Design and Fabrication of Porous Yttria-Stabilized Zirconia Ceramics for Hot Gas Filtration Applications

by

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ABSTRACT

Hot gas filtration has received growing attention in a variety of applications over the past few years. Yttria-stabilized zirconia (YSZ) is a promising candidate for such an application. In this study, we fabricated disk-type porous YSZ filters using the pore forming procedure, in which poly methyl methacrylate (PMMA) was used as the pore-forming agent. After fabricating the pellets, we characterized them to determine their potential for application as gas filters. We investigated the effect of sintering temperature, polymer particle size, and polymer-to-ceramic ratio on the porosity, pore size, gas permeability, and Vickers hardness of the sintered pellets. Furthermore, we designed two sets of experiments to investigate the robustness of the fabricated pellets – i.e., cyclic heating/cooling and high temperature exposure. This study ushers in a robust technique to fabricate such porous ceramics, which have the potential to be utilized in hot gas filtration.
GRAPHICAL ABSTRACT

Blast furnace off gas

Hot gas filter

Porous YSZ ceramic membrane

Courtesy: Tenova Goodfellow

Porous YSZ ceramic membrane

Blast furnace off gas

Hot gas filter

Porous YSZ ceramic membrane
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## TABLE OF CONTENTS

ABSTRACT .................................................................................................................................................. ii

ACKNOWLEDGMENTS ............................................................................................................................. iv

TABLE OF CONTENTS ............................................................................................................................... iv

LIST OF FIGURES ......................................................................................................................................... vii

NOMENCLATURE ......................................................................................................................................... ix

1. CHAPTER ONE – INTRODUCTION ........................................................................................................ 1
   1.1. Porous Materials .................................................................................................................................. 1
       1.1.1. Introduction to Porous Materials ................................................................................................. 1
       1.1.2. Application of Porous Materials ................................................................................................. 2
           1.1.2.1. Hot Gas Filtration ................................................................................................................. 3
   1.2. Porous Ceramics ..................................................................................................................................... 4
       1.2.1. Yttria-stabilized Zirconia ............................................................................................................. 8
       1.2.2. Fabrication Techniques .............................................................................................................. 11
           1.2.2.1. Pore Forming Agent ............................................................................................................. 12
   1.3. Powder processing .............................................................................................................................. 14
       1.3.1. Mixing and blending .................................................................................................................... 15
       1.3.2. Powder compaction .................................................................................................................... 16
           1.3.3.1. Stages of sintering ............................................................................................................... 18
   1.3. Research Objective ............................................................................................................................ 25
   1.4. Thesis Overview .................................................................................................................................... 26

2. CHAPTER TWO – MATERIALS AND EXPERIMENTAL PROCEDURES .................................................. 27
   2.1. Materials .............................................................................................................................................. 27
   2.2. Fabrication of Porous YSZ .................................................................................................................. 27
   2.3. Characterization of the Fabricated Pellets .......................................................................................... 29
       2.3.1. Scanning Electron Microscopy (SEM) ....................................................................................... 29
       2.3.2. Vickers Hardness ....................................................................................................................... 29
       2.3.3. Helium Gas Pycnometer ........................................................................................................... 29
       2.3.4. Mercury Intrusion Porosimetry (MIP) ...................................................................................... 30
       2.3.5. Gas Permeability ....................................................................................................................... 30
       2.3.6. Particle Size Distribution ......................................................................................................... 32
3. CHAPTER THREE - RESULTS AND DISCUSSIONS ................................................................. 33
   3.1. YSZ Powder Characterization .................................................................................. 33
   3.2. YSZ Pellet Without PMMA - the Benchmark ......................................................... 34
   3.3. Powder Sonication in the Fabrication Process ......................................................... 35
   3.4. Sintering Temperature ............................................................................................. 36
       3.4.1. Microstructure .................................................................................................. 36
       3.4.2. Effect of Sintering Temperature on Porosity .................................................... 38
       3.4.3. Effect of Sintering Temperature on Vickers Hardness ..................................... 39
       3.4.4. Effect of Sintering Temperature on Pore Size ................................................. 42
       3.4.5. Pore evolution during sintering ........................................................................ 43
   3.5. Polymer Particle Size ............................................................................................... 47
       3.5.1. Effect of Polymer Particle Size on Pore Size .................................................... 47
       3.5.2. Effect of Polymer Particle Size on Porosity ...................................................... 49
       3.5.3. Effect of Polymer Particle Size on Permeability .............................................. 49
   3.6. Polymer to Ceramic Ratio ....................................................................................... 50
       3.6.1. Microstructure .................................................................................................. 50
       3.6.2. Effect of Polymer to Ceramic Ratio on Porosity .............................................. 51
       3.6.3. Effect of Polymer to Ceramic Ratio on Permeability ....................................... 52
   3.7. Robustness Investigation ......................................................................................... 53
       3.7.1. Cyclic Heating/Cooling Experiments ............................................................... 53
           3.7.1.1. Porosity and Gas Permeability .................................................................. 54
       3.7.2. High Temperature (1700 °C) Exposure Experiment ......................................... 54
           3.7.2.1. Microstructure ........................................................................................ 55
           3.7.2.2. Gas Permeability and Pore Size ............................................................... 55
4. CHAPTER FOUR - CONCLUSIONS ................................................................................. 58
5. CHAPTER FIVE - RECOMMENDATION FOR FUTURE WORK .................................. 60
REFERENCES ...................................................................................................................... 61
LIST OF TABLES

