modulus (E) GPa</th>
<th>Poisson’s ratio (ν)</th>
<th>CTE (α) (\times 10^{-6}/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dense 7YSZ top-coat</td>
<td>200</td>
<td>0.3</td>
<td>10</td>
</tr>
<tr>
<td>Vertical-crack-free SPPS top-coat</td>
<td>49</td>
<td>0.3</td>
<td>10</td>
</tr>
<tr>
<td>APS top-coat</td>
<td>40</td>
<td>0.3</td>
<td>10</td>
</tr>
<tr>
<td>Bond-coat</td>
<td>200</td>
<td>0.3</td>
<td>15.2</td>
</tr>
<tr>
<td>TGO</td>
<td>400</td>
<td>0.27</td>
<td>8</td>
</tr>
<tr>
<td>Superalloy substrate</td>
<td>213</td>
<td>0.25</td>
<td>14.5</td>
</tr>
</tbody>
</table>

### Table 4.2: Results of OOF analysis to obtain top-coat in-plane stresses due to cooling by 1100 °C

<table>
<thead>
<tr>
<th>TBC</th>
<th>Thickness (mm)</th>
<th>Average in-plane stress in top-coat (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPPS</td>
<td>0.2</td>
<td>-121</td>
</tr>
<tr>
<td>SPPS</td>
<td>1.5</td>
<td>-43</td>
</tr>
<tr>
<td>SPPS</td>
<td>4.0</td>
<td>-21</td>
</tr>
<tr>
<td>APS</td>
<td>0.2</td>
<td>-143</td>
</tr>
<tr>
<td>Interface region layer</td>
<td>Al (at.%)</td>
<td>Ni (at.%)</td>
</tr>
<tr>
<td>------------------------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>Bond-coat</td>
<td>6</td>
<td>69</td>
</tr>
<tr>
<td>Alumina</td>
<td>99.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Spinel/ mixed oxides</td>
<td>65</td>
<td>27</td>
</tr>
</tbody>
</table>

**Table 4.3:** EDS compositional analysis for the interface region of the SPPS specimen subjected to 1 thermal cycle

<table>
<thead>
<tr>
<th>Interface region layer</th>
<th>Al (at.%)</th>
<th>Ni (at.%)</th>
<th>Cr (at.%)</th>
<th>Y (at.%)</th>
<th>Zr (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond-coat</td>
<td>4.1</td>
<td>70</td>
<td>25</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Alumina</td>
<td>87</td>
<td>9.7</td>
<td>3.3</td>
<td>0.6</td>
<td>0</td>
</tr>
<tr>
<td>Spinel/ mixed oxides</td>
<td>54</td>
<td>36</td>
<td>6.8</td>
<td>0.9</td>
<td>2.3</td>
</tr>
</tbody>
</table>

**Table 4.4:** EDS compositional analysis for the interface region of the SPPS specimen subjected to 140 thermal cycles
Figure 4.1: (A) SEM micrograph of an APS coating. (B) binary image of Figure 4.1(A) indicating “splat” boundaries and porosity in white ceramic matrix. (C) OOF mesh of a small region of the APS micrograph. Finer mesh can be observed near the ceramic/pore boundary. (D) Thermal map of the top-coat showing in-plane stress distribution. Lighter areas indicate tensile regions while darker regions are compressive.
**Figure 4.2:** An optical micrograph of a 4-mm thick SPPS TBC (A) and its binary image identifying vertical cracks from remainder of the top-coat (B). Note that the light regions contain ceramic phase along with included porosity.

**Figure 4.3:** SEM micrograph of a thin SPPS TBC showing un-branched vertical cracks.
Figure 4.4: Variation in the steady-state strain energy release rate of SPPS and APS TBCs as a function of top-coat thickness. The average experimental critical strain energy release rates for SPPS and APS coatings are drawn by dashed and dotted lines, respectively.
Figure 4.5: A cross-sectional SEM image of a 1.5 mm-thick SPPS TBC subjected to 40 thermal cycles. Arrows indicate the areas where small delaminations have occurred. It can be noted that cracks are primarily present above the concave bond-coat asperities.

Figure 4.6: Interface of the schematic used for OOF analysis to observe the effect of top-coat thickness on TBC interface stresses.
Figure 4.7: The interfacial stresses in the top-coat as function of top-coat thickness and TGO presence. The TGO thickness used for the results shown here was 6 µm. The maximum values of the out-of-plane stresses in the concave and convex asperity are plotted.
Figure 4.8: Bond-coat surface of the failed (A) thick APS coating showing remnant top-coat (light phase) and porosity in it (dark phase) and; (B) thick SPPS coating showing remnant top-coat (light phase) and TGO (dark phase).

Figure 4.9: Thermal cycling durability of 1.5 mm thick APS and SPPS TBCs deposited on bond-coated superalloy substrates. The histograms represent the average of three specimens and the error bars represent the data range.
Figure 4.10: SEM micrographs showing the cross-sections of the interfaces of 1.5 mm thick SPPS TBCs subjected to: (A) 0, (B) 10, (C) 40, (D) 140, (E) 400, (F) 500 and, (G) 600 thermal cycles. Each of the images clearly shows substrate, top-coat and TGO. Figure (H) shows higher magnification image of a TGO/top-coat interface for a specimen subjected to isothermal heat-treatment at 1121 °C for 105 hrs.
Figure 4.11: XRD pattern of the bond-coat side of a 1.5 mm thick SPPS specimen subjected to complete failure

Figure 4.12: SEM cross-sectional images of the 1.5 mm thick SPPS specimen subjected to 10 thermal cycles show: (A) bond-coat asperity region (pointed by an arrow) and; (B) diffusively isolated “splat” of the bond-coat material (pointed by an arrow).
Figure 4.13: TGO thickness as a function of thermal cycling in combined “asperity regions” and “diffusionally-isolated splats” regions of the bond-coat/top-coat interface for APS and SPPS TBCs. Grey TGO is mixed oxide phase whereas the dark TGO is $\alpha$-alumina.
Figure 4.14: TGO thickness as a function of thermal cycling in “planer regions” and for “diffusionally-isolated splats” regions of the interface for APS and SPPS TBCs.
Figure 4.15: (A) A low-magnification dark-field TEM micrograph of the interface region of the SPPS specimen subjected to 1 thermal cycle. Based on image contrast, five different regions are numbered along the line A-B. (refer to text for details). (B) EDS scan shows relative amounts of different elements present along the line A-B in (A).
**Figure 4.16:** Higher magnification of TEM image of the bond-coat/alumina interface region shown in Figure 4.15(A). Insets shows diffraction patterns obtained from $\alpha$-$\text{Al}_2\text{O}_3$ grains.

