Study of microstructure effect on the thermal properties of Yttria-stabilized-Zirconia thermal barrier coatings made by atmospheric plasma spray and pressing machine

Monica Bohorquez de Silva
Louisiana State University and Agricultural and Mechanical College

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STUDY OF MICROSTRUCTURE EFFECT ON THE THERMAL PROPERTIES OF YTTRIA-STABILIZED-ZIRCONIA THERMAL BARRIER COATINGS MADE BY ATMOSPHERIC PLASMA SPRAY AND PRESSING MACHINE

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

In

The Department of Mechanical Engineering

by

Monica Bohorquez de Silva

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ABSTRACT

Thermal barrier coatings (TBCs) are used in gas turbine engines to achieve a higher working temperature and thus lead to better efficiency. Yttria-Stabilized-Zirconia (YSZ), a material with low thermal conductivity, is commonly used as the top coat layer to provide the thermal barrier effect. In this dissertation the thermo-physical properties of a variety of TBCs samples made out of different fabrication techniques were investigated and compared. The first set of samples was fabricated using a pressing machine device to fabricate 0.5 inch diameter disk shaped YSZ-Al₂O₃ samples. The YSZ-Al₂O₃ powder mixture was made of 0, 1, 2, 3, 4 and 5 wt% Al₂O₃/YSZ powder ratio. The second set of samples was fabricated by Atmospheric Plasma Spray process for two different microstructure configurations, standard (STD) and vertically cracked (VC), and two different thicknesses, 400 and 700 μm respectively. A laser flash system was used to measure the thermal properties of the coatings. Experiments were performed over the temperature range from 100°C to 800°C. The porosity of the YSZ samples was measured using a mercury porosimetry analyzer, POREMASTER 33 system. A Scanning Electron Microscope (SEM) was used to study the microstructure of the samples. An analytical model is proposed to estimate the effective thermal conductivity of the TBCs. Results showed that the change of thermo-physical properties is directly linked to the microstructure of the samples, demonstrated by the porosity measurements and SEM images. The addition of alumina was effective to suppress sintering behavior of YSZ ceramic. The YSZ-Al₂O₃ composite samples reported lower thermal conductivity values compared to pure YSZ, this due to the increase of porosity of the samples. For the TBCs, the thermal diffusivity and thermal conductivity increased for the VC-TBC samples in comparison to the STD-TBC samples over the temperature range tested. The analytical predictions were compared to the experimental data.
CHAPTER 1: INTRODUCTION

1.1. The Gas Turbine Engine and TBCs

Power generation is a prominent industry which uses different approaches in order to generate power or electricity. Gas turbines are widely used for power generation due to the large amount of power that can be obtained from a relatively small physical size. Examples are jet engines, turbofan engines, local power plans, ship engines, helicopter engines, etc.

A gas turbine is a rotary engine that extracts energy from the working fluid to produce work. The main components of an aero gas turbine are shown in Figure 1.

![Gas Turbine Main Components](image)

Figure 1. Gas Turbine Main Components

Air enters to the compressor at atmospheric conditions, which is compressed to high pressure and directed into the combustion chamber or combustor. At the combustor, fuel is burned to produce gas flow at high temperature and high pressure. The hot combustion products are then directed to the turbine, which extracts the energy from the hot gas in the form of shaft power. During this process, the engine components are subjected to significant temperature extremes. Thus, the engine components experience high thermal loads, which may cause failures of the components. Severe heat load affects the durability and efficiency of the engine. Typically, the hot gases can achieve temperatures between 800°C to 1700°C. In addition, degradation of materials occurs due to the oxidizing and corrosive environments. For more than
three decades, gas turbine manufacturers engineered and developed different methods to protect the metallic components of the engine, such as the employment of high temperature superalloy materials. These developments lead to improved engine efficiency and durability.

One way to increase power and improve the efficiency of gas turbines is by increasing the turbine inlet temperature. This can be achieved by using air cooling techniques combined with thermal barrier coating (TBC). A TBC combine with air cooling will reduce the metal temperature and lead to higher inlet temperature to the gas turbine engine; then durability and efficiency of the engine will be improved.

Thermal barrier coatings (TBCs) are routinely used in the engine hot sections. A typical TBC system is composed of a thin layer of oxidation resistant bond coat and a top coat layer of an insulative ceramic, as shown in Figure 2.

![Figure 2. Cross Section of Thermal Barrier Coatings (TBCs)](image)

The evolution of this technology leads to the development of thermal barrier coatings capable of providing thermal insulation about 165°C to 170 °C [1]. According to Pratt & Whitney, one of the three major jet engine manufacturers, TBCs are first introduced on the burner in the JT8D engines in 1963. This TBC consisted of zirconia stabilized with 22wt% MgO (22MSZ) [1]. Later on they incorporated other materials in order to achieve higher temperatures in the combustor chamber. In current systems, the 22MSZ was replaced by 7 %wt yttria partially
stabilized zirconia (7YSZ). This was due to the susceptibility to destabilization and low temperature capability of MSZ.

Another problem that has to be faced with the TBCs is the spalling from the substrate. The bond coat is used to prevent oxidation and spalling of the TBC system from the superalloy element. In their designs, a variation of NiCoCrAlY composition for the bond coat has been applied by atmospheric plasma spray (APS). The failure of this bond coat was typically due to the oxidation over the thermocyclic exposure, mainly caused by the formation and growth of oxide nuclei during the APS. They eliminated this failure by incorporating another fabrication technique, low pressure chamber plasma spray (LPPS).

W.A. Nelson and R.M. Orenstein [2] presented a detailed study on the use of TBCs in power generation. They mainly reported the experiences at General Electric Power Generation (GE PG) with the uses of TBCs. First of all, the evaluation at GE PG was performed by actual operating machines. GE PG conducted more than 80 rainbow tests since the 1950s. According to GE PG report, the typical operating hours for power generation components is about 24,000 h, and for commercial aircraft it is about 8,000 h. The results of the tests lead to a confirmation of the superior behavior of the YSZ and especially, with 6 to 8 wt% yttria. Several engine operation changes occur with the uses of TBCs. It was reported [3] that the coating applied to engine components enhanced the engine performance and reduced the maintenance.

Thermal barrier coatings (TBCs) characterization is an important technique used to provide a better understanding of the relationship between the microstructure and thermal properties of the plasma spray coatings. The thermal properties of the TBC depend strongly on the microstructure and porosity. The APS technique used to make the coatings usually leads to lamellae microstructure comprised of the stacking of lamellae separated by imperfect interfaces. This microstructure enhances the thermal resistance. The thermal diffusivity of the coatings is
typical decreased with the increase of porosity, which is understandably due to the increased interfacial thermal resistance. Also higher thermal diffusivity can be obtained by using a thicker lamellae type of coating\[^4\]; thus the need for optimizing the coating thickness.

There are several failures mechanisms of TBCs. To study the failure mechanism, thermal cycling tests are usually preformed to evaluate the behavior of the TBCs. During these tests thermal barrier coatings samples can be heated by electrical furnaces to a controlled temperature for a certain period of time. The tensile adhesion test (ASTM C633-79) is used to asses the adhesive/cohesive strength of the APS coatings. The adhesive failure is due to fractures between the coating and the substrate, and the cohesive failure is due to the fractures within the coatings. A study reported that the adhesion strength of APS coatings (made of YSZ on a steel substrate without bond coat) was reduced by 25% after heat treatment at 1150°C for 10 h\[^5\]. The use of different bond coat compositions leads to different failures. For example, the use of NiCr(19%)Al(6%) results in a fracture in surfaces adjacent to the coat/bond interface, which is an adhesive type of failure\[^6\]. The degradation in bond strength and failure is related to the composition of the bond coat. This is due to the different coefficients of thermal expansions between the bond coat and the ceramic coat.

1.2. Present Study

The reliability of thermal barrier coatings (TBCs) is determined by the composition of the coating and their mechanical and thermal properties.

The objectives of the present study are as follows:

- To study the thermal properties including thermal conductivity, thermal diffusivity, and specific heat of thermal barrier coating samples made by atmospheric plasma spray technique and the samples made by using a pressing machine.
- To study the physical properties of atmospheric plasma spray TBC samples with standard
and vertically cracked microstructures.

- To examine the porosity effects on the thermal-physical properties of the thermal barrier coatings.
- To understand the effect of the addition of Al₂O₃ to pure YSZ to TBC’s thermal properties.
- To establish the relationship between microstructure and thermal properties such as thermal diffusivity, thermal conductivity, and specific heat of the TBC samples.
- To develop a model to estimate effective thermal conductivity using the microstructure details of the coatings.

This investigation provides a better understanding of the thermal-physical properties of the Thermal Barrier Coating samples made by two fabrication techniques: by atmospheric plasma spray (APS) and by using a pressing machine. In addition, one of the main goals of this study is to investigate the effect of the addition of Al₂O₃ on the thermal-physical properties of YSZ based TBCs, such as microstructure changes, porosity effect, and the change of thermal properties. A laser flash system (FL5000) was used to measure the thermal properties for all samples. A POREMASTER 33 system manufactured by Quantachrome Instruments was used to measure porosity, pore size distribution, and pore number fraction. The microstructure of the different samples was studied by Scanning Electron Microscope (SEM) images.

1.3. Structure of the Dissertation

This dissertation is organized in nine (9) different chapters to cover the research work done, results obtained, conclusion, and recommendations.

In Chapter 1: Introduction, a clear background on Gas Turbines and Thermal Barrier Coatings (TBCs) is presented. In addition, it includes the scope of the present study and structure of the dissertation.
In Chapter 2: Thermal Barrier Coatings (TBC), a Literature Survey, a theoretical background and the development of TBCs over the years is presented. The chapter is organized in six (6) sections, which included a broad scope of TBCs. It also includes the structure of the TBCs, the benefits of using TBCs, the different fabrication techniques used to make TBCs, the development of novel materials for TBCs applications, the characterization, and the future development of TBCs.

In Chapter 3: Thermal Properties Measurement, a detailed description of the Laser Flash Method used to measure thermal properties of the samples is presented. A description of the test apparatus used, FL5000, is also included. In the last part, the uncertainty analysis is presented.

In Chapter 4: Porosity Measurements, a detailed description of the Mercury Porosimetry Method is presented, which is the method used to measure porosity, pore size, and pore size distribution of the samples. In addition, a description of the test apparatus POREMASTER 33 is included.

In Chapter 5: Effective Thermal Conductivity Theoretical Models, a proposed model to estimate the effective thermal conductivity of the coatings is presented. Five different methods found in the literature are used. The model proposed included the microstructure details obtained by porosity measurements. It included the effects of details, such as, grain size, pore size, volume fraction of pores, and interfacial resistance into the effective thermal conductivity model. A comparison between experimental values and theoretical calculation is also presented.

In Chapter 6: Sample Preparation, a detailed description of the materials and methods used to prepare the samples is presented. Two techniques were used: Pressing Machine and Atmospheric Plasma Spray (APS). This chapter also includes all the steps used in the thermal properties and the porosity tests.

In Chapter 7: Results of YSZ—Al₂O₃ Composite Samples, this chapter presents the
physical properties measured: thermal diffusivity, thermal conductivity, porosity, and microstructure analysis for the composites samples prepared by using the pressing machine. In addition, the results for the effective thermal conductivity models are included.

In Chapter 8: Results of the Atmospheric Plasma Spray Samples, the results of the APS samples are presented. The results included are physical properties, thermal diffusivity, thermal conductivity, porosity, and microstructure analysis for all the samples prepared. In addition, the effective thermal conductivity predictions are included.

In Chapter 9: Conclusion, a detailed summary of the goals achieved with the work done and the contribution to the field is presented.
CHAPTER 2: THERMAL BARRIER COATINGS, A LITERATURE SURVEY

2.1. Thermal Barrier Coatings (TBCs)

Coating materials have been widely used for industrial applications, such as aerospace, automotive engines, energy applications, biomedical coating, dental and bone implants, to cite some [7]. The most common purpose of the thermal barrier coatings is to provide a protective layer to shield the substrate or metallic components from corrosive and erosive atmosphere. A TBC is a system made of two layers of coatings: a metallic bond coating and a ceramic top coat layer. The bond coating is sprayed into the superalloy substrate intended to inhibit oxidation and improve adherence of the top coat to the substrate [1]. The ceramic top layer is mainly used to create an insulative layer to create the thermal barrier effect. This layer is made of yttria-stabilized zirconia (YSZ) powders, a material with low thermal conductivity and high coefficient of thermal expansion. The thermal conductivity of the YSZ ceramic layer is ten times lower (2.0 W/mK for bulk YSZ) compare to the typical superalloy used in gas turbines (21 W/mK for Inconel IN738).

2.2. Benefit of Using Thermal Barrier Coatings

Gas turbine hot sections are typically subjected to significant temperature extremes and degradation in oxidizing and corrosive environments. To improve the engine durability and efficiency, thermal barrier coatings (TBCs) are routinely used in the engine hot sections. The engine component temperature is affected by the mainstream temperature and the heat fluxes from the mainstream flow to the metal substrate. Coatings may also provide a thermal barrier effect, in which the large temperature gradient and temperature drop take place across the coating layers, thus a low substrate temperature is achieved. The reduced heat flux can effectively increase the engine life and enhance the engine performance by reducing the thermal
fatigue load \cite{8}, thus the use of TBCs in today’s gas turbine is prevalent. By using TBCs, the turbine inlet temperature can be increased by \( \sim 150^\circ C \) to \( 200^\circ C \) \cite{1,9}. Alternatively, the cooling air usage can be reduced. It has been reported that YSZ coating with a 125 \( \mu m \) thickness could reduce the turbine blade cooling requirements by \( 36\% \) \cite{10}.