Table 1. Polymer decomposition temperatures (temperatures for 50% polymer evaporation during heating in nitrogen) .................................................... 23
Table 2. Experimental matrix of pellets fabrication ................................................................. 28
Table 3. Relationship between Young's modulus and porosity ................................................. 41

LIST OF FIGURES

Figure 1. Backscattered scanning electron micrographs of mullite-alumina ceramics: (a) MA0G, (b) MA20G, (c) MA40G and MA60G (the value after MA is the volume percentage of graphite that was added as the pore forming agent) .......................... 6
Figure 2. SEM images of the surfaces of porous reaction bonded mullite specimens sintered at (a) 1450 °C, (b) 1550 °C, (c) 1650 °C. ........................................................................................................... 7
Figure 3. Surface morphology for the tubular membrane sintered at various temperatures for 1 h: (a) 1050 °C, (b) 1150 °C, (c) 1200 °C. ........................................................................................................... 8
Figure 4. ZrO$_2$-Y$_2$O$_3$ phase diagram: t = tetragonal phase; m = monoclinic phase; c= cubic phase. ............................................................................................................... 9
Figure 5. Schematic representation of transformation toughening in YSZ ........................................ 10
Figure 6. The three techniques for powder mixing: diffusion, convection, and shear ............ 16
Figure 7. Schematic illustration of the different stages of powder compaction .................. 17
Figure 8. Idealized models for the three stages of sintering, (a) initial stage, (b) near the end of the initial stage, (c) intermediate stage, (d) final stage ................................................................. 19
Figure 9. SEM images taken during (a) initial, (b) intermediate, (c) final stages of sintering ... 22
Figure 10. Relative density as a function of sintering time to illustrate the selection of optimum isothermal sintering temperature. ................................................................. 24
Figure 11. Schematic of the gas permeability measurement setup ........................................... 31
Figure 12. (a) Low magnification, (b) medium magnification, (c) high magnification SE images of as-received YSZ powder ................................................................. 33
Figure 13. Particle size distribution of the as-received YSZ .................................................... 34
Figure 14. Surface SEM micrographs of pure YSZ pellets sintered at 1400°C without adding PMMA as the pore former ................................................................. 35
Figure 15. Surface SEM micrographs of the fabricated pellets at 1400 °C, PMMA-to-YSZ ratio of 30/70 (%v/%v), PMMA particle size of 3 µm: (a) with sonication, (b) without sonication ................................. 36
Figure 16. Secondary electron images of the polished cross sections at various sintering temperatures: (a) 1300, (b) 1400, (c) 1500, (d) 1600, (e) 1700 °C ................................................................. 37
Figure 17. Effect of sintering temperature on the porosity of the sintered YSZ pellets .......... 38
Figure 18. Effect of sintering temperature on the density of the sintered pellet ...................... 39
Figure 19. Effect of sintering temperature on the Vickers micro hardness of the sintered YSZ pellets, ................................................................................................................. 40
Figure 20. Relationship between porosity and hardness of the sintered YSZ pellets ............ 40
Figure 21. Effect of sintering temperature on the pore size of the sintered YSZ pellets. ....... 42
Figure 22. (a) Schematic illustration of grain growth leading to pore coalescence, (b) grain
growth and pore coalescence in a sample UO₂ after 2 min, 91.5% dense, and 3 h, 91.9% dense