**Figure 4.17:** A grain of aluminum-yttrium-garnet surrounded by $\text{Al}_2\text{O}_3$ grains in the SPPS TBC specimen subjected to 1 thermal cycle. The inset shows diffraction pattern for the garnet.
Figure 4.18: High magnification TEM image of coarse nickel-aluminate spinel at the interface region of the SPPS specimen subjected to 1 thermal cycle. The inset shows SAED pattern obtained from the indicated grain.
Figure 4.19: EELS maps obtained from the TEM specimen of the SPPS TBC subjected to 1 thermal cycle. Figures consist of: (A) DF TEM image, (B) Al map, (C) Ni map and, (D) Cr map in the coarse-grain spinel layer in the interface area. Arrow in (C) shows a NiO island identified besides pore in the coarse spinel layer.
Figure 4.20: Higher magnification TEM micrograph of the pore region in Figure 4.19(A) is shown in (A). NiO grains transforming to NiAl$_2$O$_4$ grains was observed by orientation relationship between two types of grains as shown in (B).

Figure 4.21: TEM micrograph of a layer of the fine grain nickel-aluminate-spinel in contact with coarse grain layer of the spinel. Inset shows ring diffraction pattern obtained from the circular area marked on the micrograph.
**Figure 4.22:** (A) TEM image showing the top-coat/fine spinel layer interface for the SPPS TBC subjected to 1 thermal cycle. Arrow indicates a 7YSZ particle embedded in the spinel layer. (B) EDS line-scan corresponding to line A-B in (A) shows presence of Zr.
Figure 4.23: (A) Bright field TEM image shows Cr$_2$O$_3$ and Cr$_2$Ni(Al)O$_4$ grains embedded in primarily nickel-aluminate-spinel grains. SAED pattern corresponding to (B) Cr$_2$O$_3$ grain and; (C) Cr$_2$Ni(Al)O$_4$ grain.
Figure 4.24: (A) TEM micrograph showing 7YSZ/fine-gained-spinel interface for the SPPS specimen subjected to 1 thermal cycle; EELS maps of this area are shown for (B) Zr, (C) Al, (D) Cr, (E) Ni, (F) combined Zr-Ni-Cr.
**Figure 4.25:** (A) The interface of 1.5 mm thick SPPS TBC subjected to 140 thermal cycles. Five different layers in the low-magnification TEM micrograph are marked. The figure also shows diffraction patterns corresponding to (B) alumina (layer #2) and (C) coarse nickel-aluminate spinel (layer #3).
**Figure 4.26:** BF TEM micrograph shows boundary between two columnar grains of $\alpha$-alumina. Arrow indicated the Ni-rich region at the grain boundary.

**Figure 4.27:** Crack lengths in bond-coat/top-coat interface regions for 1.5 mm thick SPPS TBCs as a function of thermal cycling. Total cross-section scanned in each case ~ 6000 µm.
Figure 4.28: SEM micrographs showing cross-section of the interface of 1.5 mm thick APS TBCs subjected to (A) 1, (B) 140 and, (C) 520 thermal cycles.
**Figure 4.29**: Low magnification TEM cross-sectional image of a 1.5 mm thick APS TBC subjected to 1 thermal cycle. Based on the phases present, the interface region is divided into four different layers.
Figure 4.30: Cross-sectional SEM image of the SPPS specimen subjected to 40 thermal cycles. Arrow indicates a passage of mixed oxides (grey phase) inside the dark TGO.

Figure 4.31: Effect of thickness of rectangular “diffusion cell” size on chemical failure life of TBC. The solid line represents FDM analysis results and the markers represent experimental evidence from SPPS TBCs subjected to 1 and 10 thermal cycles.
5.1 Introduction

The role of thermal conductivity of TBC top-coat materials is vital in heat transfer process and determines design and safe operation of TBCs. Although SPPS TBCs have been found to be highly durable in cyclic heating/cooling laboratory tests where thermal gradients were not involved, these have thermal conductivities higher than APS TBCs [110]. This provides the motivation for reducing the thermal conductivities of SPPS TBCs for use in the engine environment where steep thermal gradients across the TBC are desired.

In this context, we exploit the versatility of the SPPS process in depositing layered TBCs with engineered microstructures for reduced thermal conductivities. Here we have used the SPPS method to deposit 7YSZ TBCs with alternating layers of low and high porosities. The layered-SPPS TBCs have been found to have thermal conductivities
lower than those of both SPPS TBCs and APS TBCs of the same chemical composition. Analytical modeling and object-oriented finite element (OOF) package has been used to analyze microstructural effects on the thermal conductivities of the TBCs studied here. This is in an effort to support and guide microstructural design of low-thermal-conductivity TBCs.

5.2 Experimental

5.2.1 Specimen Fabrication

SPPS and APS coatings were deposited, using the same procedure described earlier in section 3.2.1 at Inframat Corp. (Farmington, CT). Additionally, by modifying certain processing parameters for the SPPS process a new type of coatings with alternate layers of low and high porosities were deposited. The substrates used here were grit-blasted, plasma-preheated (preheating temperature ~200 °C) 304 stainless steel disk substrates (diameter 25.4 mm, thickness 4 mm). The final coating thickness for all three types of coatings (APS, SPPS, and layered-SPPS) deposited here was 1.3 mm.

5.2.2 Characterization

Cross-sections of the three types of coatings were cut and polished to 1 μm final finish using routine metallographic techniques. The cross-sectional coating microstructures were observed in an optical microscope and a scanning electron microscope (SEM; Quanta, FEI, Hillsboro, OR). Quantitative image analysis was performed on the SEM images (at least 25 micrographs per coating) using a image-
analysis software (Clemex Vision, Clemex Technologies Inc., Longueuil, Canada) and stereological formulations [163].