### 2.3. Fabrication Techniques Used to Make the TBCs

TBCs are commonly made by melt-spray techniques. In the 1900s the melt atomization process was introduced to produce metal powders; by the 1920s a thick layer of free-standing material was produced \cite{11} using metal spray. Since that time, different fabrication techniques have been developed to manufacture the TBCs’ layers. The currently used TBCs are commonly made by atmospheric plasma sprayed (APS) or deposited by electron beam physical vapor deposition (EBPVD).

\[ \text{Figure 3. Schematic of Plasma Spray Process} \]

In atmospheric plasma spray process, Figure 3, a gas mixture is ionized to the plasma state by electrical current. The powder particles introduced into the plasma jet interact with the streaming plasma while traveling towards the substrate. The high temperature of the plasma jet melts the injected ceramic/metallic powders. The temperature is reported to be around 12,000 K at the center of the jet \cite{7}. Upon impact at the surface, a splat coating is created when the particle flattens, adheres, and solidifies, Figure 4.
The splats constitute the basic building elements of a TBC coating, whose shape and adherence to the surrounding material have a marked effect on the microstructure, thus in turn, affect the life, the mechanical properties, and the thermal properties of TBCs. A structure of the splat is presented in Figure 4. Notably, the porous, defected, layered microstructure of the plasma sprayed coatings can substantially reduce the already low intrinsic thermal conductivity of YSZ by as much as 60% (typical thermal conductivities of plasma spray YSZ is about 1 W/m-K compared with the bulk value of 2.2 W/m-K) [12, 13, 14].

![Figure 4. Schematic Diagram of Plasma Sprayed Coating](attachment:image.png)

Fig. 4. Schematic Diagram of Plasma Sprayed Coating

Plasma spray is a very complex process which is determined by several control parameters. The most common control parameters are: power input, arc gas pressure (argon, nitrogen), auxiliary gas (hydrogen, helium), powder gas pressure (argon), powder feed rate, grain size/shape, injection angle, surface roughness, substrate heating or cooling, spray distance, spray divergence, and spray atmosphere (air, low pressure, inert gas, water, etc.). Figure 5, shows a list of these control parameters. These parameters will influence the properties and microstructure of the coating [15, 16, 17]. APS coatings are characterized by various defects, such as pores and cracks of different sizes. The substrate temperature influences the splat flattening and cooling process. For a high substrate temperature, the degree of porosity will be lower and it is suggested that the high temperature could also enhance the contact between splats [16]. Friis et. al. [16] reported that
at high substrate temperature the grains grow perpendicular to the substrate, which prevents delimitations inside the lamellae structure. Thus, the TBC coating will result in a dense structure. On the other hand, at low substrate temperature, it has been reported by Ya-Zhe Xing et. al. \[15\] that the coating will have distinguished lamellae structure with a mean thickness of individual splats about 1 μm.

![Figure 5. Plasma Spray Operational Parameters](image)

Furthermore, many different techniques have been studied to develop coatings with improved characteristics. One particular problem that has to be addressed while manufacturing these TBCs is the substantial difference in the coefficient of thermal expansion between the gas turbine metal components and the ceramic thermal barrier layer. The TBCs will invariably fail under severe thermal cycling. To overcome this problem, one approach is that of grading the coating from essentially all metal at the metal surface to all ceramic at the outer surface of the coating \[18\]. The graded coating is believed to be able to reduce the thermal stress level \[19\]. However, some discrete metal particles were typically founded in the graded coating, which produce unacceptable stresses in the coating after oxidation. Another approach is to use so-called
vertically cracked or columnar structure in the coating. It has been reported by Bunshah \cite{20} that by using vapor deposition, columnar grains or "columnar defects," which are poorly bonded to each other, may occur. Fairbanks et al. \cite{21} reported that columnar growth defects were also observed at sputtered ceramic coatings. Some researchers argued that such structure was detrimental because the exposed columnar surface gently increases the surface exposed to the environment and also that the gaps between the columns could adversely affect the mechanical properties. However, it is also widely accepted that vertically cracked structure made by EBPVD and APS could permit stress relaxation of the coating and thereby enhance coating life.

According to the literature \cite{22}, thermal cycling will induce tensile stress in TBC normal to the surface. For the small region around the apex of the rough bond coating layer/TBC interface, assuming no cracks, the stress is compressive. Elsewhere, the TBC experiences a relatively uniform tension. The stresses increase as the system cycles, because of the displacements caused by the thickening of the thermally grown oxide (TGO) and the peak tension next to the apex that increases in a normally linear manner with the number of cycles \cite{22}. For TBCs with vertical cracks, since the cracks will open under tension, thus tensile stress will be relaxed. In addition, during compression test, it was found \cite{23} that increasing the compressive stress results in micro cracks closing up. The opening and closing of the vertical cracks is the key to preserve the integrity of the TBC, which leads to an improved in-plane tensile strength.

Many patents have been filed to produce a coating with a columnar structure. Ulion et. al. \cite{24} presented a patent on the fabrication of columnar grain ceramic thermal barrier coatings on polished substrates by APS. Gray et. al.\cite{25} presented a thermal barrier coating with an improved columnar microstructure made by APS. By increasing the deposition surface temperature from 600 °C to 950 °C, an increasing degree of columnnarity was found in the TBCs, which improved spallation resistance of the TBCs.
The basic theory for forming a vertically cracked structure is the temperature control in both substrate and the coating particles. Gray et al. [25] published a patent to improve the columnar microstructure of TBCs made by 8YSZ using APS. During plasma spray process, if the substrate temperature is kept at about 300 °C (573 K) which is 0.2 $T_m$, where $T_m$ is the absolute melting temperature of zirconia ($T_m \approx 2988$ K), cohesion of the lamellae layers occurs and presence of the vertically oriented columnar grains is observed. Increasing the substrate temperature is found to promote the formation of continuous columnar structure. The combination of high particle temperature and high substrate temperature results in long solidification time for the splats. This promotes localized re-melting of the deposition surface in the area under the pre-deposited particles and it will create a stronger bond between individual splats.

General Electric Power Generation (GEPG) employed TBCs coatings to extend the life of components [2]. GEPG use top coats made of 6-8 wt% YSZ, while the bond coat is made with Ni(Co)-Cr-Al-Y alloys. The uses of these materials have been successful in improving the high-temperature resistance and thermal cycle life of TBCs.

Ulion et al. [26] presented a patent on the fabrication of columnar grain ceramic thermal barrier coatings on polished substrates. The TBC system is formed by a superalloy substrate, a dense bond coat made of MCrAlY, an alumina layer, and an adherent columnar ceramic coating applied by vapor deposition. The innovative feature presented by this invention consisted of a polished interface between the MCrAlY and the alumina layer, low surface roughness which is less than 25 $\mu$inches RMS. This TBC system presented superior performance in comparison with any other known high temperature coatings at this time.

H. P. Dillon II [18] presented an invention to provide an improved refractory coating to withstand severe high temperature. The coating is composed of several layers of coatings starting
from essentially all metal at the metal surface to all ceramic at the outer surface of the coating; this structure is described as lamellar composite coating. The intended coating provided higher bond strength, thermal shock resistance, and maximum protection to the base from high temperature damage.

2.4. Development of Novel Materials for TBCs Application

Although TBC materials have been developed for more than three decades, there are still many challenging problems facing the development of a robust TBC. The reliability of thermal barrier coatings is determined by the composition of the coating and their mechanical and thermal properties. Yttria-Stabilized-Zirconia is the most common material used for TBCs. Several researchers also have tried adding specific components to improve the properties for novel mixtures suitable for TBCs.

D. Zhu et al.\textsuperscript{[8]} developed advanced multi-components low thermal conductivity TBCs by incorporating multi-components, paired-cluster oxide dopants into zirconia and yttria or hafnia-yttria oxide system. In addition, they investigated the thermal conductivity by laser high-heat-flux technique and sintering behavior of the intended novel TBC material made by atmospheric plasma spray (APS) and by Electron Beam-physical vapor deposited (EB-PVD). The tests were run under high temperature conditions and engine-like heat fluxes including real-time monitoring.

X. Ma et al.\textsuperscript{[27]} developed an innovative thermal barrier coating with low thermal conductivity and high durability. They achieved this objective by co-doped zirconia ceramic with rare earth oxides such as yttrium and gadolinium oxide. They implemented a new process, the solution precursor plasma sprayed process (SPPS), to produce the desirable microstructure, which includes ultrafine splats, high volume porosity, and vertical cracks. The obtained microstructure led to a lower thermal conductivity and good durability in comparison to
Atmospheric Plasma Sprayed (APS) and Electron Beam-physical vapor deposited (EB-PVD) coatings.

Recent studies demonstrated that YSZ--Al₂O₃ composite layer could reduce the oxygen diffusion through the TBCs by lowering the grain-boundary resistivity of YSZ. Hassan, et al. reported the effect on the microstructure provided by adding 0.77 to 1.0 wt% Al₂O₃ to YSZ. In this study, the porosity of YSZ layer was reduced, thus a better gas-tight YSZ layer was obtained. They studied the effect of milling time on the mean particle size of the YSZ powder fired at different temperatures. They found that the mean particle size decreased with milling time, but this change is not noticeable after 48 hrs. In addition they found that the powder fired at 1300°C had the coarser mean particle size, while the powder fired at lower temperature gives a cracked layer, which is the desirable structure for gas turbine application. With reference of the microstructure of the specimens, they reported that the pure YSZ showed a homogeneous monophase structure, while in the specimens with added alumina presented a second phase spots. They concluded that a small amount of alumina enhances the densification of the specimen, which reduces the leak rate for solid oxide fuel cell applications. They also found a reverse effect if the concentration of Al₂O₃ exceeded the solubility limits of 0.5 mol%.

X.-J. Lu et al. studied YSZ with Al₂O₃ prepared by electrophoretic deposition (EPD) for TBC applications. They reported sintering mechanism under compressive stress and the constrained sintering mechanism of the composite coating. The mechanical properties hardness and Young’s modulus of the coating were measured using the nano-indententer XP. The density of the sample was estimated by the Archimedes method. They reported a densification process of the sample. The density changed from 72% to 76% after firing the coatings at 1000°C. The hardness along the cross section increased from the coating/substrate interface up to a distance of 30 μm and slightly up to the top of the surface. This is due to the change in microstructure of the
coating along the thickness, where the porous structure is presented at the zone within 30\(\mu\)m from the interface. Also, they reported that both hardness and Young’s modulus increased after thermally treated at 1000\(^\circ\)C on the time range 30 h - 500 h.

Chen et al.\(^{[31]}\) studied YSZ samples prepared with added alumina made by solution precursor plasma spray process (SPPS). They reported that at 1500 \(\circ\)C processing temperature, \(\text{Al}_2\text{O}_3\) and \(\text{ZrO}_2\) grain sizes were around 350 and 170 nm, respectively. The mismatch of grain sizes between \(\text{Al}_2\text{O}_3\) and \(\text{ZrO}_2\) might be the reason for the high porosity. They found that the typical lamella structure presented in the APS samples was not presented in the SPPS samples, besides it had a dense structure with porosity only of 4.4%.

N. Bansal et al.\(^{[32]}\) studied hot pressing samples made by adding \(\text{Al}_2\text{O}_3\) to YSZ in concentrations varying from 0 to 30 mol\%. Based on the scanning electro microscope (SEM) micrographs, they reported that the density decreased with alumina content. The alumina particulates were dispersed throughout the material. In addition, they detected only cubic zirconia and \(\alpha\)-alumina phases on the specimens indicating that no chemical reaction had occurred during the hot pressing process with x-ray diffraction technique. By adding alumina, they found a stronger material in terms of higher flexure strength and elastic modulus.

H. Guo et al.\(^{[33]}\) prepared and studied \(\text{Al}_2\text{O}_3 – \text{YSZ}\) thermal barrier coatings by co-deposition of \(\text{Al}_2\text{O}_3\) and YSZ onto NiCoCrAlY bond coat by EB-PVD. They reported changes in the structure and composition distribution across the thickness of the coating; it also presented a micro-porous structure. With this study the authors found that the \(\text{Al}_2\text{O}_3 – \text{YSZ}\) samples presented lower thermal conductivity in comparison with pure YSZ samples.

B. Liang et al.\(^{[34]}\) studied zirconia-30 vol.% alumina coatings made by atmospheric plasma spraying using nanosize 3YSZ powders with a mean diameter of 50 \(\mu\)m and alumina powder with mean diameter of 20 \(\mu\)m. They reported microstructure of the coatings and
mechanical properties. The APS coatings presented a smooth surface; the average roughness (Ra) was about 6.03 μm. It showed an excellent bonding between the substrate and the coating. The coating exhibited a lamellar structure with 6% porosity. The microhardness of the compositd coatings was 1.5 times higher than zirconia coating deposited using the same nanosized zirconia powders.

S.R. Choi et al. [35] studied zirconia/alumina composites fabricated by hot pressing with alumina particles or platelets with compositions varies from 0-30 mol%. They reported that the flexure strength and fracture toughness increased by increasing the alumina contents. Another important contribution from this study was that the thermal cycling did not show any strength degradation of the 30 mol% platelet composites.

S. Sodeoka et al. [36] studied thermal and mechanical properties of ZrO₂-CeO₂. By adding CeO₂, which is a material with a higher thermal expansion coefficient and lower conductivity than zirconia, they produced advanced TBCs with high fracture resistance and high heat protective capacity.

2.5. Characterization of Thermal Barrier Coatings

The characterization of the thermal barrier coatings is performed by conducting physical, mechanical, and thermal properties measurements. The physical properties studied are density, porosity, and microstructure. The mechanical properties studied include hardness, Young’s modulus, and failures mechanism. The thermal properties studied include thermal diffusivity, thermal conductivity, thermal expansion coefficient, and thermal cycling.

M. Radovic et al. [37] reported the thermo-physical properties of YSZ and Ni-YSZ as functions of temperature and porosity in the 20-1000°C temperature range. In that study, they determined the specific heat (Cp) by differential scanning calorimetry (DSC). The laser flash method was used to determine the thermal diffusivity (α), while the thermal conductivity was
found as a function of $C_p, \alpha$, and the density of the material. The coefficient of thermal expansion (CTE) was determined using a thermo mechanical analyzer (TMA), while the elastic moduli were determined by resonant ultrasound spectroscopy (RUS). It was found that all the properties changed non-linearly with temperature. They also reported a significant drop in elastic module for both YSZ and Ni-YSZ in the 25 – 600 °C temperature range, attributed to the oxygen vacancies because of order/disorder transition in YSZ.

The porosity effect on thermal properties has also been studied by many researchers. D. Zhu et al. [38] reported porosity effect and thermal conductivity on thermal barrier coatings (TBCs) and environmental barrier coating materials (EBCs), which were used to protect metallic based and Si-based ceramic components in gas turbine engines, respectively. Their experiments were conducted using a laser steady-state heat flux technique to evaluate the thermal conductivity at high temperature for hot-pressed and plasma spray TBC and EBC materials. In their test, the specimen surface was heated by a uniformly distributed heat flux from a high power laser. The plasma spray coatings showed lower initial conductivity values (1.4 W/m-K for EBCs and 1.0 W/m-K for TBCs) as compared to the hot-pressed coating materials due to higher porosity.