at 1600°C. .................................................................................................................. 43
Figure 23. Circular pore surrounded by four grains. ...................................................... 44
Figure 24. Pore stability in two dimensions for dihedral angle of 120°. ......................... 45
Figure 25. Conditions for pore stability in three dimensions as a function of pore coordination.
........................................................................................................................................ 46
Figure 26. Effect of sintering temperature on the gas permeability of the sintered YSZ pellets.
........................................................................................................................................ 47
Figure 27. Effect of polymer particle size on the pore size of the sintered YSZ pellets ....... 48
Figure 28. Effect of polymer particle size on the porosity of the sintered YSZ pellets......... 49
Figure 29. Effect of polymer particle size on the permeability of the sintered YSZ pellets..... 50
Figure 30. BSE images of various PMMA-to-YSZ (%v/v): (a) 50/50, (b) 40/60, (c) 30/70, (d)
20/80, (e) 10/90, (f) 0/100. .......................................................................................... 51
Figure 31. Effect of polymer to ceramic ratio on porosity of the sintered YSZ pellets. ....... 52
Figure 32. Effect of polymer to ceramic ratio on the permeability of the sintered YSZ pellets.53
Figure 33. (a) Effect heating (1400 °C-1h)/cooling (150 °C, 30 min) number of cycles on
porosity. (b) Effect heating (1400 °C-1h)/cooling (150 °C, 30 min) number of cycles on
porosity ............................................................................................................................ 54
Figure 34. SEM images of the porous YSZ ceramics after exposure to 1700 °C for: (a) 1 h, (b)
2 h, (c) 3 h, (d) 4 h. ...................................................................................................... 55
Figure 35. Effect of high temperature exposure dwelling time on the (a) permeability, (b)
porosity of the sintered YSZ pellets. ............................................................................. 56
NOMENCLATURE

LIST OF SYMBOLS

\( \mu \)  Dynamic viscosity
\( k \)  Darcian permeability
\( v \)  Fluid velocity

ABBREVIATIONS

YSZ  Yttria Stabilized Zirconia
PMMA  Poly Methyl Methacrylate
SEM  Scanning Electron Microscopy
PSD  Particle Size Distribution
DI Water  Deionized Water
MIP  Mercury Intrusion Porosimetry
**1. CHAPTER ONE - INTRODUCTION**

Many industrial processes, such as fluidized beds, cement production, minerals processing, and metals smelting (e.g., iron blast furnace) emit off gas streams, consisting of mixed gases with particulate matters of variable composition and size. Many of these off gas streams are at very high temperatures (more than 1000 °C, even up to 1800 °C). Managing and cleaning these off gas streams is a necessary step in many industrial processes.

Because many of these processes run at elevated temperatures, ceramic filters are the material of choice, due to their excellent physical properties, such as high thermal stability, high mechanical strength, and chemical stability. Most ceramic filters available in the market can operate up to a maximum temperature of 1000 °C; however, some applications (such as blast furnace) require a material that can sustain temperatures of up to 1800 °C. Thus, developing a porous ceramic filter that can sustain such harsh conditions is highly of interest.

**1.1. Porous Materials**

**1.1.1. Introduction to Porous Materials**

Porous materials are defined as solids containing pores. Generally, porous materials have a porosity of 20-95%. Porosity is defined as the fraction of pore volume to total volume. Pores are categorized into two types: closed pores, which do not communicate with the surface and are isolated from the outside, and open pores that are connected to the outside of the material. Penetrating pores are a type of open pores, which have at least two openings at two sides of the porous materials.