5.2.3 Thermal Conductivity Measurement

Thermal conductivity measurements were performed using a method described in earlier studies [110, 164, 165]. Briefly, free-standing coatings of as-sprayed APS, SPPS, and layered-SPPS were obtained by dipping the specimens in a 40% HNO₃ solution for 2 hrs, where the acid selectively attacked the partially-attached metal/ceramic interfaces. These were then cut and ground into plates (8.8×8.8×1 mm³). Thermal diffusivity (κ) of each plate specimen was measured at various temperatures in the range 100 to 1000 °C during heating using the laser-flash technique (Thermaflash 2200, Holometrix, Bedford, MA) in Ar atmosphere. Prior to thermal diffusivity measurements, the front faces of each specimen were coated with thin layers of gold to prevent direct transmission of the laser beam through the translucent specimens. In addition to this, back faces of each specimen were coated with thin layer of carbon to prevent an infrared (IR) detector from viewing into the sample and thus not giving an accurate temperature rise curve for the rear surface. Appropriate corrections were made in the thermal diffusivity calculations to account for the presence of these layers. The precision of the thermal diffusivity measurements is ±5%. The specific heat capacities (c) as a function of temperature for 7YSZ was obtained from a previous study [110]. Densities (ρ) of the plate specimens were measured using the Archimedes principle, with deionized water as the immersion medium. The thermal conductivity (k) is given by: \( k = \kappa \rho c \).
5.3 Results and Discussion

5.3.1 Microstructures

Figure 5.1A and Figure 5.1B are SEM micrographs of the APS coating at low and high magnifications, respectively, showing splats, splat boundaries/cracks, vertical micro-cracks, and pores. These microstructures are similar to those described in the section 1.3.2. The density of the APS coating was found to be 5.16 Mg.m\(^{-3}\), or 0.15 volume-fraction porosity, assuming the density of fully dense 7YSZ to be 6.07 Mg.m\(^{-3}\).

Figure 5.2A and Figure 5.2B show SEM microstructures of the SPPS coating at low and high magnifications, respectively. Note the absence of large splats and splat boundaries/cracks that are always present in the APS coatings. The porosity in the SPPS coating appears to be distributed, but with a somewhat horizontal texture. The 1.3 mm thick SPPS coatings are also characterized by through-thickness vertical cracks (Figure 5.2).

Figure 5.3A, Figure 5.3B, and Figure 5.3C show microstructures of the layered-SPPS coating at low (optical), medium (SEM), and high (SEM) magnifications, respectively. The interleaved low- and high-porosity layers, and the through-thickness vertical cracks, are clearly visible in Figure 5.3A. Figure 5.3B and Figure 5.3C show that the pores within the high-porosity layers are not continuous. The dashed lines in Figure 5.3C mark the approximate locations of the high- and low-porosity layers, where the high-porosity layers contain elongated pores primarily, while the low-porosity layers contain mainly round pores.
For analytical modeling of microstructural effects on thermal conductivity, detailed image analysis of the SPPS coatings was performed with the following assumptions: (i) elongated pores are approximated by disks, with diameter \( d \) and thickness \( t \), and aspect ratio \( d/t > 1.25 \) and (ii) round pores of \( d/t < 1.25 \) are approximated by spheres. In the case of layered-SPPS coating the following assumptions are made: (i) high-porosity layers of thickness \( L_{\text{Disk}} \) contain only disk-shaped pores and (ii) low-porosity layers of thickness \( L_{\text{Sphere}} \) contain only spherical pores. All disk-shaped pores are assumed to be parallel to the substrate/coating interface and perpendicular to the heat flux. These assumptions, depicted schematically in Figure 5.4, are essential for striking a balance between simplifying the representation of complex microstructures for analytical modeling and capturing the key microstructural characteristics.

Table 5.1 summarizes the data from the detailed image analyses of the SPPS and layered-SPPS coatings.

The densities of the SPPS and the layered-SPPS coatings were measured to be 4.73 Mg.m\(^{-3}\) and 4.13 Mg.m\(^{-3}\), respectively. The corresponding porosity volume fractions of 0.22 and 0.32 for SPPS and layered-SPPS coatings, respectively, compare with those estimated from image analysis (\( \phi \) in Table 5.1).

### 5.3.2 Thermal Conductivity: Experimental Data

Figure 5.5 is a plot of thermal conductivity as a function of temperature for APS, SPPS, and layered-SPPS coatings. Thermal conductivity data for fully dense, hot-pressed 7YSZ from a previous study [164] are included in Figure 5.5 for comparison. Overall,
although the thermal conductivities in Figure 5.5 are seen to decrease with temperature, they are not a strong function of the temperature, which has been attributed to strong phonon scattering in zirconia ceramics [166-168].

The thermal conductivity values for the APS coating (0.8 to 1.0 W.m\(^{-1}\).K\(^{-1}\)) in Figure 5.5 compare with the data obtained by others on 7YSZ APS coatings [169-171]. The thermal conductivities of the SPPS coating (1.0 to 1.2 W.m\(^{-1}\).K\(^{-1}\)) are found to be higher than those of the APS coating. Note that the SPPS coating is thermally more resistive than TBCs fabricated using electron-beam physical vapor deposition (EB-PVD); thermal conductivities of 7YSZ EB-PVD coatings are in the range 1.5 to 2.0 W.m\(^{-1}\).K\(^{-1}\) (not shown here) [170-172]. In Figure 5.5 it can be seen clearly that the layered-SPPS coating is thermally more resistive (thermal conductivity 0.7 to 0.8 W.m\(^{-1}\).K\(^{-1}\)) than both the APS and the SPPS coatings in the temperature range studied.