H.B. Guo, et al. [39] studied thick TBC made by plasma spray technique. This study provided a complement to the thermo-physical properties by including the thermal cycling behavior, and failure mechanisms. They studied in detail the microstructure of the cross-sections of the plasma sprayed samples. They found three different types of cracks in the coating microstructures: segmentation cracks (cracks running perpendicular to the coating surface and penetrating at least half of the coating thickness), branching cracks (cracks parallel to the coating plane starting form the segmentation cracks), and horizontal delamination (boundary between lamellae); this is due to the different processing conditions during spraying. A high substrate
temperature during the APS process led to a coating with a high segmentation cracks density which improved the contact between the intersplats; on the other hand, a low substrate temperature during the APS process led to a coating with poor contact resistance between the intersplats. Another important finding was that during the thermal cycling experiments the samples with higher segmentation cracks density achieved longer lifetime compared to other coatings.

S.M. Guo, et al. [40] studied the microstructure changes on Yttria-stabilized-Zirconia (YSZ) specimens made by compressing the YSZ powders in a pressing machine. All the samples were then subjected to different sintering processes starting from 1100°C up to 1600°C. The importance of this study was to establish the relationship between the life, mechanical properties and thermal properties of the YSZ related to their microstructure. They reported a gas tight structure of YSZ prepared under high processing temperature; a dense coating should be capable of stopping the crack propagation while conserving the pore network structure for lowering heat conduction. Another important finding was that the percentage of porosity decreased with increase in the heat treatment temperature.

2.6. Thermal Barrier Coating Future Development

Although thermal barrier coating has been developed for the last three decades, there are still many challenging problems facing the development of a robust TBC. In the past ten years, the developing of new coating materials has led to an increase in coatings’ life about 10 to 20 times than previous coatings. The life of the coatings depends on composition, thickness, and the standard of evenness to which it has been deposited [41].

Most of the new coatings have been applied by the atmospheric plasma spray technique; this process itself needs improvements in order to provide an extremely even coating. Several studies have provided in a prospective view specific deficiencies that in the plasma spray process
It is well known that during the plasma spray process, the particles fed into the spray jet must be uniformly heated and accelerated before impacting the substrate. This issue has not been solved yet. In the actual plasma spray process, a variation in properties as temperature, velocity, viscosity, species distribution, etc is observed \([11]\). Normally the particles are injected radially, which induces small differences in the particle trajectory producing an uneven deposited material. This problem should be solved by addressing the feedstock entry and preventing powders and particles from having different thermal-kinetic histories. There is a need to develop new designs for spray torch to provide uniformly distributed feed materials.

Another weakness of the plasma spray process is during the deposition process. The dynamic of the splat’s solidification determines the microstructure of the coating, which influences the properties and durability of the coatings. The formation of the splats depends strongly on the melt-flow characteristics and solidification conditions. Different materials and operation conditions, such as temperature and velocity, can lead to a columnar structure, which is not desirable for certain applications. Future research in the area of deposit formation needs to be done in order to predict the relationship between microstructure, properties and performance of the TBCs in terms of the plasma spray and particle parameters. The fabrication process itself has not been standardized for commercial use. In addition, these standards are key points to establish if the coatings are acceptable for particular applications. On the other hand, it is needed to establish standard methods and procedures for microstructure characterization of the TBCs due to the different strong effect in relatively small errors in measurements techniques \([11]\).

The reliability of thermal barrier coatings (TBCs) is determined by the composition of the coating, the mechanical and thermal properties, and the durability. Thus, accurate property measurements are needed to develop new materials for TBC application. Further studies are
needed to determine stress and thermo cycling modeling of the TBCs systems, especially the study of failure mechanisms by thermal cycling test in order to determine the durability of the TBCs.

Finally, the development of more corrosive-resistance materials is also needed. A new generation of gas turbine that operates at 2500–3000 °F (1371–1659 °C) bringing the double of the horsepower at half of the present engine size may not be so far [41].
CHAPTER 3: THERMAL PROPERTIES MEASUREMENT

3.1. Laser Flash Method

Laser flash method is a standard testing method to measure the thermal diffusivity of materials. The method uses an instantaneous pulsed laser source to heat up the front surface of the sample, and the temperature rise as a function of time of the rear surface is recorded by using an infrared detector. A schematic of the flash method is presented in Figure 6.

![Image of Laser Flash Method Arrangement](image.png)

Figure 6. Schematic of Laser Flash Method Arrangement

The test method was developed and performed by Parker et al. [42] in 1961. Their physical model is based on the thermal behavior of an adiabatic slab material, initially at constant temperature. The model assumes one dimensional heat flow, no heat losses from the slab’s surfaces, uniform pulse absorption at the front surface, infinitesimal short pulse, homogeneity and isotropy of the slab material. The initial temperature distribution within a thermally insulated solid of uniform thickness is given by the following equation [43],

\[
T(x,t) = \frac{1}{L} \int_{0}^{L} T(x,0) \, dx + \frac{2}{L} \sum_{n=1}^{\infty} \exp \left( \frac{-n^2 \pi^2 \alpha t}{L^2} \right) \times \cos \frac{n \pi x}{L} \int_{0}^{L} T(x,0) \cos \frac{n \pi x}{L} \, dx
\]

where \( \alpha \) is the thermal diffusivity in cm\(^2\)/s. If a pulse of radiant energy is instantaneously and
uniformly absorbed in the small depth \( g \) at the front surface \( x=0 \) of a thermally insulated solid of uniform thickness \( L \), the temperature distribution is given by the following equations \(^{42}\),

\[
T(x,0) = \frac{Q}{DCg} \quad \text{for} \quad 0 < x < g \quad \text{and} \\
T(x,0) = 0 \quad \text{for} \quad g < x < L
\]  

(2)  

where \( Q \) is the pulse radiant energy in cal/cm\(^2\), \( D \) is the density in g/cm\(^3\), and \( C \) is the heat capacity in cal / g °C.

With this initial condition, we can write Equation 1. as follows \(^{42}\),

\[
T(x,t) = \frac{Q}{DCL} \left[ 1 + 2 \sum_{n=1}^{\infty} \cos \left( \frac{n\pi x}{L} \right) \sin \left( \frac{n\pi g}{L} \right) \frac{\sin(n\pi g / L)}{(n\pi g / L)} \exp \left( -\frac{n^2 \pi^2}{L^2} \alpha t \right) \right]
\]  

(4)  

For this particular case, since \( g \) is very small number for opaque materials, then \( \sin(n\pi g/L) \approx (n\pi g/L) \). At the rear surface, \( x = L \), then the temperature distribution can be written as follows \(^{42}\),

\[
T(L,t) = \frac{Q}{DCL} \left[ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \frac{\sin(n\pi g / L)}{(n\pi g / L)} \exp \left( -\frac{n^2 \pi^2}{L^2} \alpha t \right) \right]
\]  

(5)  

If we define two dimensionless parameters, \( V \) and \( \omega \) as follows \(^{42}\),

\[
V(L,t) = \frac{T(L,t)}{T_M}
\]  

(6)  

\[
\omega = \frac{\pi^2 \alpha t}{L^2}
\]  

(7)  

where \( T_M \) is the maximum temperature at the rear surface.

We can combine Equations 5, 6, and 7 to obtain,

\[
V = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2 \omega)
\]  

(8)  

Based on this model, when \( V \) is equal to 0.5, \( \omega \) is equal to 1.38, and the thermal
diffusivity ($\alpha$) can be estimated using the following expression \cite{42},

$$
\alpha = 0.1388 \frac{L^2}{t_{1/2}}
$$

(9)

where $L$ is the thickness of the sample (cm) and $t_{1/2}$ is the half time (s), which is the time required for the rear surface to reach half of the maximum temperature rise. This value is obtained from the detector signal raw data. A typical plot of the rear surface temperature detector signal is shown in Figure 7.

![Figure 7. Detector Signal (Volt) as a Function of Time (sec) for YSZ+1 wt % Al$_2$O$_3$ at 400°C](image)

The specific heat ($C_p$) of the samples was measured using FL5000 with the help of an alumina reference sample, whose $C_p$ values are known accurately under different temperatures. The method used for this purpose is based on the fact that the energy received by the YSZ samples and the reference sample is the same under identical laser shots. This can be expressed by the following equation,

$$
(m \times Cp(T) \times \Delta T)_{ref} = (m \times Cp(T) \times \Delta T)_i
$$

(10)
where m is the mass (kg) of all the samples, Cp is the specific heat (J/kg-K), ΔT temperature rise of the sample. For a linear sensor, the detector signal (Volts) is proportional to the temperature change. In above equation, ref indicates the reference material, and i indicates the sample tested.

The thermal conductivity (k) is calculated using the following equation,

$$k(T) = \alpha(T) \times Cp(T) \times \rho$$

(11)

where K is the thermal conductivity (W/m-K), α is the thermal diffusivity (m²/s), Cp is specific heat (J/kg-K), and ρ is the density (kg/m³).

The laser flash method can be applied to determine the thermal diffusivity values in a range that varies from $10^{-7}$ to $10^{-3}$ m²/s in a wide range of temperature (75 K up to 2800 K) according to ASTM E1461-01, which is the standard test method designation for laser flash method.

Other investigators contribute later on in the development of various theories to better describe the real process. The finite pulse effect, for example, only occurs when thin samples of high thermal diffusivity are tested. Thus, the accuracy of the data strongly depends on the mathematical model used to represent the experimental models [44]. Several corrections have been applied to Parker’s equation. In 1962, Cowan included radiative heat loss from the sample surface after the heat pulse was delivered to Parker’s approximation. Cowan’s theory uses a parameter five times the half-times to calculate the time response of the sample rear surface in addition to the half-time parameter. Then, the thermal diffusivity is calculated by the following equation [44],

$$\alpha t_{1/25} = C d^2$$

(12)
where C is the ratio between the temperature change of the half-time and the new temperature parameter.

In 1975, the radiative heat losses were also studied by Clark and Taylor \cite{45}. They made the assumption that the rear surface temperature had a non-constant decreased temperature with time. They established several points during the heating process: 0.2*ΔT, 0.3*ΔT, 0.4*ΔT, 0.7*ΔT, and 0.8*ΔT. Then, they determined different values of the “C” parameter. The values used by them are: T_{0.3}/T_{0.2}, T_{0.7}/T_{0.3} and T_{0.8}/T_{0.4}.

In 1981, Koski \cite{46} improved the previously technique by including the laser pulse width correction into the corrections made by Cowan, and by Clark and Taylor. He also included a parameter “L” to consider the heat loss from the front surface to the rear surface. The parameter “L” is determined by the following equation,

\[ L = \left[ \frac{4 \sigma \varepsilon T^3 d}{k} \right] \]  

(13)

where \( \sigma \) is the Stefan-Boltzman constant, \( \varepsilon \) is the emissivity, T is the average temperature of the sample, d is sample thickness, and k is the thermal conductivity.

Laser pulse in terms of time is represented as a triangular shape signal, but the actual pulse is a finite pulse. Some researchers have proposed various procedures to consider the effect of the actual finite pulse to get a better approximation \cite{47,48}.

3.2. Thermal Properties Test Apparatus

A laser flash system (FlashLine™5000) manufactured by ANTER Co was used to measure the thermal properties for all the samples. The main components of the system,
including the laser power supply, the fiber delivery wand (FDW), the furnace head, and furnace assembly are shown in Figure 8. The system also includes an operating and data analysis software package using the Windows™ platform.

Figure 8. Laser flash System Schematic (FL5000)

Laser pulse source consists of a remote-controlled Class I Nd: glass laser (approximately of 35 joules maximum power with 1.06 wavelength). Standard configuration employs a 200-300 µs pulse width. The output of the laser is channeled through a flexible fiber delivery wand (FDW) to the selected furnace. Pulse delivery through the fiber produces outstanding flux uniformity up to 95%, which greatly improves the data.

The furnace assembly includes a furnace, specimen support, and infrared detector. The furnace is a Kanthal Super Furnace designed and manufactured by Anter Corporation for this application. It can operate up to 1600°C under vacuum or inert gas atmosphere. The temperature control is provided by a Type S thermocouple, it uses two separated thermocouples, one for the furnace and one for the sample.
The specimen support is a multi-sample alumina carousel capable of holding up to six (6) samples of 12.7 mm in diameter at a time, as it is shown in Figure 9.

![Figure 9. Picture of the Specimen Support or Carousel](image)

The infrared detector consists of a liquid nitrogen (LN$_2$) cooled device with an InSb detector. The detector size is 1 sq. mm and fast reaction type according to the manufacturer.$^{[44]}$

![Figure 10. Schematic of the InSb Liquid Nitrogen Cooled Infrared Detector](image)
A pneumatic operated aperture restrictor is interposed between the universal detector assembly (UDA) and the beam-bending mirror. The purpose of the aperture restrictor is to attenuate the radiant power that reaches the UDA to extend its operating range. The beam bending mirror is a front surface IR mirror used to reflect the energy from the sample to the UDA.

3.3. Uncertainty Analysis

An uncertainty analysis was performed to determine the accuracy of all the calculated quantities in terms of the measured quantities. For a calculated quantity (y), the error will be represented by (dy) if (y) is a function of a set of measured quantities (x_1, x_2, x_3, …, x_n), then we can write,

\[ y = f(x_1, x_2, x_3, \ldots, x_n) \]  

(14)

Then using the chain rule we found the derivatives as follows,

\[ dy = \left( \frac{dy}{dx_1} dx_1 + \frac{dy}{dx_2} dx_2 + \frac{dy}{dx_3} dx_3 + \cdots + \frac{dy}{dx_n} dx_n \right) \]

(15)

In order to find the error then we use the following expression,

\[ dy = \left( \left( \frac{dy}{dx_1} dx_1 \right)^2 + \left( \frac{dy}{dx_2} dx_2 \right)^2 + \left( \frac{dy}{dx_3} dx_3 \right)^2 + \cdots + \left( \frac{dy}{dx_n} dx_n \right)^2 \right) \]

(16)

The uncertainty should be expressed as a percentage by using the following expression,
\[ \frac{dy}{y} \times 100\% \]  \hspace{1cm} (17)

The method presented above is the standard procedure to calculate uncertainty of the results from the experimental tests. Now, we need to apply this method to all the quantities calculated in the present study.