Porous materials can be classified by different criteria, such as pore size, pore shape, as well as materials and production techniques\(^1\). The international Union of Pure and Applied Chemistry (IAUPC) has recommended specific nomenclature for characterizing porous materials, i.e., materials with pore size smaller than 2 nm, between 2 nm and 50 nm, and higher than 50 nm are considered as microporous, mesoporous, and macroporous, respectively. The properties of porous materials, for example mechanical strength, depend on the nature of the material, pore geometry, porosity, and pore size\(^2\). Classification on the basis of material’s nature,
e.g., metals, glasses, ceramics, paper, and cloth is an important factor when designing porous materials. Materials are selected depending on their properties, including mechanical strength, chemical stability, and high temperature resistance. Recently, porous ceramics with high temperature stability, strength, catalytic activity, as well as erosion and corrosion resistance have been developed. These properties make the porous materials excellent candidates for applications under harsh environments.

1.1.2. Application of Porous Materials

Porous materials are used in wide range of applications, e.g., purifying drinking water by activated carbon and removing dusts from high purity process gases in semiconductor production. In many industrial applications of porous materials, open pores are required. Filters and carriers for catalysts and bioreactors require a high fraction of open pores, whereas thermal insulators require closed pores. Filters require relatively narrow pore size distribution to allow selective filtration. Bimodal pore size distribution is beneficial for bioreactors, where small pores are used to immobilize enzymes and bacteria, while large pores are used as channels to transport reactants and products.

Porous materials are also used for wide ranges of applications, such as bioreactors, gas sensors, thermal insulators, electrodes, among others. In many applications of porous materials, high open porosity is desirable to increase the specific surface area or fluid permeability. However, increasing the porosity negatively affects the mechanical properties, limiting the applicability of the porous material. A combination of high porosity and high strength is required to make the porous material suitable for severe operating conditions.

Porous materials are used as catalysts or as their carrier. High specific surface area is required for the catalytic applications to increase the surface area in contact with reactants. At high temperatures, the surface area decreases because of surface diffusion or evaporation-condensation. High thermal stability is important for high temperature applications, such as catalysts used in automobile exhausts gases. Another main application of porous materials is filtration. Porous filters are used in a wide range of applications from dairy production to high-
tech processing. High penetrating porosity, high fluid permeability, narrow pore size distribution, and high mechanical strength are required properties for porous material filters.

Advanced ceramics are useful materials for filters, because they have high thermal resistance, high chemical stability, and high mechanical strength. Porous ceramic filters are used in new fields, e.g., ceramic foams are used to filter molten metals for casting. For such applications, alumina, aluminum titanate and silicon carbide have been used. When the molten metal passes through a ceramic foam, inclusions are removed and the flow of the molten metal is rectified.

Ceramic materials that can resist extreme temperatures are considered a great candidate for applications under harsh environments, such as hot gas filtration, because of their thermo-mechanical and chemical stability. High-density and low-density ceramics are available as filter media. The porosity of the high-density and low-density ceramics is about 40% and 90%, respectively. Low-density ceramic have a high internal surface area because of the fiber structure.

1.1.2.1. Hot Gas Filtration

Gas filtration at temperatures above 260 °C is considered hot gas filtration, according to the VDI (Verein Deutscher Ingenieure, Association of German Engineers) guidelines 3677-3, and it is usually performed at temperatures of up to 900 °C and pressures of up to 8 MPa in both oxidizing and reducing atmospheres with chemically aggressive compounds. Such operating conditions require materials with high mechanical strength as well as thermal and chemical stability. The filter media and the vessel materials must be stable against temperature, pressure, and chemical composition of the gas and dust.