5.3.3 Thermal Conductivity: Analytical Modeling

The porous coating can be treated as a composite of 7YSZ dielectric and air confined in the pore space. First consider the thermal conductivity contribution of the air in the pore space, \(k_{\text{Gas}}\), which is given by [173]:

\[
k_{\text{Gas}} = \frac{k_{\text{Gas}}^0}{1 + \frac{BT}{tP}}
\]

where \(k_{\text{Gas}}^0\) is the conductivity of air in open space, \(B\) is a constant, \(t\) is the thickness of the pore, \(T\) is the temperature, and \(P\) is the pressure. The largest contribution from pore-air conductivity is expected at the lowest temperature (100 °C), and for coating with the
thickest pores (average \( t \) for layered-SPPS is \( \sim 1.9 \) μm). Thus, using \( B=2.5\times10^{-5} \) Pa.m.K\(^{-1}\) and \( k^0_{\text{Gas}} \) values for air (ambient pressure) [174] the largest \( k_{\text{Gas}} \) is estimated to be 0.02 W.m.K\(^{-1}\) (Figure 5.6). This is negligible, and hence the contribution from pore-air conductivity is ignored in the ensuing calculations.

Second, consider the scattering of photons by pores in radiative conduction. The total radiative thermal conductivity, \( k_{\text{Rad}} \), of a porous dielectric is given by [175]:

\[
k_{\text{Rad}} \approx \frac{16}{3} n^2 \delta \sigma T^3
\]

where \( n \) is the refractive index (\( \sim 2.2 \) for 7YSZ [176]), \( \delta \) is the radiation penetration depth (\( \sim 10 \) μm for plasma-sprayed coatings [174]), and \( \sigma \) is the Stefan-Boltzmann constant. Figure 5.6 shows the plot of radiative thermal conductivity for a plasma-sprayed coating for the temperature range of 100-1000 °C. It can be seen that, at the highest measurement temperature (1000 °C) \( k_{\text{Rad}} \) is estimated to be 0.03 W.m.K\(^{-1}\), which is negligible. Thus, the photon scattering by pores is also ignored in the following calculations.

Finally, the pore sizes are orders-of-magnitude too large to scatter phonons in phonon thermal conductivity.

Thus, the reduced thermal conductivity of the coatings relative to the dense 7YSZ is solely due to the missing dielectric medium in the form of pores. This is described by the Maxwell equation for materials with spherical, non-interacting pores of volume-fraction porosity \( \phi_{\text{Sphere}} \) [177]:
Consider the SPPS coating which contains both spherical and disk-shaped pores. The combined effect of the two different types of porosities on the thermal conductivity SPPS is given by [180]:

\[
k_{SPPS} = \frac{1}{2} \left\{ f_4 \left( \frac{\phi_{\text{Disk}}}{1 - \phi_{\text{Sphere}}} \right) f_3(\phi_{\text{Sphere}}) + f_3 \left( \frac{\phi_{\text{Sphere}}}{1 - \phi_{\text{Disk}}} \right) f_4(\phi_{\text{Disk}}) \right\} k_{\text{Dense}}
\]  

(5.5)

where \( f_3 \) and \( f_4 \) are functions representing Equations. 5.3 and 5.4, respectively. Using Equations 5.3-5.5 and the microstructural data from Table 5.1, the calculated thermal conductivity of the SPPS coating is plotted in Figure 5.5. The calculated thermal conductivities are within 12.7% of the experimental values, and they are consistently lower than the experimental values. This could be due to various reasons, including (i) overestimation of the porosities in the coatings and (ii) assumption of all disk-shaped pores being aligned normal to the heat flux, which may not be strictly valid.
Consider the layered-SPPS coating, which contains alternating layers of spherical pores (low porosity) and disk-shaped pores (high porosity) (Figure 5.3 and Figure 5.4). Thus, the conductivity of the layered-SPPS coating is given by a series model equation:

\[
k_{\text{LayeredSPPS}} = \left( \frac{f_3(\phi_{\text{Sphere}})f_4(\phi_{\text{Disk}})(L_{\text{Sphere}} + L_{\text{Disk}})}{f_3(\phi_{\text{Sphere}})L_{\text{Disk}} + f_4(\phi_{\text{Disk}})L_{\text{Sphere}}} \right) k_{\text{Dense}} \quad (5.6)
\]

Using Equations 5.3, 5.4, and 5.6, and the microstructural data from Table 5.1, the calculated thermal conductivities of the layered-SPPS coating are also plotted in Figure 5.5. The agreement between the calculated and the experimental values is within 11.3%, which is better than that in the SPPS-coating case. Once again, the calculated values are consistently lower than the experimental values, which can be attributed also to the aforementioned reasons. Nevertheless, the agreement between the calculated and experimental thermal conductivities is noteworthy considering that there are no adjustable parameters in the Equations 5.3, 5.4, and 5.6.

Note that the vertical cracks in both SPPS and layered-SPPS coatings have a negligible effect on the thermal conductivity, as determined using the expression by Lu et al. (Equation 18a in Ref. [173]) and the data in Table 5.1.

The model described for the layered-SPPS coatings has been used to carry out parametric studies. It is assumed that layers of disk-shaped pores and spherical pores have equal thicknesses \((L_{\text{Disk}} = L_{\text{Sphere}})\).

Figure 5.7 shows the effect of varying aspect ratio on the normalized thermal conductivity \((k_N = k_{\text{Dense}}/k_{\text{LayeredSPPS}})\) of layered-SPPS coating for equal amount of
porosity fractions in two types of layers. It can be seen that effect of reduction in the 
thermal conductivity with increased aspect ratio becomes more prominent with increase 
in total porosity content of the material. The effect of total porosity and fraction of disk-
shaped porosity of the total porosity on the thermal conductivity of the layered-SPPS 
coatings has been shown in Figure 5.8. The map shows equal thermal conductivity lines 
at the aspect ratio \((d/t = 4)\) of disk-shaped pores equal to 4. As it can be observed from 
the figure, lower thermal conductivity regions are favored with increase in both the 
variables. Such maps drawn for different aspect ratios can serve as reference to design 
the microstructure of the layered-SPPS coatings for a desired thermal conductivity. 
Effect of aspect ratio on such a map can be superimposed as shown in the Figure 5.9. 
The effect has been shown for only one normalized thermal conductivity value \((k_N = 0.3)\) 
line for clarity purpose. It can be observed that the equal thermal conductivity line moves 
more and more towards the origin with increase in aspect ratio of the disk-shaped pores.