First we need to express the results in terms of the measure quantities. The density is function of the following variables: thickness, diameter, and weight. The thickness and diameter were measured using an outside micrometer, range 0-1 in, graduations 0.001 in, and the mass was measured with a balance, graduation 0.0001 g. Then, the density (\( \rho \)) is calculated with the following equation,

\[ \rho = \frac{m}{v} \]  \hspace{1cm} (18)

where \( m \) is the mass (kg), and \( v \) is the volume (m\(^3\)). The volume (\( V \)) is calculated with the following equation,

\[ V = \frac{\pi}{4} D^2 \times t \]  \hspace{1cm} (19)

where \( D \) is the diameter (m) and \( t \) is the thickness (m).

To determine the uncertainty of the volume and density calculations, first we found the derivatives, \( (dp/dm) \), \( (dp/dV) \), \( (dV/dD) \), and \( (dV/dt) \); using the following expressions,
\[
\frac{d\rho}{dm} = \frac{1}{V}
\]
\[
\frac{d\rho}{dV} = -\frac{m}{V^2}
\]
\[
\frac{dV}{dD} = \frac{\pi}{2} D \times t
\]
\[
\frac{dV}{dt} = \frac{\pi}{4} D^2
\]

(20)

The final uncertainty equations for volume and density can be written as:

\[
d(V) = \left[ \left( \frac{\pi}{2} D t d(D) \right)^2 + \left( \frac{\pi}{4} D^2 d(t) \right)^2 \right]^{\frac{1}{2}}
\]

(21)

\[
d(\rho) = \left[ \left( \frac{1}{V} d(m) \right)^2 + \left( \frac{m}{V^2} d(V) \right)^2 \right]^{\frac{1}{2}}
\]

(22)

From the instrumentation used, we have \(d(m) = 0.0001 \text{ g}\) and \(d(D) = d(t) = 0.0001 \text{ in}\), then the uncertainties are 1\% for volume and 4\% for density calculations.

The uncertainty for the thermal diffusivity, thermal conductivity and specific heat has been provided by ANTER Corporation. The accuracy for the thermal diffusivity measurements is within ±5\% and a reproducibility of ±3 \%. The specific heat values calculated using a reference material using the laser flash system (FL5000) has an accuracy of ±6\% and a reproducibility of ±4 \%, according to the manufacturer [44].
CHAPTER 4: POROSITY MEASUREMENTS

4.1. Mercury Porosimetry Method

The porosimetry method is a non-destructive method used to investigate any type of porous materials, including soft, frail, and powders; this includes the quantification of pore diameter, total pore volume and bulk and absolute density. This method provides the widest range of measurable pore radii (from 0.3 nm to $3 \times 10^5$ nm) $^{[49]}$. The accuracy of the methods depends primarily on the accuracy of the measuring of the pore size distribution curve of the standard samples, which is 1% of the total pore volume and the reproducibility of the method is less than 1%.

The mercury porosimetry method is based on the measurement of the volume of mercury intruded or extruded into the pores of the samples. According to Washburn equation, which represents the capillary flow in porous materials, the pore radius is calculated as a function of the pressure given by the as follows $^{[50]}$,

\[
P r = -2 \gamma \cos \theta
\]

where $P$ is the pressure, $r$ is the radius, $\gamma$ is the surface tension of the mercury, and $\theta$ is the contact angle between mercury and sample. A rearrangement of the equation in terms of $r$ leads to the following expression $^{[50]}$,

\[
|r| = \frac{(2900.753\gamma) \cos \theta}{P}
\]

where the pressure is in Psia, $\theta$ in degrees, and $\gamma$ in erg/cm$^3$. 


The volume of mercury intruded/extruded can be normalized by dividing the mercury (Hg) volume by the sample weight (cm$^3$ Hg /g of sample). In addition, the percent volume of mercury intruded/extruded is the volume of mercury intruded/extruded normalized 100% (full scale).

The first derivative of the volume vs. pressure data is represented as dV/dP, this value is used in the calculation of the distribution function. It can be calculated by using the following expression $^{[50]}$,

$$\frac{dV}{dP} = \frac{\text{volume}(i) - \text{volume}(i-1)}{\text{pressure}(i) - \text{pressure}(i-1)}$$  \hspace{1cm} (25)

Finally, these quantities are used to estimate the porosity, pore size distribution and pore number fraction of the sample.

The porosity is evaluated by measuring the total volume of mercury intruded up to the maximum pressure, and calculated using the following equation $^{[50]}$,

$$\text{Porosity}(\%) = \frac{V_t}{V_b} \times 100$$  \hspace{1cm} (26)

where $V_t$ is the total volume of mercury intruded and $V_b$ is the bulk volume of the sample.

The pore number fraction is found by dividing the number of pores in a small interval by the total number of pores. The value obtained is a dimensionless quantity, and represents the fractional amount of pores which are found in that particular interval $^{[50]}$.

The pore size distribution is determined by the calculation of volume pore size distribution function (Dv(r)), which is defined as the pore volume per unit interval radius. It is
estimated using the following equation \[^{[50]}\],

\[
D_v(r) = \frac{P}{r} \frac{dV}{dP}
\]  

(27)

where \(D_v(r)\) is the volume pore size distribution function, \(P\) is the pressure applied, \(r\) is the pore radius, and \(dV/dP\) is the first derivative (slope) of the volume vs. pressure data.

**4.2. Porosity Test Apparatus**

A POREMASTER 33 system manufactured by Quantachrome Instruments was used to measure porosity, pore size distribution, and pore number fraction. The main components of the equipment, the two low pressure stations, and the high pressure station are shown in Figure 11. The system also includes an operating and data analysis software package using the Windows XP platform.

![Figure 11. POREMASTER 33 Main Components \[^{[50]}\]](image)

The POREMASTER 33 equipment is designed to measure pore volumes in the range of about 1000 to 0.0070 \(\mu\)m diameter. The low pressure stations work in a pressure range from 0.2
– 50 psia. For measurements of pore volume smaller than 7 μm, the high pressure station should be used. The high pressure station works in a pressure range from 20 – 33000 psi. For unknown materials both test are required to be run. The system also is provided with a vapor cold trap, to prevent mercury contamination. A schematic of the cold trap is shown in Figure 12. The cold trap is filled with liquid nitrogen to prevent mercury vapor running in the system.

The accuracy for the porosity measurements is within ±0.11% fso (full scale output) and the resolution is 0.000763 psia [50].

![Figure 12. Cold Trap Assembly](imageurl)
CHAPTER 5: EFFECTIVE THERMAL CONDUCTIVITY MODELS

5.1. Thermal Conductivity of Porous Materials

Thermal conductivity is the property of a material that describes its ability to conduct heat. For isotropic materials the thermal conductivity has a constant value throughout the material. In the case of composite materials the thermal conductivity depends on the thermal conductivity of each of the constituent materials. For porous materials the thermal conductivity would be determined by the continuous solid matrix in combination with the thermal conductivity of the pores or dispersed phase within the materials, which is called effective thermal conductivity.

Many researchers have developed theoretical models to estimate the thermal conductivity of a porous material \([51, 52, 53, 54, 55, 56, 57, 61, 64]\). In order to model these porous structures, the microstructure of the coating has to be well known. For this purpose two different fabrication techniques are used in order to produce two distinct and unique microstructures.

The first technique uses a “Pressing Machine,” in which the sample is made using the sintering process of powder. For this purpose powder are compressed with a uni-axial pressure to produce the disk shape samples, then the samples are heated below the melting point until the particles adhere to each other. A particular advantage of this method is the great uniformity of the material and the possibility of creating a material with uniform and controlled porosity.

The second technique used to make the samples is “Atmospheric Plasma Spray,” in which the coatings are made using a melting technique. During this process the powders are melted by a plasma jet and drawn toward the substrate. Upon contact, the molten particle flattens, adheres, and solidified. During this process the so called splats are formed; multiple layers of splats are needed to create the coating. Due to the process of splat formation the
microstructure is characterized by a lamellae structure, which consist of many layers of splats on top of each other. The unique structure has distinctive features such as: globular pores, and defects in between the layers. A very complex microstructure is formed and the porosity and the thermal conductivity are linked to the microstructures.

For thermal modeling of these coatings, the pertinent of the approximation to the real microstructure determines the validity of the proposed model. Five different models to estimate the effective thermal conductivity are presented as follows:

5.2. Series Model

If we consider that the continuous phase and the dispersed phase are arranged such as a series composite wall formed by an alteration of two different layers. A schematic is presented in Figure 13.

![Figure 13. Schematic of Series Model Used to Determine Effective Thermal Conductivity](image)

The effective thermal conductivity for porous materials considers conduction as the only heat transfer mechanism for the structure shown above. The thermal resistance between the layers cannot be estimated. The effective thermal conductivity can be estimated using the following equation \[^{[51]}\],

$$
ke = \frac{1}{\frac{\nu_1}{k_1} + \frac{\nu_2}{k_2}}
$$

(28)

where: ke is the effective thermal conductivity, \(\nu_1\) and \(\nu_2\) are the volume fraction of each phase,
and \( k_1, k_2 \) are the thermal conductivity of each phase.

### 5.3. Parallel Model

If we consider that the continuous phase and the dispersed phase are arranged such as a parallel composite wall formed by an alternation of two materials. A schematic is presented in Figure 14.

![Schematic of Parallel Model](image_url)

**Figure 14. Schematic of Parallel Model Used to Determine Effective Thermal Conductivity**

The effective thermal conductivity for a porous material considering conduction as the only heat transfer mechanism within the structure shown above without thermal resistance between the layers can be estimated using the following equation \[^{51}\],

\[
k_e = \nu_1 k_1 + \nu_2 k_2
\]

where, \( k_e \) is the effective thermal conductivity, \( \nu_1 \) and \( \nu_2 \) are the volume fraction of each phase, and \( k_1, k_2 \) are the thermal conductivity of each phase.

### 5.4. Simplify Model of Heat Conduction in Solid with Two Phases

This model considers a single sphere with thermal conductivity \( k_s \) and radius \( R \) in a solid matrix of a continuous material of thermal conductivity \( k_m \) with a temperature gradient in the \( z \)-direction, as shown in Figure 15.

Assumptions:

i) Steady state

ii) \( k_s \neq k_m \)
iii) Center of the sphere is located in the origin

![Figure 15. Single Sphere in a Solid Continuous Material](image)

The temperature distribution within the region of constant thermal conductivity under steady state conditions is governed by Laplace’s Equation, which can be written in polar coordinates by the following expression \[^{[51]}\]

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial T}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 T}{\partial \phi^2} = 0 \quad (30)$$

Since there is symmetry along the z-axis then the temperature \(T\) is independent of \(\phi\), then the solution for the Laplace’s Equation for this condition can be written as follow:

$$T = A + \frac{B}{r} + C r \cos \theta + \frac{D}{r^2} \cos \theta \quad (31)$$

where, A, B, C and D constant are determined using the boundary condition.

**Boundary Conditions:**

i) At \(r = 0\), the temperature \(T_s \neq 0\)

ii) At \(r = R\), \(k_s \frac{\partial T_s}{\partial r} = k_m \frac{\partial T_m}{\partial r}\) and \(\frac{\partial T_s}{\partial \theta} = \frac{\partial T_m}{\partial \theta}\)
iii) $r >> R$, $T_m = b^z = b \cos \theta$ where, b: magnitude of the temperature gradient in the continuous systems

Plugging back the boundary conditions and rearranging the terms, the temperature distribution can be written as follow,

Temperature Distribution within the Sphere:

$$T_s = b \frac{3k_m}{k_s + k_m} r \cos \theta$$ \hspace{1cm} (32)

External Temperature Distribution:

$$T_m = b \cos \theta - bR^3 \frac{k_s - k_m}{k_s + 2k_m} \frac{\cos \theta}{r^2}$$ \hspace{1cm} (33)

This model is for a single sphere within a solid matrix, then Maxwell $^{[52]}$ – Eucken $^{[53]}$ developed a model to include multiple inclusions and estimate the effective thermal conductivity for two phase materials.

For this model, Maxwell - Eucken consider the dispersed phase as multiples n small spheres with radius $R_2$ and with thermal conductivity $k_2$ contained within a single large sphere with radius $R_1$ and thermal conductivity $k_1$. In addition, for this model the contact between the inclusions is not considered, then the heat conduction pathway in the porous material will follow the continuous phase or solid matrix. The disturbance into the temperature distribution due to the inclusion does not affect other inclusions. Maxwell – Eucken model has a maximum bias throughout the continuous phase. A schematic of this representation is shown in Figure 16.
Assumptions:

i) Multiples inclusions are represented by n spheres with radius $R_2$ and thermal conductivity $k_2$ contained within a large sphere with radius $R_1$ and thermal conductivity $k_1$.

ii) Dispersed phase could never form a continuous conduction pathway.