Hot gas filtration has been attracting growing attention in a wide variety of processes over the last decades. The main reasons are the increase in emissions level, the possibility to simplify or to intensify processes, issues with supplying and cleaning the wash waters for wet scrubbing, as well as the development of new processes. Hot gas filtration can improve the quality of products, process efficiency, and process economics. In many processes, high temperature filtration is necessary to avoid undesirable condensation or de-sublimation reactions.
The only disadvantage of hot gas filtration is the high cost of the filter system, because of the need for high quality materials as well as higher gas volume at high temperature. Moreover, the pressure drop is increasing because of the higher viscosity at higher temperature. However, the advantages dominate in most cases, and the higher capital cost is also compensated by the reduction in the overall process costs. More than 25 large hot gas filtration setups are in service in coal gasification plants worldwide, among which 20 were installed in China over the last 8 years. The total number of hot gas filters installed in many different applications is in the order of few hundreds.

At low temperature, dust properties, such as particle size distribution, adhesion and cohesion forces as well as compressibility of the dust determines the pressure drop, which is the controlling factor of the filtration efficiency. In contrast, at higher temperatures, the thermal properties of dust influence the filtration efficiency. The filter media must have high mechanical strength, good thermal shock resistance and chemical stability against gases, such as H_{2}S, HCl, NH_{3}, Cl_{2}, and H_{2}O. Porous ceramics are promising candidates for this application because of their excellent physical properties, such as high thermal stability, high mechanical strength, and chemical stability, which will be discussed in further detail in the next section.

1.2. Porous Ceramics

The development of porous ceramics, also known as cellular ceramics, started in the 1970s. Generally, porous ceramics pore size spans from angstrom to millimeter, the porosity spans from 20% to 95%, and the service temperature ranges from room temperature to 1700 °C. In general, porous ceramics are divided into two categorizes: honeycomb ceramics and ceramic foam. The former has polygonal columnar pores that form a two-dimensional structure and the latter has hollow polyhedron pores that form a three-dimensional structure.

There are two types of ceramic foams: the open-cell arranged ceramic foams, and the closed-cell bubble-like ceramic foams. When the solid foam body is comprised only of pore structure, the connective pores generate arranged structures, resulting in open-cell ceramic foams. In the closed-cell ceramic foam, pores are separated by solid cell walls. Such differences can be clearly seen by comparing the fluid penetrability through these two foamed bodies. The
difference between the two types depends on whether the pore is covered by solid cell walls or not. In addition, there are half open-cell ceramic foams.  

Porous ceramic foam structures can be adjusted at a relatively low level of bulk density and thermal conductivity, as well as various levels of fluid penetrability, which could be high for the open-cell body. By properly matching the ceramic raw material and the fabrication technique, porous ceramics with relatively high mechanical strength, corrosion resistance, and stability under high temperatures can be fabricated.

Ceramic foams are important types of porous ceramics, and the open-cell type of ceramic foams has a three-dimensional structure with connective pores, resulting in a large specific surface area, high fluid contact efficiency, and a small loss of fluid pressure. In particular, these materials have many connective pores and have high specific surface energy on the inside, so they perform well in terms of filtration and adsorption under low fluid resistance loss conditions. They can be used in many fields, including metallurgy, chemical engineering, environment protection, energy, and biology, as well as in metal melt filtration, high-temperature gas purification, and catalyst support. Moreover, the porosity, density, fluid resistance loss, and penetrability of these materials can be tailored by various processing techniques, and the commonly used materials include alumina and cordierite. Cordierite is used as a raw material with the primary purpose of improving the heat fluctuation resistance of products. As the demand for thermal stability increases for such products, porous silicon nitride and silicon carbide ceramics become of interest.

Several ceramic materials are used as the substrate, including silicon carbide, cordierite, silicon nitride, mullite, and aluminum titanate, among which silicon carbide (SiC) is most popular, because of its superior properties in terms of high melting temperature (2730 °C), high hardness, low coefficient of thermal expansion, high heat transfer capability. However, despite these advantageous properties, SiC does not resist highly oxidizing atmospheres. Alumina (α-Alumina, corundum) is also not a suitable material for hot gas filtration because of low thermal shock resistance, which is a required property in this application.