Thermal conductivity of the APS coating was not analyzed using the above 
models because the microstructural parameters for that coating could not be quantified 
adequately. Instead, the newly developed object-oriented finite element (OOF) method 
[138] was used to analyze the thermal conductivity of the APS coating. For comparison, 
the thermal conductivities of the SPPS and layered-SPPS coatings were also analyzed 
using OOF.

5.3.4 Thermal Conductivity: Object-Oriented Finite Element (OOF)

In this study the inputs for two-dimensional OOF were digitized SEM images of
the APS, SPPS, and layered-SPPS coatings. The microstructures were converted into binary images consisting of only two distinct phases — 7YSZ and pores (air) (Figure 5.10A). The 7YSZ phase was assigned dense-7YSZ thermal conductivity from Figure 5.5 for a given temperature, and the pore phase was assigned a diminishingly small thermal conductivity value at all temperatures.

As described earlier in section 4.3, the binary images were then meshed using an adaptive meshing procedure, which allowed the subdivision of the elements and movement of nodes to conform to the microstructure. A finer mesh is created at the 7YSZ/pore interfaces where higher temperature gradients are expected. A typical OOF mesh for the layered-SPPS coatings consisted of up to 220000 triangular elements for the 7YSZ phase, and up to 75000 elements for pores, depending on the complexity of specific microstructure. The top and the bottom of the meshed micrographs were assigned constant temperatures of $T_1$ and $T_2$, such that a thermal gradient of 10 °C ($T_1-T_2$) is set up across the meshed micrographs, in the direction of the expected heat flow in an actual TBC. The two vertical sides of the micrographs were kept adiabatic. OOF command files used for thermal conductivity determination are given in Appendix B. The resultant heat flux from the analysis was used to obtain the average thermal conductivity of the microstructure. Figure 5.10B shows an example of a microstructure (layered-SPPS) with superimposed thermal gradient.

The thermal conductivity results from the OOF analysis for the APS, the SPPS, and the layered-SPPS coatings are plotted in Figure 5.11. In the cases of the APS, SPPS, and layered-SPPS coatings the agreements between the experimental data and the OOF
results are within 7.5%, 6.2%, and 10.9%, respectively. These agreements are better than those obtained using analytical modeling, despite the fact that OOF is a two-dimensional model. This can be attributed to the fact that “real” microstructures are used as input in OOF, instead of the approximated, ideal microstructures used in the analytical modeling. This demonstrates the utility of OOF in capturing accurately the effect of real microstructures on the thermal conductivities of plasma-sprayed TBCs.

Although the total porosity fraction in APS coatings is smaller compared that of the SPPS coatings, very high aspect ratios (>10) of the “splat” boundaries in APS coatings result into effective thermal barrier. This results in lower overall thermal conductivity of the APS coatings. However, due to the large local variation in the microstructure of APS coatings, corresponding variation in the thermal conductivity values have been observed. This causes a standard deviation of 0.38 in the thermal conductivity values for this type of coatings. The standard deviation values for layered-SPPS coating and SPPS coatings were 0.11 and 0.13, respectively.

As mentioned earlier, in section 3.3.2, vertical branched cracks are characteristics of a thick SPPS coating. Effect of such microstructure (isolated vertical crack and associated in-plane branching cracks) on the thermal conductivity of layered-SPPS coatings with IPBs was studied. Figure 5.12 shows one such microstructure used for OOF calculations. Due to the crack-like porosity in the direction perpendicular to the heat-flow, very steep gradients of temperature were observed in that direction. The effective room temperature thermal conductivity of this region is found to be 0.61 W m$^{-1}$ K$^{-1}$, which is $\sim$ 22 % less than regions away from vertical cracks.
Due to the anisotropy of plasma-sprayed microstructures, thermal conductivity values in the direction parallel to the coating-substrate interface (in-plane) and direction perpendicular to it are expected to be different. By applying the temperature gradient on the left and right sides of a microstructure and keeping other two sides adiabatic, thermal conductivity in the in-plane direction can be calculated by using OOF. Considerable increase in the thermal conductivity was calculated for all three types of coatings in the in-plane direction compared to the direction perpendicular to it and is attributed to lower resistance to heat flow in the in-plane direction. Percentage increase in the in-plane thermal conductivity values for layered-SPPS, SPPS and APS coatings is 70-80, 35-70 and 45-65, respectively. It should be noted that for these thermal conductivity values for SPPS and layered-SPPS coatings were obtained from microstructures without vertical cracks present in them. In reality, where vertical cracks are present in both the types of coatings, one should expect very high resistance to the heat flux and thus negligibly small thermal conductivity in the in-plane direction.
<table>
<thead>
<tr>
<th>Microstructural Parameter</th>
<th>Sym.</th>
<th>SPPS</th>
<th>Layered-SPPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity Volume Fraction from Disk-Shaped Pores</td>
<td>$\phi_{\text{Disk}}$</td>
<td>0.17</td>
<td>0.24</td>
</tr>
<tr>
<td>Porosity Volume Fraction from Spherical Pores</td>
<td>$\phi_{\text{Sphere}}$</td>
<td>0.07</td>
<td>0.06</td>
</tr>
<tr>
<td>Total Porosity Volume Fraction ($\phi_{\text{Disk}}+\phi_{\text{Sphere}}$)</td>
<td>$\phi$</td>
<td>0.24</td>
<td>0.30</td>
</tr>
<tr>
<td>Ave. Aspect Ratio of Disk-Shaped Pores</td>
<td>$d/t$</td>
<td>2.84</td>
<td>3.34</td>
</tr>
<tr>
<td>Ave. Thickness of High-Porosity Layer</td>
<td>$L_{\text{Disk}}$</td>
<td>-</td>
<td>6 $\mu$m</td>
</tr>
<tr>
<td>Ave. Thickness of Low-Porosity Layer</td>
<td>$L_{\text{Sphere}}$</td>
<td>-</td>
<td>4 $\mu$m</td>
</tr>
<tr>
<td>Ave. Vertical Crack Spacing</td>
<td>$W$</td>
<td>170 $\mu$m</td>
<td>300 $\mu$m</td>
</tr>
<tr>
<td>Ave. Vertical-Crack Gap Thickness</td>
<td>$u$</td>
<td>0.11 $\mu$m</td>
<td>0.13 $\mu$m</td>
</tr>
</tbody>
</table>