Incorporating Maxwell - Eucken model assumptions to the single sphere model, Eq. (33), the temperature distribution within the continuous medium can be expressed by the equation \[^{[51]}\]

$$T_m = b \ r \cos \theta - bnR_2^3 \ \frac{k_2 - k_1}{k_2 + 2k_1} \ \frac{\cos \theta}{r^2}$$  \hspace{1cm} (34)$$

The volume fraction of the small spheres ($v_2$) within volume fraction of the large sphere can be expressed using the following equation \[^{[51]}\]

$$v_2 = \frac{nR_2^3}{R_1^3}$$  \hspace{1cm} (35)$$

Then Eq. (33) became \[^{[51]}\].
\[ T_m = b \, r \cos \theta - b v_2 R_1^3 \frac{k_2 - k_1}{k_2 + 2k_1} \frac{\cos \theta}{r^2} \] (36)

If the large sphere is filled with a material with thermal conductivity \( k_e \) then Eq. (33) can be written as follow \(^{[51]}\),

\[ T_m = b \, r \cos \theta - b R_1^3 \frac{k_e - k_1}{k_e + 2k_1} \frac{\cos \theta}{r^2} \] (37)

Then, in order to produce the same results, Eq. (36) is equal to Eq. (37), then \(^{[51]}\),

\[ b \, r \cos \theta - b v_2 R_1^3 \frac{k_2 - k_1}{k_2 + 2k_1} \frac{\cos \theta}{r^2} = b \, r \cos \theta - b R_1^3 \frac{k_e - k_1}{k_e + 2k_1} \frac{\cos \theta}{r^2} \] (38)

Eq. (38) can be rearranged in terms of \( k_e \), and then the effective thermal conductivity can be written as follow \(^{[51]}\),

\[ k_e = k_1 \frac{2k_1 + k_2 - 2(k_1 - k_2)\nu_2}{2k_1 + k_2 + (k_1 - k_2)\nu_2} \] (39)

Maxwell – Eucken Model (ME1) as represented by Eq. (39) represents the case when the thermal conductivity of the small spheres (dispersed phase) is lower than the thermal conductivity of the continuous phase. Similarly, the expression for the effective thermal conductivity in the case that the thermal conductivity of the small spheres (dispersed phase) is
higher than the thermal conductivity of the continuous phase, Maxwell – Eucken Model (ME2) can be expressed by the following equation\textsuperscript{[51]}:

\[
k_e = k_2 \frac{2k_2 + k_1 - 2(k_2 - k_1)(1 - \nu_2)}{2k_2 + k_1 + (k_2 - k_1)(1 - \nu_2)}
\]

(40)

The equations developed by Maxwell and Eucken (EM1 and EM2) are mathematically equivalent to the Hashin – Shtrikman bounds\textsuperscript{[51, 54]}, commonly known as more strict upper and lower limit for effective thermal conductivity calculations in two phase materials.

5.5. Effective Medium Theory

The effective medium theory (EMT) was developed by Landauer\textsuperscript{[55]}. The most important contribution in this model is that there is connection between the inclusions. Starting from the single sphere model, Laundaeur incorporated the multiple inclusions by assuming random distribution of the components\textsuperscript{[51]}. A schematic showing a random distribution is presented in Figure 17.

Figure 17. Schematic of Random Distribution for Effective Medium Theory
Assumptions:

i) Multiples inclusions are represented by a completely random distribution of components.

ii) The effect of local distortions to the temperature distribution caused by individual inclusion could be averaged over a large volume (V).

iii) The temperature distribution within the material could be approximated by a material having a uniform temperature and thermal conductivity $k_e$.

The Effective Medium Theory assumes random distribution of inclusion with an overall uniform temperature distribution. According to the single sphere model, Eq. (33), the net effect from the second term in the right hand side must be zero in order to obtain a uniform temperature distribution. Then,

$$
\int \frac{k_i - k_e}{k_i + 2k_e} p(k_i) dk = 0
$$

(41)

where: $k_i$ is the thermal conductivity of the i component, and $p(k_i)$ is the probability function the component at an arbitrary location within the heterogeneous material with conductivity equals $k_i$.

The random distribution probability function is proportional to the volume fraction $\nu_i$ of the components for $w$ components then Eq. (41) can be written as follow for $w$ components $^{[55]}$,

$$
\sum_{i=1}^{w} \nu_i \frac{k_i - k_e}{k_i + 2k_e} = 0
$$

(42)

For two components then the Eq. (42) can be written as follow,
The Effective Medium Theory Model (EMT) considers that each component has same size and thermal conductivity. The EMT model can be adjusted to take into account microstructural details, such as pore size, pore size distribution, as well as interfacial thermal resistance due to grain boundaries.

**Adjusting the EMT Model with the Interfacial Thermal Resistance:**

In order to adjust the EMT model with the interfacial thermal resistance, the thermal conductivity of the solid phase is estimated as a polycrystalline solid phase. Many researchers have shown that the effective thermal conductivity is affected by the interfacial thermal resistance \[^{[56, 57]}\]. Then the effective thermal conductivity can not be simply calculated using Eq. (43). The polycrystalline thermal conductivity can be calculated using the following equations \[^{[54]}\],

\[
\frac{1}{k_{\text{polycrystalline}}} = \frac{1}{k_{\text{single crystal}}} + n R_{\text{int}}
\]  \quad (44)

and

\[
n = \frac{1}{\phi_{\text{grain}}}
\]  \quad (45)

where, \(n\) is the number of interfaces per unit length, \(\phi_{\text{grain}}\) is the mean grain size diameter, and \(R_{\text{int}}\) is the interfacial thermal resistance of the grain boundaries.
**Adjusting the EMT Model with the Bimodal Pore Size Distribution:**

The effective thermal conductivity model considers a mixture of two homogeneous phases with a similar size of individual phase. According to porosity measurement this is not the case for ceramics thermal barrier coatings. In order to estimate the effective thermal conductivity for TBC materials a two step calculation will be performed.

Step 1:

For the first step, the thermal conductivity of (solid-mesopore), mixture of phases, will be estimated using the volume fraction of mesopore as the dispersed phase and solid matrix data from the porosity test. Then, the following equation (which is the same as Eq. (43) for the EMT model) will be used,

\[
k_{(\text{solid+mesopore})} = \frac{1}{4} \left[ k_2 (3\nu_2 - 1) + k_1 [3(1 - \nu_2) - 1] + \sqrt{(k_2 (3\nu_2 - 1) + 3[(1 - \nu_2) - 1]k_1)^2 + 8k_1 k_2} \right]
\] (46)

where: \(k_1\) is the thermal conductivity of solid, \(k_2\) is the thermal conductivity of air, \(\nu_1\) is the volume fraction of solid, and \(\nu_2\) is the volume fraction of mesopore.

Step 2:

For the second step, the effective thermal conductivity will be determined using (solid+mesopore) as the continuous phase and macropore as the dispersed phase.

Then, the effective thermal conductivity will be estimated using the following equation (which is the same as Eq. (43) for the EMT model),

\[
k_e = \frac{1}{4} \left[ k_2 (3\nu_2 - 1) + k_1 [3(1 - \nu_2) - 1] + \sqrt{(k_2 (3\nu_2 - 1) + 3[(1 - \nu_2) - 1]k_1)^2 + 8k_1 k_2} \right]
\] (47)
where, $k_1$ is the thermal conductivity of (solid+mesopore), $k_2$ is the thermal conductivity of air, $\nu_1$ is the volume fraction of (solid+mesopore), and $\nu_2$ is the volume fraction of macropore.

Since EMT model considers two heterogeneous phases with similar size of individual phases, this approximation adjusts the model to consider the different sizes of pores.

**Adjusting the EMT Model with the Pore Size:**

Another important effect that may change the effective thermal conductivity of porous materials is the fact that the thermal conductivity of air changes as a function of pore size. This is known as Knudsen Effect $^{[54]}$. In order to consider this effect into the EMT model, the thermal conductivity of air will be estimated using the following equations,

$$k_{\text{air}} = \frac{k_{\text{air,o}}}{1 + 2\beta k_n}$$

(48)

$$k_n = \frac{\bar{l}}{d}$$

(49)

where, $k_{\text{air,o}}$ is the thermal conductivity of air at room temperature (0.026 W/m-K $^{[58]}$), $\beta$ is a constant equal to 1.5 for air, and the $\bar{l}$ is the mean free path of the gas (air = $1\times10^{-7}$ m), and $d$ is the mean size pore diameter.

**5.6. Series and Parallel Model Including Contact Resistance for Atmospheric Plasma Spray Samples**

The APS thermal barrier coatings samples were modeled using one-dimensional heat conduction. The heat transfer equation can be written as,

$$q = UA \Delta T$$

(50)
where \( q \) is the heat transfer by conduction, \( U \) is the overall heat transfer coefficient, \( A \) is area of the wall normal to the direction of the heat transfer, and \( \Delta T \) is the temperature gradient across the plane wall.

The overall heat transfer coefficient \( (U) \) is expressed by the following equation,

\[
U = \frac{1}{R_{\text{tot}}}
\]

(51)

where \( R_{\text{tot}} \) is the total resistance.

For the Standard (STD) plasma spray process, a splat coating is created when the particle flattens, adheres, and solidifies. Each splat has a typical thickness in the order of one micron. Multiple splats will form a laminar structure. Thus the STD-TBC samples can be modeled as a series composite wall formed by a solid layer of material and an air gap, Figure 18, the so-called unit cell. This unit cell describes a splat and the air gap is used to model the porosity in the STD-TBC. To simulate the lamellae structure of the STDT-BC, the unit cell will be repeated \( n \) times to give correct TBC thickness.

The total thermal resistance for the STD-TBC samples, which include the thermal contact resistance between materials, is calculated using the following equation,

\[
R_{\text{tot}} = n \left( \frac{L_s}{K_s A} + \frac{R_{i,c1}}{A} + \frac{L_a}{K a} + \frac{R_{i,c2}}{A} \right)
\]

(52)

where \( R_{\text{tot}} \) is the total thermal resistance, \( n \) is the number of series layers of the composite wall, \( L_s \) is the thickness of each layer of solid material, \( K_s \) is the solid material thermal
conductivity, $K_a$ is the air thermal conductivity, $R''_{tc,1}$ and $R''_{tc,2}$ are the thermal contact resistance between the materials, and $A$ is the area perpendicular to the heat flux.

![Diagram](image.png)

**Figure 18. Heat Transfer Model for the STD-TBC and the Equivalent Thermal Circuit**

The VC-TBC samples were modeled as a parallel composite wall. It is formed by a solid layer and an air gap layer, as shown in Figure 19. We will call this model a unit cell as well, which will repeat $m$ times to cover the desired coating surfaces.

The thermal resistance for the VC-TBC samples is calculated using the following equation,

$$
R_{tot} = \frac{1}{m \left( \left[ \frac{R_{tc,1} + R_{tc,2}}{A_s} \right]^{-1} + \left[ \frac{L}{K_s A_s} \right]^{-1} + \left[ \frac{L}{K_a A_a} \right]^{-1} \right)}
$$

(53)

where $R_{tot}$ is the total thermal resistance, $m$ is the number of parallel cells to form a unit TBC area, $L$ is the thickness, $K_s$ is the solid material thermal conductivity, $K_a$ is the air thermal conductivity, $R''_{tc,1}$ and $R''_{tc,2}$ are the thermal contact resistance between the materials, $A_s$ is the area perpendicular to the heat transfer of solid material layers, and $A_a$ is the area perpendicular to the heat transfer of air layers.
In order to compare the values for the total thermal resistance of the TBC samples, we will assume the following parameters:

\[
n = 100, \quad m = 100
\]

\[
L = 200 \mu m, \quad Ls = 2 \mu m, \quad \text{and} \quad La = 0.1 Ls
\]

\[
A = 0.0125 m, \quad As = 125 \mu m, \quad Aa = 0.1 As \quad \text{(per unit with)}
\]

Thermal Conductivity\textsuperscript{[59]}

\[
K_a = 0.067 \text{ W/m-K at 1000K}
\]

\[
K_s = 1.5 \text{ W/m-K (Zirconia)}
\]

Thermal Contact Resistance between Silicon Chip/aluminum\textsuperscript{[60]}

\[
R_{tc} = 0.9 \times 10^{-4} \text{ m-K/W}
\]

Plugging back all parameters in Eq. (52) and Eq. (53), the result for the total resistance for STD-TBC is about 1.474 K-m /W and for VC-TBC it is about 0.0248 K-m /W. A lower total thermal resistance will lead to a higher thermal conductivity for VC-TBC samples. From this ideal model, it is demonstrated that the total resistance for the VC-TBC is lower than the STD-TBC, which facilitates the heat conduction.

The models presented above represent a good approximation of the effective thermal conductivity of porous ceramics. All the methods presented made a distinction between solid matrix and dispersed phase or pores in their calculations, assuming that the pores are spherical
shape. In addition, the porosimetry method assumes that all the pores have spherical shape, which is not always the case for the TBC made by atmospheric plasma spray. For these samples, due to the nature of the APS process, the coatings are made by the adhesion of consecutive layers of molten droplets of materials. The microstructures of the coatings are more complicated than a homogenous phase with spherical intrusions. Some of the characteristics of the pores found in APS coatings are as follows: lamellae pores, closed pores, globular pores, microcracks, intersplat crack, vertical crack, branch cracks, etc, to mention some. Burggeman et. al. [61] presented a correction of the Maxwell-Eucken equation by representing the dispersed phase as ellipsoid. In order to get a better approximation for TBCs, a computer aided image analysis is required to statistically map the distribution of those characteristics, thus the agreement between analytical results and experimental values will be improved [62, 63, 64].
CHAPTER 6: SAMPLE PREPARATION

6.1. Description of Sample Preparation by Using the Pressing Machine

A set of samples was prepared using a mixture of YSZ and aluminum oxide (Al₂O₃). It was prepared using YSZ powders provided by Tosoh Corporation and Al₂O₃ powders (99.99%) provided by SIGMA-ALDRICH. The YSZ powders used in this study are Solid Oxide Fuel Cell grade powders with a higher concentration of Y₂O₃ than the standard TBC grade YSZ. The composition of used YSZ powders provided by the manufacturer is shown in Table 1.

<table>
<thead>
<tr>
<th>Result of Analysis</th>
<th>Y₂O₃</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>Na₂O</th>
<th>Ig-loss</th>
<th>Specific Surface Area</th>
<th>Crystallite size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol 8% (13.30 wt%)</td>
<td></td>
<td>Max 0.005 wt %</td>
<td>0.004 wt %</td>
<td>Max 0.002 wt %</td>
<td>0.070 wt %</td>
<td>0.83 wt %</td>
<td>13.2 m²</td>
<td>240 Angstrom</td>
</tr>
</tbody>
</table>

A high-energy ball mill (SPEX 8000) was operated for 30 minutes to make the YSZ-Al₂O₃ mixture in a stainless steel vial. Vial size is 2-1/4 inch in height and 2 inch in diameter. The ball to YSZ-Al₂O₃ powder weight ratio is 10:1 and a combination of 1/4” and 1/8” stainless steel balls were used. The mixtures were prepared for 0, 1, 2, 3, 4 and 5 wt% Al₂O₃/YSZ powder ratios. The equivalent mol% of there rations are presented in Table 2. During ball milling, the process was kept relatively short, thus the contamination from the stainless steel balls is not
significant. A 0.7 inch diameter stainless steel die was used to make disk shaped samples under uniaxial pressure of 30 MPa on a 16T pressing machine.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt% Al₂O₃</td>
<td>1.28</td>
</tr>
<tr>
<td>2 wt% Al₂O₃</td>
<td>2.56</td>
</tr>
<tr>
<td>3 wt% Al₂O₃</td>
<td>3.83</td>
</tr>
<tr>
<td>4wt% Al₂O₃</td>
<td>5.09</td>
</tr>
<tr>
<td>5 wt% Al₂O₃</td>
<td>6.35</td>
</tr>
</tbody>
</table>

A sequence of the steps needed to make the samples is shown in Figure 20.