Lattella et al. fabricated mullite-alumina (2Al₂O₃·SiO₂) ceramics, using slip casting for potential use as filters in hot gas filtration. They used graphite as the pore forming agent. The
microstructure and mechanical properties were characterized at ambient and elevated temperatures. It was shown that gas permeability increases with increasing porosity and pore size, and the maximum Darcian permeability (which is calculated using Darcy’s law in which a fluid is passed through a porous medium and using the inlet and outlet pressure as well as the flow rate, the permeability is determined through the Darcy’s equation) was $k=2.5 \times 10^{-14} \text{ m}^2$ for a porosity of 71%, with the average pore size of 22 µm. The main disadvantage of the fabricated membrane was that it did not possess sufficient strength, i.e., very low hardness of only 3 Hv. They could achieve a higher hardness of 175 Hv, with lower porosity and pore size, 43% and 6 µm, respectively. The backscattered scanning electron microscopy images are presented in Figure 1.

**Figure 1.** Backscattered scanning electron micrographs of mullite-alumina ceramics: (a) MA0G, (b) MA20G, (c) MA40G and MA60G (the value after MA is the volume percentage of graphite that was added as the pore forming agent).

Although alumina and SiC alone have their own disadvantages, their combination in mullite has proven to be a good candidate for hot gas filtration. She and the co-workers fabricated a porous mullite ceramic by reaction bonding technique, using the mixture of Al₂O₃ and SiC.
powders and graphite was used as the pore forming agent. They achieved a strong structure high surface area of 12.4 m$^2$ g$^{-1}$ but low porosity of 32%. They found that pore size was increasing with increasing the sintering temperature. The SEM images of the surface of fabricated mullite are shown in Figure 2.

![SEM images of the surfaces of porous reaction bonded mullite specimens sintered at (a) 1450 °C, (b) 1550 °C, (c) 1650 °C.](image)

**Figure 2.** SEM images of the surfaces of porous reaction bonded mullite specimens sintered at (a) 1450 °C, (b) 1550 °C, (c) 1650 °C.

A porous filter was fabricated using cordierite powder by an extrusion method. The effect of operating condition on the durability of the filter for hot gas cleaning purpose was investigated, and it was found that thermal shock has the most detrimental effect on durability, whereas the pressure shock does not have a significant effect.

Dong and co-workers fabricated micro filtration cordierite porous ceramics on tubular macro porous cordierite supports, using waste fly ash and basic magnesium carbonate as the

7
starting materials by spray coating followed by dip casting. The sintering temperature for the tabular membrane was in the range of 1150-1200 °C with the pore size in the range of 3.6-6.4 µm. The SEM micrographs of tubular membrane are shown in figure 3.

![SEM micrographs of tubular membrane](image)

**Figure 3.** Surface morphology for the tubular membrane sintered at various temperatures for 1 h: (a) 1050 °C, (b) 1150 °C, (c) 1200 °C.

1.2.1. **Yttria-stabilized Zirconia**

One promising candidate for ceramic materials is yttria-stabilized zirconia (ZrO$_2$-Y$_2$O$_3$) (YSZ), which exhibits excellent physical properties, including high melting temperature (~2700 °C), high tensile strength (745 MPa), high thermal shock resistance, and high resistance to chemical attack and corrosion at elevated temperatures.

YSZ exhibits phase transformations at high temperatures. At room temperature, the stable phase of ZrO$_2$ has a monoclinic symmetry. During heating, it first transforms into a tetragonal phase (in the 1000-1100 °C temperature range), then into a cubic phase (above 2000 °C). However, noticeable changes in volume are associated with these transformations: during the monoclinic to tetragonal transformation, 5% volume decrease occurs when zirconium oxide is heated; reversely, 3% increase in volume is observed during the cooling process. This last retransformation into the monoclinic phase is of the same nature as the martensitic transformation occurring in steel and can be compared to that.