**Table 5.1:** Results from the microstructural characterization of the SPPS and layered-SPPS coatings
Figure 5.1: SEM micrographs of the APS coating at: (A) low and (B) high magnifications. Arrows in (B) indicate splat boundaries.
Figure 5.2: SEM micrographs of the SPPS coating at: (A) low and (B) high magnifications. Arrows in (A) indicate vertical cracks.
Figure 5.3: (A) Low magnification optical micrograph of the layered-SPPS coating showing alternate layers and vertical cracks (arrows). SEM micrographs at: (B) low and (C) high magnifications, showing the alternate layers of low and high porosities. Dashed lines in (C) demarcate approximate boundaries between low and high porosity layers.
Figure 5.4: Schematic diagram showing the different types of porosities (spherical- and disk-shaped) present in the SPPS and the layered-SPPS coatings. The direction of heat flow ($Q$), and the thicknesses of the low ($L_{\text{Sphere}}$) and high ($L_{\text{Disk}}$) are indicated. The disk-shaped pores are assumed to have a diameter $d$ and thickness $t$. 

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Figure 5.5: Thermal conductivity as a function of temperature. The symbols represent experimentally measured data, and they are connected with dashed lines. Error bars represent ±5%, which are about the size of the symbols for SPPS, layered-SPPS, and APS coatings. The solid lines represent results from the analytical modeling for SPPS and layered-SPPS coatings. Experimental data for the dense 7YSZ is from Ref. [30].
Figure 5.6: Thermal conductivity of Ar gas in the coating pores and, radiative thermal conductivity of the plasma-sprayed ceramic as a function of temperature.

Figure 5.7: Effect of aspect ratio of disk-shaped porosity on the normalized thermal conductivity of the layered-coatings for three different total porosity contents. It is assumed that in all the three cases fractions of disk-shaped porosity and spherical porosity are equal.
Figure 5.8: Equal normalized thermal conductivity lines as a function of fraction of disk-shaped porosity and total porosity in layered-coatings. Arrows indicate various thermal conductivity regions bound by these lines. Aspect ratio of disk-shaped pores is assumed to be 4 for the calculations.
**Figure 5.9:** Effect of aspect ratio of disk-shaped pores on equal thermal conductivity lines shown in Figure 5.8. Arrows indicate the equal thermal conductivity lines for various aspect ratios ($d/t$).
Figure 5.10: (A) Binary image of the SEM image of a layered-SPPS coating shown in Figure 5.3B. Dark phase is ceramic whereas the light is pores. (B) OOF microstructure of the layered-SPPS coating with a superimposed thermal gradient of (T_1-T_2). The white regions represent porosity.
Figure 5.11: Thermal conductivity as a function of temperature. The symbols represent experimentally measured data, and they are connected with dashed lines. Error bars represent ±5%, which are about the size of the symbols for SPPS, layered-SPPS, and APS coatings. The solid lines represent results from OOF modeling for APS, SPPS and layered-SPPS coatings. Experimental data for the dense 7YSZ is from Ref. [30].

Figure 5.12: Branched-vertical crack in the layered-SPPS TBC. Arrows show prominent branches associated with the crack.
SUMMARY AND CONCLUSIONS

6.1 Processing and Mechanical Properties of Thick TBCs

The SPPS method has been used to demonstrate the feasibility of depositing highly durable, thick (4 mm thickness) 7YSZ TBCs on bond-coated superalloy substrates. The microstructures of these coatings are characterized by branched vertical cracks, a lack of horizontal “splat” boundaries and cracks, and porosity of ~22%. The indentation-toughness (mode-I) of the SPPS coating was found to be over five times that of the reference 7YSZ APS coating in the most critical in-plane orientation. While the indentation-toughness of the SPPS coating is isotropic, the indentation-toughness anisotropy in the APS coating is highly pronounced. Critical strain energy release rates \( (G_c) \) were obtained by direct measurements for APS and SPPS coatings under mode-II loading. The average apparent \( G_c \) value for the APS coatings is much higher than that for the SPPS coatings. This is primarily attributed to the extra energy absorption due to crack face friction in the APS TBCs. Uniaxial compression of the SPPS coatings is characterized by an initial non-linear stress-strain response and permanent deformation.
This is followed by a linear-elastic response, before the ultimate compressive failure occurs. The ultimate compressive strengths of SPPS and APS coatings in the in-plane orientation were found to be comparable, while the strength of the SPPS coating was found to be lower than that of the APS coating in the out-of-plane orientation. Heat-treatment of the SPPS coating resulted in a significant increase in the ultimate compressive strength in the in-plane orientation, which is most likely due to the complete pyrolysis of the unpyrolyzed material present in the as-sprayed SPPS coatings. The average thermal-cycling life of the SPPS TBCs was found to be 820 cycles, while that of a reference APS TBC deposited on identical bond-coated superalloy substrate was found to be 40 cycles.

### 6.2 Fracture Mechanics Analysis of Thick TBC Failure

Fracture mechanics analysis for the thick SPPS and APS TBCs has been carried out based on the experimental results and finite element analysis (FEA). It is shown that steady-state strain energy release ($G_{ss}$) for 4 mm thick APS TBC was much higher than its critical strain energy release rate ($G_c$) under mode-II type of loading. This explains the experimentally observed premature spallation of the thick APS TBC. On the contrary, due to the presence of branched vertical cracks and therefore, reduced in-plane stresses, the 4 mm thick SPPS coatings developed insufficient $G_{ss}$ to drive its instantaneous failure. Further, its failure under mode-I type of loading is delayed due to significantly high in-plane local fracture toughness. Failure occurs along the top-coat/TGO interface in the thick SPPS TBCs whereas it occurs within the ceramic top-coat in the thick APS TBCs.


6.3 **Interfacial Damage and TGO Development**

Interfacial damage and TGO developments for 1.5 mm thick APS and SPPS TBCs have been studied using the interrupted-thermally-cycled specimens. Interfacial delaminations start forming at multiple locations, within the ceramic top-coat, during early stages of thermal cycling. They grow in size with further thermal cycling and join each other through the TGO to result in TBC failure.