Figure 20. Sequence of the Steps to Prepare the Sample by Pressing Machine

The sequences of steps are:

- Put short pushing rod into the die from bottom and stand the die with the short pushing rod on the support plate.
• After sitting the die (steel sleeve) on the support plate put the powder into the die.
• Place the long pushing rod into the die after the powder loaded.
• Then, put another support plate on the top of long pushing rod before pressing operation on pressing machine.
• Bring the die loaded with powder, both support plates, and pressing rods onto the pressing machine. Make the die alignment with spinning screw before pressing operation.
• After pressing operation put the opened steel cylinder on the support plate for taking off pressed sample from the die (drawing of patterns).

A total of five sets of samples each set with 5 samples were prepared, which then were fired to 1600ºC using a MTI-KSL1700X high temperature box furnace. The sintering settings are presented in Table 3. After firing, the samples were grinded to the required diameter of 0.5 inch.

<table>
<thead>
<tr>
<th>Table 3. Setting for the Sintering Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (ºC)</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>Step 1</td>
</tr>
<tr>
<td>Step 2</td>
</tr>
<tr>
<td>Step 3</td>
</tr>
<tr>
<td>Step 4</td>
</tr>
<tr>
<td>Step 5</td>
</tr>
<tr>
<td>Step 6</td>
</tr>
</tbody>
</table>
6.2. Description of Sample Preparation by Atmospheric Plasma Spray

The Atmospheric Plasma Spray samples were prepared by Material Solution International, Texas. The samples were prepared using Atmospheric Plasma Spraying (APS) with bond coat on selected superalloy inconel IN 738 disks. The substrate disks were 0.5 inch diameter and 0.125 inch thickness. The bond coating composition used for the preparation of YSZ APS samples was a standard powder Sultzer Metco powder 386 of nominal composition Ni-22Co-17Cr-12.5Al-0.25Hf-0.4Si-0.6Y (weight %). This bond coating was used for both the standard (STD-TBC) and the vertically cracked (VC-TBC) samples.

The top coat uses 7.65% Y$_2$O$_3$-ZrO$_2$ powders. For the top coat formulations, different procedures were used to form the distinct standard lamellae and the vertically cracked microstructures in the ceramic top coat. Typically, atmospheric plasma spray coatings have morphology characterized by a lamellae structure, in which multiple layers of splats are on top of each other. These layers are formed during the plasma process by applying several passes of melted particles with the plasma spray gun into the substrate. For each gun pass a layer is form, the melted powder will adhere to the previous layer and while it’s cooling down, it flattens to form the layer. The above structure has a low thermal conductivity and it will provide a good thermal barrier effect between the hot gases and the metallic components of the engine. The major disadvantage is that this structure is not strong enough to prevent from peeling or spallation from the substrate. Another kind of structure, vertically cracked structure, is used to prevent and face this issue. In order to obtain these structures the substrate is heated up, during plasma spray process, which will produce a re-melting of the particles already deposited on the substrate. By increasing the temperature of the substrate, a columnar growth of the grain within the coating microstructure is promoted to produce a columnar structure. The benefit is to prevent spallation of the coating and extend the life of the coating, but the major disadvantage is that
these columnar structures will enhance conduction within the coating, thus the thermal conductivity of vertically crack structure is higher compare with standard structure.

All the samples were sprayed using a SG-100 air plasma spray gun with internal powder feed injection. The samples were sprayed using a FANUC 710i robot for precise gun-to-part motion and for repeatability of process. Two sample thicknesses, about 400 microns and 700 microns respectively, were prepared for both STD-TBC and VC-TBC cases. Due to the proprietary nature of this process, no detailed process information was included in this thesis.

For thermal property measurements, the TBC layers were separated from the IN738 substrates using hydrochloric acid solution; then all the TBC samples were sputtering coated with a thin layer of nickel less than 1 micron. The sputtering process was carried in a conventional sputtering system with a 4 inch target of Nickel for about 50 minutes of each side of the sample. Then these samples were sprayed with high temperature grade graphite to eliminate any reflectivity provided by the nickel coating. This process was carried out by hand spraying several layers of graphite on each side of the samples. A key requirement is that the surface of the samples must be smooth and even. It is recommended to wait one or two minutes in-between each application to allow the graphite to dry.

6.3. Thermal Properties Test

A laser flash system (FL5000) was used to measure the thermal diffusivity for all the samples. The FL5000 uses an instantaneous pulse laser source to heat up the front surface of the sample and records the rear surface temperature using an infrared detector.

During the test, three different laser shots at each temperature are performed to measure the thermal diffusivity. In our test, the laser power was set at 1600 V, the acquisition rate used was 10,000 Hz, and the total acquisition time was set to be 20 sec for all the samples due to the low thermal response of the material.
In order to run the test, first we need to turn the laser source power on. Second, we upload the samples in the carousel. The first sample to be loaded is the reference sample, then up to five samples should be loaded in counterclockwise direction. During this step, a verification of sample concentricity with energy beam is required. Third, we need to close the furnace by bringing down the furnace head. Fourth, we need to start the vacuum pump for about 30 min and at the same time fill detector dewar with liquid nitrogen (LN$_2$). The average hold time for the LN$_2$ is 8 hours. Fifth, we need to open compressed air valve up to 40 psi. Sixth, the test is run under a controlled atmosphere by using argon, thus we need a continuous flow rate of 10 cfm and a pressure less than 5 psi. The equipment is provided with a clear glass exit bubbler filled with oil to verify the flow of argon by distinguished visible bubbles in the oil. Seventh, we need to launch the FlashLine software. The software is made in Windows environment which allows us to specify the sample’s characteristics and to establish the temperature range to be tested.

### 6.4. Porosity Test

The porosity of the samples was measured using a mercury porosimetry analyzer, POREMASTER 33 system manufactured by Quantachrome Instruments. The system uses the mercury intrusion method to quantify the total volume of mercury intruded in the pores of the sample material. A high hydrostatic pressure is applied in order to force the mercury to penetrate the void spaces of the material. The low pressure station works from 0.2 to 50 psi and the high pressure station works from 20 psi to 33000 psi, depending on the requirements.

In order to run a test, first we select a penetrometer cell, which is a sample cell used to place the sample and run the porosity test, according to the anticipated intruded volume. Second, we need to weigh a sufficient amount of sample to use, which is typically about 50-80% of the penetrometer stem volume. For unknown samples, a 2 cm$^3$ penetrometer cell is used. The glass bulb is half fill with the sample material. Third, we need to load the sample into the
penetrometer. Fourth, we need to assemble the sample cell for low pressure analysis. A schematic of this assembly is shown in Figure 21. Fifth, we need to place the sample cell in the low pressure station as it is shown in Figure 22, and sixth we run the low pressure analysis.

![Figure 21. POREMASTER Sample Cell Assembly for Low Pressure Analysis](image)

Fifth, we need to place the sample cell in the low pressure station as it is shown in Figure 22, and sixth we run the low pressure analysis.

![Figure 22. Sample Cell Assembly Loaded in the Low Pressure Station](image)

Once the low pressure analysis is completed, the evacuation and refill processes are preformed in order to prepare the sample for the high pressure analysis. For high pressure analysis, the assembly of the sample cell is shown in Figure 23. After removing the sample cell
from the low pressure station, we transfer it to the high pressure cavity, and then we run the high pressure analysis test. The data for low and high pressure analysis are merged by the software.
CHAPTER 7: RESULT OF YSZ-AL$_2$O$_3$ COMPOSITE SAMPLES

7.1. Basic Physical Properties

All the samples were weighed and their geometries were measured before and after the sintering process in order to obtain the bulk density of the material. The density calculations are presented in Table 4, which shows that the YSZ samples have a highest density value around 5700 kg/m$^3$. The standard deviation due to the average of 5 measurements is ± 3.0%.

For comparison, the density value for YSZ - 1% wt Al$_2$O$_3$ is 5296 ± 4, which is lower than pure YSZ samples (5699 ± 4). The density value for YSZ - 2% wt Al$_2$O$_3$ is about 5262 ± 4, and for YSZ - 3% wt Al$_2$O$_3$ the density value is about 5174 ± 4.

According the experimental data obtained, the density decreased with alumina content as expected. The addition of alumina was effective to suppress sintering behavior of YSZ ceramic samples.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Thickness (cm)</th>
<th>Diameter (cm)</th>
<th>Weight (g)</th>
<th>Density (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>0.29</td>
<td>1.26</td>
<td>2.0599</td>
<td>5699 ± 4</td>
</tr>
<tr>
<td>YSZ+1%Al2O3</td>
<td>0.2675</td>
<td>1.26</td>
<td>1.7655</td>
<td>5296 ± 4</td>
</tr>
<tr>
<td>YSZ+2%Al2O3</td>
<td>0.2667</td>
<td>1.26</td>
<td>1.7492</td>
<td>5262 ± 4</td>
</tr>
<tr>
<td>YSZ+3%Al2O3</td>
<td>0.295</td>
<td>1.26</td>
<td>1.9027</td>
<td>5174 ± 4</td>
</tr>
<tr>
<td>YSZ+4%Al2O3</td>
<td>0.293</td>
<td>1.26</td>
<td>1.9256</td>
<td>5282 ± 4</td>
</tr>
<tr>
<td>YSZ+5%Al2O3</td>
<td>0.294</td>
<td>1.26</td>
<td>1.9115</td>
<td>5216 ± 4</td>
</tr>
</tbody>
</table>

The volumetric shrinkage is about 46% for YSZ samples and from 30 to 35% for YSZ-Al$_2$O$_3$ samples. These results are presented in Figure 24.
7.2. Thermal Diffusivity Data

As shown in Figure 25, there is a decrease in thermal diffusivity with the increase of temperature for all the samples prepared; there is temperature dependence in the range tested from 100 - 1000° C.

It appears the addition of Al₂O₃, up to 5% wt, has a smaller impact to the thermal diffusivity of YSZ based TBCs. The values are averaged from a total of 5 measurements; the standard deviation for all the samples is about ± 3.0%.
7.3. Thermal Conductivity Data

The thermal conductivity results which are presented in Figure 26, increase as the temperature increases for the range tested (100 °C–800 °C). The thermal conductivity values for both YSZ and YSZ- Al₂O₃ samples increases with temperature. With the data available, it appears the YSZ- Al₂O₃ samples have a slightly smaller value of thermal conductivity, in comparison to the pure YSZ samples.

![Figure 26. Thermal Conductivity for YSZ Samples Prepared with Addition of Al₂O₃](image)

The YSZ pure sample has higher thermal conductivity than the samples with addition of Al₂O₃. The thermal conductivity value for pure YSZ reported for (100°C – 500°C) varies from 1.69 and 1.97 W/m-K [40]. The thermal conductivity value for YSZ-Al₂O₃ samples at 100°C varies between 1.32 and 1.699 W/m-K. At higher temperature, at 400°C, the thermal conductivity value varies from 1.46 and 1.97 W/m-K. For 600 °C, the thermal conductivity value varies from 1.6 and 2.08 W/m-K. And, finally, for 800°C, the thermal conductivity value varies from 2.08 and 2.63 W/m-K for the YSZ- Al₂O₃ samples.

The lowest thermal conductivity values were found for YSZ-3wt% Al₂O₃ samples, which
are 1.46 W/m-K, 1.6 W/m-K and 2.08 W/m-K at 400°C, 600°C, and 800 °C respectively. At high temperatures, phonon conductivity (radiation) becomes the predominant mechanism of energy transfer. This is a rapid sequence of absorptions and emissions of photons that travel at the speed of light. This mode of conduction is especially important in glass, transparent crystalline ceramic, and porous ceramic at high temperature. In these materials, thermal conductivity increases with increased temperature. The values are averaged from a total of 5 measurements; the standard deviation for all the samples is less than ± 0.1.

7.4. Porosity Data

The porosity results are presented in Table 5. As shown, the porosity for the pure YSZ sample is about 2.3% and the average porosity for the YSZ-Al₂O₃ sample is about 5.37%. The maximum porosity was obtained for YSZ-3 wt% Al₂O₃. Chen et al. [9] reported that at 1500 °C processing temperature, Al₂O₃ and ZrO₂ have grain sizes around 350 and 170 nm, respectively. The mismatch of grain sizes between Al₂O₃ and ZrO₂ may be the reason for the high porosity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>2.32</td>
</tr>
<tr>
<td>YSZ + 1 wt% Al₂O₃</td>
<td>5.79</td>
</tr>
<tr>
<td>YSZ + 2 wt% Al₂O₃</td>
<td>5.59</td>
</tr>
<tr>
<td>YSZ + 3 wt% Al₂O₃</td>
<td>5.96</td>
</tr>
<tr>
<td>YSZ + 4 wt% Al₂O₃</td>
<td>4.82</td>
</tr>
<tr>
<td>YSZ + 5 wt% Al₂O₃</td>
<td>4.69</td>
</tr>
</tbody>
</table>

The mercury porosimetry measurement can lead to a better understanding of the microstructure of the sample. In addition, it gives detail information about the distribution of
pores within the solid matrix. The method measures the volume of mercury intruded into the porous material, thus the results show data for pore size distribution function, pore number fraction, volume fraction of pores, and porosity.

The cumulative volume graph presented in Figure 27, confirms that the samples exhibit bimodal pore size distribution. The pores are divided into two categories, mesopore and macropore. For the YSZ- Al$_2$O$_3$ sample, it is constituted by mesopore (fine pores) with diameter less than 0.1 μm and by macropore (large pore) with diameter larger than 4μm.

![Cumulative Pore Volume of YSZ- Al$_2$O$_3$ Samples](image)

Figure 27. Cumulative Pore Volume of YSZ- Al$_2$O$_3$ Samples

The volume fraction of mesopore and macropore can be determined from Figure 27 and it is presented in Table 6. The results showed that the volume fraction of mesopore increases with porosity. For YSZ + 3 wt % Al$_2$O$_3$, samples with highest porosity, the volume fraction of mesopore is about 0.0115 cm$^3$/g (0.059 cm$^3$) and the volume fraction of macropore is about
0.0005 cm$^3$/g ($0.00045$ cm$^3$). The porosity increases due to the fine pores within the solid matrix. SEM images obtained for all the YSZ-$\text{Al}_2\text{O}_3$ samples also confirm these microstructure characteristics.