Early transient oxidation of the bond-coat results in ~1 µm thick layer of Ni/Cr-rich mixed oxides above equi-axed layer of Al₂O₃ layer. This is followed by growth of α-Al₂O₃ in the columnar form resulting from inward oxidation of anions. Regions of bond-coat asperity and “diffusionally isolated splats” have showed presence of significantly thick non-protective mixed oxide layer above the protective α-Al₂O₃ TGO in both, APS and SPPS TBCs subjected to failure. This chemical failure of the TGO has been correlated with breaking of the α-Al₂O₃ TGO along with lack of sufficient Al in the subsurface bond-coat regions. Based on the experimental and numerical analysis, mechanisms for the chemical failure of the TGO have been proposed. Finally, it has been concluded that the TGO growth kinetics and its chemical failure are independent of the top-coat deposition method. They are primarily governed by bond-coat morphology and its chemical composition for given test conditions.

6.4 **Thermal Conductivity Reduction by Microstructural Tailoring of TBCs**

The microstructures of SPPS TBCs have been tailored to contain alternate layers of high and low porosities (layered-SPPS), in an effort to reduce the thermal conductivity
of SPPS TBCs. The thermal conductivities of the 7YSZ layered-SPPS coating are found to be lower than those of both the SPPS coating and the APS coating of the same composition, in the temperature range 100-1000 °C. Analytical modeling and OOF have been used to analyze the experimental thermal conductivity data. Although the calculated thermal conductivities from both analytical modeling and OOF compare with the respective experimentally measured thermal conductivities, OOF captures accurately the effect of real microstructures on the thermal conductivities of plasma-sprayed TBCs.


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92. Ramachandra C, Lee KN, Tewari SN. Durability of TBCs with a surface environmental barrier layer under thermal cycling in air and in molten salt. Surface & Coatings Technology 2003;172:150.


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CHEMICAL FAILURE OF APS COATED OVERLAY COATINGS
USING FINITE DIFFERENCE METHOD

Equations based on balance of fluxes have been used to obtain numerical solutions for time required for chemical failure of diffusion cells.

Based on microstructural observation of cross-sections of the TBCs deposited on APS bond-coats, different types of scenarios are presented. For the purpose of the modeling following four different types of ‘cells’ of bond-coat material have been considered: a) a region with convex bond-coat asperity separated from the bulk of the bond-coat by an elongated open pore, b) a circular region having very small contact with bulk of the bond-coat, c) a rectangular region almost completely surrounded by top-coat and open porosity, d) a rectangular region having only one long side in contact with the bulk of the bond-coat. Figure A. 1 shows schematics of different types of ‘cells’ and corresponding SEM images. It should be noted that these ‘diffusion cells’ are primarily found to form only at the BC/top-coat interface. Their thickness or diameter varies in the range of (~2-40 µm).
Following assumptions have been made for the numerical analysis: 1. reduction in aluminum level due to initial spinel (NiAl2O4) formation is neglected; 2. Al2O3 formation occurs only at the max hold temperature; 3. alumina grows uniformly at all the sites along the sides of the cell; 4. the BC/Topcoat interface concentration is slightly less than rest of the BC at time=0.

Applicable differential equation for one dimensional non-steady state mass flow is given by Fick’s second law as:

\[
\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial x^2} \right) \quad (A.1)
\]

where diffusion coefficient, \( D \), is \( D_{\text{AlAl}} \) and is given by [181]

\[
D_{\text{AlAl}} = \left( 1.81 + 0.39C'_{At} + 0.03C'_{Cr} + 0.01C'^2_{At} - 0.0005C'^2_{Cr} \right) \times 10^{-10} \text{ (cm}^2\text{s}^{-1}) \quad (A.2)
\]

An equation for solving one-dimensional diffusion problem using explicit scheme can be given as follows:

\[
C'_{k+1} = C'_{k} + D \frac{\Delta t}{\Delta x^2} \left( C'_{k+1} - 2C'_{k} + C'_{k-1} \right) \quad (A.3)
\]

We can use this scheme to explicitly compute all \( C'_{k+1} \) given values from the previous time-step \( (C'_{k}) \). Subscript \( k \) represents relative location of a node. The terms \( \Delta t \) and \( \Delta x \) are the time interval and distance between two nodes, respectively. In order to obtain composition of BC/top-coat interface mass balance equation derived from energy equation has been used [181].
The term \( C_{\text{alumina}} \) is Al concentration in alumina. Due the inward growth of alumina and consumption of aluminum in the BC, the bond-coat/oxide interface keeps shifting. The corrected composition for the new node position can be obtained by Murray and Landis equation [182] as follows:

\[
C'_k = C'_k \left(1 - \frac{C'_{k-1} - C'_{k+1}}{(1 - k)/n} \right) \Delta L
\]

where \( \Delta L = \frac{dZ_N}{PBL} \)

\( dZ_N \) : Incremental increase in the oxide thickness obtained from Figure 4.13.

\( PBL \) : Pilling-Beadworth Ratio for alumina formation (~ 1.27)

\( n \) : Total number of nodes

For the calculations of concentration profiles in rectangular profiles two dimensional FDM in Cartesian coordinate system has been used. For a two dimensional Cartesian coordinate system:

\[
\frac{\partial C}{\partial t} = D_x \left( \frac{\partial^2 C}{\partial x^2} \right) + D_y \left( \frac{\partial^2 C}{\partial y^2} \right)
\]

If a rectangular “diffusion cell” is completely secluded from the remainder of the bond-coat, it becomes an isolated rectangle as shown in Figure A. 1. Due to symmetry involved in the problem only quarter of the rectangle can be considered.
Numerical solution for the interior nodes of the rectangle can be found as:

\[
C_{x,y}^{t+\Delta t} = \Delta t \left[ \frac{x - 1}{\varepsilon_x} \times \frac{C_{x+1,y}^{t} - C_{x-1,y}^{t}}{2} + \frac{y - 1}{\varepsilon_y} \times \frac{C_{x,y+1}^{t} - C_{x,y-1}^{t}}{2} \right] + \Delta t \left[ \frac{D}{\Delta x^2} \left( C_{x+1,y}^{t} - 4C_{x,y}^{t} + C_{x-1,y}^{t} + C_{x,y+1}^{t} + C_{x,y-1}^{t} \right) \right] + C_{x,y}^{t} \tag{A.7}
\]

For external surface nodes the solution becomes,

\[
C_{x,y}^{t+\Delta t} = \frac{4D\Delta t}{\Delta x^2} \left[ C_{x+1,y}^{t} - 3C_{x,y}^{t} + C_{x,y+1}^{t} \right] - \frac{4\Delta t C_{\text{Al min}}}{\Delta x} + C_{x,y}^{t} \tag{A.8}
\]

Appropriate solutions for the nodes at corners of the rectangular cell have been applied. Another solution for oxidation of rectangular cell from three sides (representing a closed pore present on the fourth side) has been calculated using similar scheme of equations. In this case, composition of the nodes along the non-oxidizing close pore is given by:

\[
C_{x,y}^{t+\Delta t} = \frac{4D\Delta t}{\Delta x^2} \left[ C_{x+1,y}^{t} - 3C_{x,y}^{t} + 2C_{x,y-1}^{t} - 2C_{x,y+1}^{t} \right] + C_{x,y}^{t} \tag{A.9}
\]

A “diffusion cell” is termed as failed when \(C_{\text{Al}} < 5\) at.% at the center of the cell. The results of analysis for rectangular “diffusion cells” with oxidizing at all sides and three sides are given in Figure 4.31 and Figure A.2, respectively.

In order to calculate concentration profiles for circular/ semi-circular shaped bond-coat “diffusion cells” (Figure A.1), one dimensional FDM in polar co-ordinate
system can be used. Here differential equation for diffusion in one dimensional polar co-
ordinate system is given by:

\[
\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} \right) + \frac{1}{r} \frac{\partial C}{\partial r} \quad (A.10)
\]

Numerical solution to the above partial differential equation for explicit finite
difference method can be given based on the boundary conditions involved in the present
problem.

For interior nodes:

\[
C_{k}^{t+\Delta t} = \Delta t \left( \frac{n}{\varepsilon} \right) \left( \frac{C_{k+1}^{t} - C_{k-1}^{t}}{2} \right) + \frac{\Delta L}{\Delta t} + \frac{D}{\Delta r^2} \left[ C_{k+1}^{t} - 2C_{k}^{t} + C_{k-1}^{t} + \frac{\Delta r}{2r} \left( C_{k+1}^{t} - C_{k-1}^{t} \right) \right] + C_{k}^{t} \quad (A.11)
\]

Here \( \Delta r \) is the distance between the two nodes and \( \varepsilon \) is the radius of the circle of
"diffusion cell". Also, similar to the case of one dimensional Cartesian coordinate
system, the concentration of the boundary node (outside node or node #1) can be
calculated by:

\[
C_{1}^{t+1} = \frac{2}{\Delta r} \left[ \left( 1 - \frac{\Delta r}{2r} \right) \times D \left( \frac{C_{2}^{t} - C_{1}^{t}}{\Delta r} \right) \Delta t - \Delta YC_{alu_{min}} \right] + C_{1}^{t} \quad (A.12)
\]

For the central node (\( C_c \)):

\[
C_{c}^{t+\Delta t} = C_{c}^{t}(1 - 4F_o) + 4F_o \times C_{2}
\]

where

\[
F_o = \frac{D \times \Delta t}{(\Delta r)^2},
\]

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The results of analysis for circular and semi-circular “diffusion cells” are given in Figure A. 3.
Figure A. 1: SEM images of bond-coat/top-coat interface of 1.5 mm thick SPPS TBCs subjected to 10 thermal cycles. The bond-coat “diffusion cell” morphologies indicated by arrows here are: (A) rectangular, (B) circular, (C) rectangular with three sides getting oxidized, (D) semicircular with curved portion getting oxidized. Corresponding schematics, used in the modeling, are shown on the right of the images. The dark lines in schematics show sides undergoing oxidation constantly. The lighter lines show effective barrier which is not undergoing active oxidation.
Figure A. 2: Effect of thickness of rectangular “diffusion cell” with three-sides-oxidizing on chemical failure life of TBCs. Results for three different lengths of the cell are shown here.

Figure A. 3: Effect of diameter of circular and semi-circular “diffusion cells” (in Figure A.2 (B) and (D)) on chemical failure life of TBC.
APPENDIX B

OOF COMMAND-FILES FOR THERMAL CONDUCTIVITY ANALYSIS

In OOF, portable pixel map (PPM) images were subjected to applying intrinsic material properties and meshing by using the following command file.

1 Ppm2oof Command File

ppmfile filename=/home/image.ppm
graphics 0 dashboard Select demoRGB red_value=0 green_value=0 blue_value=0 +/-__red=60 +/-__green=60 +/-__blue=60 replace=false
materials gas gray=1 planestrain=false kappa=0.01
graphics 0 dashboard Select select_complement materials isotropic gray=0 planestrain=false T0=0 young=65 poissson=0.33 alpha=1.1e-06 kappa=2.7844
pixelgroups new name=ceramic
pixelgroups new name=pore
pixelgroups add ceramic
graphics 0 dashboard Select select_complement pixelgroups add pore
adaptive_mesh create nx=150 ny=150
adaptive_mesh refine interface iterations=3
adaptive_mesh anneal T=0 delta=1 iterations=10
adaptive_mesh swap_worst
adaptive_mesh swap_worst
adaptive_mesh swap_worst
adaptive_mesh save filename=/home/OOF_Folder/save_name
2 OOF Command File

initialize file filename=/home/goof_file
modify select group ceramic
modify replace isotropic gray=0 T0=0 planestrain=false young=65 poisson=0.33 alpha=1 kappa=2.8
modify select none
modify select group pore
modify replace gas gray=1 kappa=200e-04
equilibrate maxiter = 8000
equilibrate tolerance = 1e-16
fictiveT = 0
bc free all
bc emancipate all
distort clear all
distort thermal clear all
distort thermal set reset_params
distort thermal set incremental = false
bc fix T top
bc fix T bottom
bc apply
distort thermal set top
distort thermal set T0 = 100
distort thermal set top
distort thermal set T0 = 0
distort thermal set bottom
distort thermal set reset_params
equilibrate thermal
output heatflux top
output heatflux bottom
output position top
output position bottom
log stop