Table 6. Cumulative Volume of Pores for YSZ-$\text{Al}_2\text{O}_3$ Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity (%)</th>
<th>Vmesopore (cc/g)</th>
<th>Vmacropore (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>2.32</td>
<td>0.0041</td>
<td>0.0032</td>
</tr>
<tr>
<td>YSZ +1%</td>
<td>5.79</td>
<td>0.0109</td>
<td>0.0017</td>
</tr>
<tr>
<td>YSZ +2%</td>
<td>5.59</td>
<td>0.0106</td>
<td>0.0018</td>
</tr>
<tr>
<td>YSZ +3%</td>
<td>5.96</td>
<td>0.0115</td>
<td>0.0005</td>
</tr>
<tr>
<td>YSZ +4%</td>
<td>4.82</td>
<td>0.0091</td>
<td>0.0023</td>
</tr>
<tr>
<td>YSZ +5%</td>
<td>4.69</td>
<td>0.009</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Figure 28. Pore Size Distribution in Terms of the Volume Distribution Function ($D_v(d)$)

The pore size distribution curves in terms of the volume distribution function, $D_v(d)$, of YSZ--$\text{Al}_2\text{O}_3$ are shown in Figure 28. $D_v(d)$ is defined as the volume of mercury intruded and/or extruded per unit change in pore radius. As it is shown, the $D_v(d)$ values for YSZ is close to zero, which means that the intrusion of mercury to the pores is very little or none. The results for
YSZ-\(\text{Al}_2\text{O}_3\) samples have shown the increases on the pores density, in comparison to pure YSZ.

![Figure 29. Pore Number Fraction Distribution for Pure YSZ and YSZ--\(\text{Al}_2\text{O}_3\)](image)

### 7.5. Microstructure Data

The microstructure of the YSZ samples with the addition of \(\text{Al}_2\text{O}_3\) was studied by Scanning Electron Microscope (SEM) micrograph of the fracture cross section of the samples; the results are shown from Figure 30 to Figure 35.

As shown in Figure 30, the SEM micrograph for pure YSZ, it shows a dense structure, which implies a gas-tight structure. It is noticeable small pores distribute within the solid matrix. With the addition of \(\text{Al}_2\text{O}_3\), the boundaries between grains are not clear and the microstructure is more like a porous material. The formation of an amorphous phase is shown in the grain boundary. These microstructural changes clearly influence the thermal conductivity behavior of the samples with the addition of alumina. From both SEM micrographs and porosity measurements, it can be concluded that the addition of \(\text{Al}_2\text{O}_3\) enhances the formation of pores in all YSZ-\(\text{Al}_2\text{O}_3\) samples; porosity reduces the densification, which results in a decrease of thermal conductivity, which is a desirable trend for TBC application. It is noticeable that the addition of the alumina improved the sintering behavior of the YSZ.
The SEM micrographs for YSZ-Al₂O₃ are presented from Figure 31 to Figure 35. Those images showed a change to the microstructure due to the addition of alumina. Different sizes of pores are distributed within the solid matrix.
Figure 32. SEM Micrographs of YSZ + 2 wt % Al₂O₃ Samples Fired at 1600°C

Figure 33. SEM Micrographs of YSZ + 3 wt % Al₂O₃ Samples Fired at 1600°C
Figure 34. SEM Micrographs of YSZ + 4 wt % Al₂O₃ Samples Fired at 1600°C

Figure 35. SEM Micrographs of YSZ + 5 wt % Al₂O₃ Samples Fired at 1600°C
7.6. Effective Thermal Conductivity Data

The effective thermal conductivity of the samples was estimated using the five models presented in Chapter 5. The thermal conductivity of the solid matrix for the dense YSZ-Al₂O₃ samples was estimated using the Series Model. The input value for the thermal conductivity of dense YSZ was 2.2 W/m-K \(^{[54, 65]}\), which is reported value in the literature for dense YSZ made using a die and a pressing machine. The thermal conductivity of alumina used to estimate is presented in Table 7. After estimating the thermal conductivity of the solid phase, models as described in Chapter 5 were used to calculate the effective thermal conductivity of the samples.

The thermal conductivity of air used in the models is presented in Table 7.

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>( k_{\text{air}} ) (W/m-K)</th>
<th>( k_{\text{Alumina}} ) (W/m-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.032</td>
<td>32.59</td>
</tr>
<tr>
<td>200</td>
<td>0.039</td>
<td>22.16</td>
</tr>
<tr>
<td>300</td>
<td>0.0454</td>
<td>16.35</td>
</tr>
<tr>
<td>400</td>
<td>0.051</td>
<td>13.18</td>
</tr>
<tr>
<td>500</td>
<td>0.057</td>
<td>10.53</td>
</tr>
<tr>
<td>600</td>
<td>0.062</td>
<td>8.85</td>
</tr>
<tr>
<td>800</td>
<td>0.072</td>
<td>7.36</td>
</tr>
</tbody>
</table>

The measured thermal conductivity as a function of volume fraction of alumina compared with the analytical predictions at 100, 400, 600, and 800 ºC are presented in Figure 36 to Figure 39. The experimental thermal conductivity values for samples made with addition of alumina have a better agreement with the Effective Medium Theory Model except for the results presented at high temperature (800 ºC). X. Zhaon et al. \(^{[66, 67]}\) showed that a high temperature the
energy transport in crystalline solids is transferred by lattice vibration and radiation. Clark [68] has developed an approximate method to describe the lattice vibration at high temperature as follow,

$$k_p \rightarrow 0.87 \, k_B \, N_A^{2/3} \, m^{2/3} \, \rho^{1/6} \, E^{1/2} \, M^{2/3}$$

(49)

where, $k_B$ is the Boltzman’s Constant, $N_A$ the Avogadro’s number, $M$ the molecular weight, $m$ the number of atoms per molecule, $\rho$ the material density, and $E$ the elastic modulus. This expression will give a lower value of thermal conductivity estimated at higher temperature.

Figure 36. Effective Thermal Conductivity of YSZ-Al$_2$O$_3$ samples as a Function of Volume Fraction of Alumina for Experimental Measurements and Analytical Predictions at 100 °C
Figure 37. Effective Thermal Conductivity of YSZ-Al₂O₃ samples as a Function of Volume Fraction of Alumina for Experimental Measurements and Analytical Predictions at 400 º C

Figure 38. Effective Thermal Conductivity of YSZ-Al₂O₃ samples as a Function of Volume Fraction of Alumina for Experimental Measurements and Analytical Predictions at 600 º C
Figure 39. Effective Thermal Conductivity of YSZ-Al₂O₃ samples as a Function of Volume Fraction of Alumina for Experimental Measurements and Analytical Predictions.
CHAPTER 8: RESULTS OF ATMOSPHERIC PLASMA SPRAY SAMPLES

8.1. Basic Physical Properties

The densities of the plasma sprayed samples were determined by measuring the thickness, the diameter, and the weight. The thickness was measured using a micrometer, range 0-1 in, graduations 0.001 mm. It is crucial to have the accurate thickness measurement as the overall thickness of the sample is two orders of magnitude smaller than the sample diameter. Thus, the thickness was also determined by scanning electron microscope (SEM) images. The uncertainty for density values is 4% and the standard deviation due to the average of 5 samples is ± 3%. These results are presented in Table 8. The density values are higher for VC-TBC samples compared to STD-TBC for both thicknesses. In addition, the 700 μm thick samples have higher density compared with the 400 μm thick samples. The dense structure for thicker coating has been reported due to the change in control parameter during plasma spray process, specially the high substrate temperature to growth the columnar structure in the vertical cracked samples [15, 16, 17].

<table>
<thead>
<tr>
<th></th>
<th>Density (kg/m³) (± 4%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STD-TBC400</td>
<td>4377</td>
</tr>
<tr>
<td>STD-TBC700</td>
<td>4622</td>
</tr>
<tr>
<td>VC-TBC400</td>
<td>4878</td>
</tr>
<tr>
<td>VC-TBC700</td>
<td>4954</td>
</tr>
</tbody>
</table>

8.2. Thermal Diffusivity Data

The experimental results show an increase in thermal diffusivity for the VC-TBC samples compared with the STD-TBC sample over the 100°C to 800°C temperature range tested. The
average values are presented in Table 9 and Figure 40.

Table 9. Thermal Diffusivity for STD-TBC and VC-TBC Samples as Function of Temperature

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>100 °C</th>
<th>200 °C</th>
<th>400 °C</th>
<th>600 °C</th>
<th>800 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>STD-TBC400</td>
<td>0.0038</td>
<td>0.0033</td>
<td>0.003</td>
<td>0.0028</td>
<td>0.0024</td>
</tr>
<tr>
<td>STD-TBC700</td>
<td>0.0042</td>
<td>0.0041</td>
<td>0.0031</td>
<td>0.0028</td>
<td>0.0027</td>
</tr>
<tr>
<td>VC-TBC400</td>
<td>0.0047</td>
<td>0.0044</td>
<td>0.0037</td>
<td>0.0035</td>
<td>0.0031</td>
</tr>
<tr>
<td>VC-TBC700</td>
<td>0.0051</td>
<td>0.0045</td>
<td>0.00445</td>
<td>0.0031</td>
<td>0.0038</td>
</tr>
</tbody>
</table>

The VC-TBC samples were found to have higher thermal diffusivity values than those of STD-TBC. The average thermal diffusivity value for the VC-TBC samples at 100 °C varies between 0.0047 and 0.0051 cm²/s, and for STD-TBC samples it varies between 0.0038 and 0.0042 cm²/s. At 400 °C, the average thermal diffusivity value for the VC-TBC samples varies between 0.0037 and 0.00445 cm²/s, and for STD-TBC samples it varies between 0.003 and 0.0031 cm²/s. At higher temperature, at 600°C, the thermal diffusivity value for VC-TBC samples varies between 0.0035 and 0.0031 cm²/s and for STD-TBC samples it is about 0.0028 cm²/s. Finally, at 800°C, the thermal diffusivity value for VC-TBC samples varies between 0.0031 and 0.0038 cm²/s and for STD-TBC it varies between 0.0024 and 0.0027 cm²/s. Similar behavior has been reported previously for hot pressed and plasma sprayed samples where the thermal diffusivity has a slight dependence on temperature and varies from 0.003 cm²/s at 20°C to 0.006 cm²/s [37,38,69,70,71,72,73], these data was also included Figure 40 for reference.

All the thermal diffusivity values were averaged from five measurements with standard deviation of ± 5% for STD-TBC and ± 3% for VC-TBC. The data with error bars are shown in
8.3. Thermal Conductivity Data

The average thermal conductivity results are presented in Figure 41 and Table 10. The VC-TBC samples have higher thermal conductivity than STD-TBC samples. The thermal conductivity value for VC-TBC samples at 100°C varies between 1.14 and 1.26 W/m-K and for STD-TBC it varies between 0.83 and 0.97 W/m-K. At 400°C, the thermal conductivity value for VC-TBC samples varies between 1.04 and 1.27 W/m-K and for STD-TBC it varies between 0.76 and 0.83 W/m-K. At a higher temperature, 600°C, the thermal conductivity value for VC-TBC samples varies from 1.05 and 1.25 W/m-K, and for STD-TBC it varies between 0.76 and 0.8 W/m-K. Finally, at 800°C, the thermal conductivity values for VC-TBC samples varies from 0.95 and 1.18 W/m-K and for STD-TBC it varies between 0.66 W/m-K and 0.78 W/m-K.

The thermal conductivity for the STD-TBC samples has been reported to be in the range from 1.0 to 1.4 W/m-K by other researchers [38, 74, 75]. Normally a higher value is expected for samples gone through a high temperature sintering and densification process. For the samples
tested, the STD-TBC400 samples are found to have the lowest thermal conductivity value compare with STD-TBC700 and VC-TBC400, and VC-TBC700. The thermal conductivity values vary from 0.83 W/m-K to 0.66 W/m-K. This is believed to be associated with the low heating rate during the fabrication process [15]. The values are the average of 5 samples, the standard deviation of ±3% for STD-TBC samples, ±2.0% for STD-TBC700, ±2.0% for VC-TBC400 and ±3.0% for VC-TBC700 are shown in Figure 41 as error bars.

![Graph showing thermal conductivity for STD-TBC and VC-TBC samples](image)

**Figure 41.** Thermal Conductivity for STD-TBC and VC-TBC Samples.

**Table 10.** Thermal Conductivity for STD-TBC and VC-TBC Samples

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>100 °C</th>
<th>400 °C</th>
<th>600 °C</th>
<th>800 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>STD-TBC400</td>
<td>0.83</td>
<td>0.76</td>
<td>0.76</td>
<td>0.66</td>
</tr>
<tr>
<td>STD-TBC700</td>
<td>0.97</td>
<td>0.83</td>
<td>0.8</td>
<td>0.78</td>
</tr>
<tr>
<td>VC-TBC400</td>
<td>1.14</td>
<td>1.05</td>
<td>1.05</td>
<td>0.95</td>
</tr>
<tr>
<td>VC-TBC700</td>
<td>1.26</td>
<td>1.27</td>
<td>1.25</td>
<td>1.18</td>
</tr>
</tbody>
</table>
8.4. Porosity Data

The porosimetry method measures the volume of mercury intruded into the porous material, thus the results show data for pore size distribution function, pore number fraction, volume fraction of pores, and porosity. Porosity results for all the samples are presented in Table 11.

<table>
<thead>
<tr>
<th>Table 11. Porosity Results for STD and VC Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (%) ± 5 %</td>
</tr>
<tr>
<td>STD-TBC400</td>
</tr>
<tr>
<td>STD-TBC700</td>
</tr>
<tr>
<td>VC-TBC400</td>
</tr>
<tr>
<td>VC-TBC700</td>
</tr>
</tbody>
</table>

As it is shown in the table above, the higher values of porosity are obtained for the STD-TBC samples; the values are 17% for samples of 400 µm thick and 7.8% for 700 µm thick samples. For the thicker coating the processing time is longer than thinner coatings, then the coating exhibit sintering due to the atmospheric plasma spray process. In comparison, the VC-TBC samples have lower porosity than STD-TBC samples; the values are 14.6 % for samples of 400 µm thick and 5.18 % for samples 700 µm thick samples. To prepare the vertical cracked samples, the substrate is preheated to a very high temperature. It produces a grain growth in columnar structure within the splats. During this heating process the APS ceramic coating experienced sintering, and then the samples are denser if the processing time is higher, which is the case for thicker coatings. This is also confirmed by the density values estimated by weighting-dimensions methods. A dense coat which have high density values will have lower porosity and vice verse. The porosity values presented were averaged from a set of 5
measurements each with standard deviation of $\pm 5.0$ for STD-TBC and VC-TBC for both thicknesses.

The cumulative volume graph, presented in Figure 42, provides more detailed information on the pore sizes and the volume fraction of pores. It also reveals a bimodal size distribution. The two steps presented in the graph correspond to bimodal pore size distribution. According to many researchers, due to the nature of the fabrication process, a typical TBC cross section SEM micrograph will show layers of splats, along with microcracks and pores $^{[76]}$.

![Cumulative Pore Volume of STD-TBC and VC-TBC](image)

Figure 42. Cumulative Pore Volume of STD-TBC and VC-TBC

In addition, the results show that the volume fraction of pores will increase with porosity content of the coating, Table 12.

The pore size distribution by volume and by fraction for STD-TBC and VC-TBC samples are presented in Figure 43 and Figure 44, respectively. The thicker samples have fine pores as the peak in the pore size distribution function graph is shifted to smaller values if we compare...
the STD-TBC700 with STD-TBC400. Also, the same phenomenon is observed for VC-TBC.

Table 12. Volume Fraction of Pores for STD-TBC and VC-TBC

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity (%)</th>
<th>Vmesopore (cm$^3$/g)</th>
<th>Vmacropores (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STD-TBC400</td>
<td>17.4</td>
<td>0.0365</td>
<td>0.0158</td>
</tr>
<tr>
<td>STD-TBC700</td>
<td>7.81</td>
<td>0.0149</td>
<td>0.0128</td>
</tr>
<tr>
<td>VC-TBC400</td>
<td>14.6</td>
<td>0.0248</td>
<td>0.0123</td>
</tr>
<tr>
<td>VC-TBC700</td>
<td>5.18</td>
<td>0.0102</td>
<td>0.0063</td>
</tr>
</tbody>
</table>

Figure 43. Pore Size Distribution Function for the STD-TBC and VC-TBC Samples

The samples made with 400 µm thickness have larger pore sizes compared to samples with thickness of 700 µm for STD-TBC and VC-TBC, Figure 44. This is another evidence that thicker coating experience sintering during the atmospheric plasma spray process. Also, there is a noticeable difference between the pores sizes for STD-TBC and for VC-TBC.
8.5. Microstructure Data

Thermal barrier coatings made by atmospheric plasma spray have a unique microstructure depending on the process parameters and feedstock characteristics. Many researchers had defined some microstructural properties of the coating in order to create a terminology that can be easily recognized and understood by the scientific community \[^{11, 15, 16, 17, 24, 39, 62, 63, 64}\]. Some of these properties are: globular pores, interlamellar crack or intersplat crack, segmentation cracks, branch crack, vertical crack, closed pores, lamellae pores, unmelted particles. All of these terms can be found in the literature and have been extensively used for microstructural characterization of thermal barrier coatings made by atmospheric plasma spray. This nomenclature will be used in the present study to make the characterization of the STD-TBC and VC-TBC coatings. The microstructure of the coatings is obtained using scanning electron microscopy.

Figure 44. Pore Number Fraction of the STB-TBC and VC-TBC Samples
The SEM images of STD-TBC and VC-TBC are presented from Figure 45 to Figure 47. The fractured cross-section of STD-TBC400 coatings are shown in Figure 45. As shown, the microstructure is characterized by a lamellar structure; STD-TBC400 coating showed layers or splat along the thickness of the coating. Interlamellar pores represented with letter (a) in the graph, are evident for both thicknesses. This is caused by improper adhesion during deposition and it could cause delamination between splats during operations. Other features, such as close pores, globular pores, and interlamellar cracks, can also be observed in the atmospheric plasma spray coating. These characteristics should be carefully controlled to provide better properties of the coating. Defects such as interlamellar pores will provide significantly reduction of thermal conductivity, but it will cause premature failure due to poor adhesion between splats within the coatings.

![SEM Micrograph of STD-TBC400 and STD-TBC700](image)

Figure 45. SEM Micrograph of STD-TBC400 and STD-TBC700 (a) Interlamellar Cracks, (b) Globular Pores, (c) Lamellae structure thickness, (d) Close Pores (e) Dense Structure

As expected, thicker coating STD-TBC700 has dense structure. This coating still has lamellae structure (see lamellar structure identified with letter (c) in the plot) but the adhesion between splats is better than the STD-TBC400 coating. Also, dense structures, represented by letter (e) in the graph, are observed. This defect appears because of longer processing time needed for creating the thick coating. For the STD-TBC700, there are still present some
interlamellar pores but the lamellae structure is more cohesive. Also, the thickness of the splats is reduced from ~10 μm for STD-TBC400 to ~5 μm for STD-TBC700 coatings, indicating the sintering of the coating occurring during coating deposition.

For the VC-TBC samples, the grain structures are aligned in the vertical direction with respect to the cross-section area and the coating has multiple cracks in the same direction, as it is shown in Figure 46 and Figure 47. This microstructure enhanced the heat transfer along the vertical direction and strongly influenced the increase of thermal conductivity observed for those samples. The thermo-physical property changes are directly linked to the samples microstructures demonstrated by the measured thermal properties and confirmed by SEM images.

In addition, for thicker coatings, VC-TBC700, branch cracks as well as vertical cracks are observed within the thickness of the coating.

The formation of branch cracks or vertical cracks is usually due to the mismatch between the substrate and the coating. The cracks are initiated in the surface of the coating and propagated within the thickness. As it is shown in the graphs, the VC-TBC700 has a denser structure compared to VC-TBC400.
8.6. Effective Thermal Conductivity Data

The effective conductivity of the samples was estimated using the models presented in Chapter 5 and the results are presented in Figure 48 to Figure 51. For the TBC samples, the input value for the thermal conductivity of the solid matrix of YSZ used in the models was 2.2 W/m-K (value reported in the literature for dense YSZ)\(^ {54,59}\).

![Figure 48](image_url)

**Figure 48.** Effective Thermal Conductivity for STD-TBC400 as a Function of Temperature for Experimental Measurements and Analytical Predictions
For thin coatings, STD-TBC400 and VC-TBC400, the predictions have a better agreement with the effective medium theory adding grain resistance, bimodal size distribution, and pore size model (EMT + Grain + Bimodal + Pore Size). According to the results, the effective thermal conductivity is overestimate if the changes in thermal conductivity due to pore size are not included, especially for the thin coating cases where the porosity is high, then the pore size has a strong tendency to change the effective thermal conductivity of the coating. According to the Knudsen effect \[^{[54]}\], the pore size can greatly influence the thermal conductivity of air for pore size smaller than 10 \( \mu \text{m} \).

![Thermal Conductivity VC-TBC400](image)

Figure 49. Effective Thermal Conductivity for STD-TBC700 as a Function of Temperature for Experimental Measurements and Analytical Predictions

For thicker coatings, the results for the temperature range tested 100 – 800 °C agrees with the Maxwell-Eucken Model (EM2). The results for STD-TBC700 and VC-TBC700 are presented in Figure 50 and Figure 51, respectively. The same results were obtained by Smith et. al. \[^{[57]}\].
The EM2 model assumes that the conduction path is dominated by the continuous phase, the disturbance into the temperature due to the inclusions does not affect other inclusions. The samples with thicknesses of 700 µm for both STD and VC structure are denser compared to samples with 400 µm, the processing time to create thicker coatings generated the release of gases trapped into the coating resulting in fine pores and denser coatings compared to thin coatings also this provoke some aging of the coatings.

The effective medium theory suggested a well thermally connected inclusions. If we examine closely the APS structure for thicker coating, even though the coating are denser, the microstructure is characterized by a series of different defect between the splat, such as vertical, horizontal, and branch crack. These cracks propagate as the coating is treated by longer processing time during plasma spray. The nature of the fabrication process of coating and its structure determined the appropriate model. In addition, the results obtained from the

![Thermal Conductivity STD-TBC700](image)

Figure 50. Effective Thermal Conductivity for STD-TBC700 as a Function of Temperature for Experimental Measurements and Analytical Predictions

The effective medium theory suggested a well thermally connected inclusions. If we examine closely the APS structure for thicker coating, even though the coating are denser, the microstructure is characterized by a series of different defect between the splat, such as vertical, horizontal, and branch crack. These cracks propagate as the coating is treated by longer processing time during plasma spray. The nature of the fabrication process of coating and its structure determined the appropriate model. In addition, the results obtained from the
POREMMASTER assume spherical shape pores which disagree with the actual pore shape and crack variety in these APS coatings. In order to use the effective medium theory to represent these thicker coatings, a statistical analysis including pore’s aspect ratio has to be done and it has to include a better representation of the non-spherical pore shape.

Figure 51. Effective Thermal Conductivity for VC-TBC700 as a Function of Temperature for Experimental Measurements and Analytical Predictions
CHAPTER 9: CONCLUSION

In the present study the thermo-physical properties of the TBCs samples were investigated. These samples were made of two different fabrication techniques, namely pressing machine and atmospheric plasma spray process. A laser flash system was used to measure the thermal diffusivity, thermal conductivity, and specific heat. The porosity of the samples was measured using a mercury porosimetry analyzer, POREMASTER 33 system. The test was performed to determine the porosity, pore size distribution, and the pore number fraction of all samples. A Scanning Electron Microscope (SEM) was used to study the microstructure of the samples. It was observed that the thermal conductivity values strongly depend on the porosity, density, and microstructure of the samples; especially for the STD-TBC and VC-TBC samples.

For the pressing machine samples, it can be concluded that adding Al$_2$O$_3$ would reduce the thermal conductivity values of YSZ, due to the increase of porosity in the YSZ-Al$_2$O$_3$ composite samples. Based on the SEM images, the YSZ structure is close to a gas tight structure with a porosity of only 2.3%, which is a desirable structure for solid oxide fuel cells application. Furthermore, the YSZ-Al$_2$O$_3$ composite has higher average porosities of about 5.37% in comparison with pure YSZ samples. An analytical comprehensive model to estimate the effective thermal conductivity for porous ceramics has been successfully developed. The model predictions were compared with the experimental results. The core of the model is based on the calculation of the thermal conductivity in terms of the volume fraction of each phase (solid and pore).

The experimental thermal conductivity values obtained for samples made with addition of alumina have a better agreement with the Effective Medium Theory (EMT) Model; this model considers the connection between the pores and the continuous matrix, as well as the
interconnection of the solid matrix. For the YSZ-Al$_2$O$_3$ samples, due to the high compression to
the powders using a pressing machine, the morphology of the pore network is interconnected and
not particularly oriented. Thus, the EMT model leads to a better approximation.

Addition of alumina into YSZ may lead to a desirable structure for TBC applications
because the porous composite has a better thermal barrier effect. The addition of alumina was
ineffective to suppress the sintering behavior of YSZ ceramic samples.

For the atmospheric plasma spray samples, the thermal diffusivity, thermal conductivity,
porosity, and SEM images for the STD-TBC samples and VC-TBC samples were studied. The
results show an increase in both thermal diffusivity and conductivity for the VC-TBC samples,
compared with the STD-TBC sample over the temperature range tested. In addition, there is a
temperature dependence of the thermal diffusivity and the thermal conductivity for both VC-
TBC and STD-TBC samples. The porosity measurements reveal that a thicker coating has lower
porosity, for both STD-TBC and VC-TBC samples. For the thicker coating the processing time is
longer than thinner coatings, thus the coating exhibits sintering due to the heating in the
atmospheric plasma spray process. Furthermore, the VC-TBC samples have lower porosity than
STD-TBC samples. To prepare the vertical cracked sample the substrate is preheated to a very
high temperature to promote columnar grain growth. During this process, it generated a dense
coating. In comparison to STD-TBC samples, significant increases of thermal diffusivity and
thermal conductivity values can be found for the VC-TBC samples. This is attributed to the
vertical columnar microstructure in the VC-TBC top coating, and this has been demonstrated by
the proposed STD-TBC and VC-TBC heat transfer models presented in Chapter 5, section 5.6.

The models presented to estimate the effective thermal conductivity represent a good
approximation of the effective thermal conductivity of porous ceramics if there is a good
interconnection between the pores. For STD-TBC and VC-TBC samples, due to the nature of the
APS process, the coatings are made by the adhesion of consecutive layers of molten droplets of materials. In addition, the exposure at high temperature promotes sintering phenomena within the TBC. The microstructures of the coatings are more complicated than a homogenous phase with spherical intrusions or a random distributed dispersed phase. Some of the characteristics of the APS coatings are as follows: lamellae pores, closed pores, globular pores, microcracks, intersplat crack, vertical crack, branch cracks, etc. Thus, the analytical results obtained for the effective thermal conductivity for thin coatings have a good agreement with the effective medium theory including the correction for grain resistance, bimodal size distribution, and pore size for the temperature range tested. For thicker coatings, the effective medium theory over estimate the values of the thermal conductivity, instead the Maxwell-Eucken equation 2 has a better approximation. This model takes into account that the conduction path way is thru the continuous phase, thicker coating is denser due to longer processing time, thus the layer of the coating is more cohesive and adhere to each other. It is observed that the microstructure and the porosity are directly linked with the thermo-physical properties. The pertinent approximation to the real microstructure determines the validity of the chosen model.
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VITA

Monica Bohorquez de Silva was born in Maracaibo, Venezuela, in March, 1973. She received a Bachelor of Science in Mechanical Engineering degree from University of Zulía, Venezuela, in 1998 and then she was hired as a Field Engineer at JANTESA Consulting Corporation. Between 2001 and 2004 she held faculty duties at University of Zulia, Maracaibo, Venezuela, as an Assistant Professor in the Mechanical Engineering Department. Since fall 2004, she attended Louisiana State University Graduate School to pursue her Doctor of Philosophy degree in mechanical engineering.