These phenomena have been shown to be detrimental to the mechanical behavior of zirconium oxide, because the stresses induced during the phase transformations result in crack
formation. This phase transformation of zirconium oxide can be inhibited by the addition of stabilizing oxides (CaO, MgO, Y₂O₃), and this process has become a common practice. Accordingly, in the presence of a small amount of stabilizing additive, tetragonal particles, provided they are small enough, can be maintained in a metastable state, at temperatures below the tetragonal to monoclinic transformation temperature. The transformation of small tetragonal grains, which should result in a volume increase, is prevented by the compressive stresses applied on these grains by their neighbors. In the ZrO₂-Y₂O₃ system, the extent of the stability range of the tetragonal phase in terms of temperature and amount of yttrium oxide (as shown in Figure 4) allows sintering of fully tetragonal fine-grained materials.

![Figure 4. ZrO₂-Y₂O₃ phase diagram: t - tetragonal phase; m - monoclinic phase; c - cubic phase.](image)

Using Y₂O₃ as a stabilizing agent enables the production of a zirconium oxide ceramic made of 100% small metastable tetragonal grains. The volume change related to the tetragonal to monoclinic phase transformation results in a pre-stressed material. In this respect, a propagating crack can release the stresses on the neighboring grains, which then transforms from the metastable state into the monoclinic phase. The associated volume expansion results in compressive stresses at the edge of the crack front and extra energy is required for the crack to propagate further (Figure 5). Thus, it is believed that the main energy absorbing mechanism is due to the martensitic-like transformation occurring at the crack tip.
Yttria stabilized ZrO₂ ceramics have been synthesized by different techniques in the recent years. The synthesis via the sol-gel processing routes was especially used for high-purity ZrO₂ powder preparation as well as for thin-film applications, such as porous membranes for gas filtration\textsuperscript{22}, dense coating layers for corrosion protection, or reflective coatings for optical applications\textsuperscript{21}. For synthesis of zirconia nanopowders, the sol-gel method leads to a homogeneous particle size distribution and a good sinterability after shaping\textsuperscript{24}. Additionally, partially stabilized ZrO₂ fibers can be obtained via the sol-gel process for manufacturing of zirconia matrix composites with improved mechanical properties\textsuperscript{25}.

Yttria stabilized zirconia (YSZ) exhibits excellent physical properties, including high melting temperature (\sim 2700 °C), high tensile strength (745 MPa), high thermal shock resistance, and high resistance to chemical attack and corrosion at elevated temperatures. Porous YSZ-based materials are used in several applications, that include molten metals filters\textsuperscript{26}, thermal insulators\textsuperscript{27-29}, liquid-phase filtration\textsuperscript{30}, solid oxide fuel cells (SOFCs)\textsuperscript{31}, controlled virus retention\textsuperscript{32}, among others; however, to the best of our knowledge, no previous study has been undertaken to develop porous single phase YSZ to be applied in high temperature gas filtration.
1.2.2. Fabrication Techniques

Properties of the porous ceramics can be tailored for each specific application by controlling the composition and microstructure. All microstructural features are in turn highly influenced by the processing route used for the fabrication of the porous materials.

The conventional solid-state porous ceramic developing technologies include partial sintering and pore forming inclusion technique. In recent years, other techniques, such as foaming after sintering and direct foaming, gel casting, and freeze casting have been also investigated; however, they are still at the development stage and have not yet been commercialized.

The most straightforward processing route for the preparation of porous ceramics is the partial sintering of initially porous powder compacts or the sintering of powder mixtures, which undergo solid state reactions that lead to pore formation. This method often results in a relatively low porosity with pores uniformly distributed within the microstructure. However, this technique faces several drawbacks, namely lack of control over the pore size and degree of porosity, which directly depend on the sintering temperature and applied pressure. Furthermore, ceramics fabricated using this technique lack strength, because the connection in the ceramic body is by necking of powders.

Direct foaming involves mixing a pre-ceramic polymer with precursors for polyurethane (polyols and isocyanates) in a common solvent, which also acts as a physical foaming agent for the system. Then foam is blown out by vigorous stirring of the mixture and putting the sample into an oven. Gel casting is also used for fabricating ceramic bodies by means of in-situ polymerization, through which a macromolecular network is created to hold the ceramic particles together. The resultant porous ceramic is strong enough to be machined forming the complex-shaped advanced ceramic materials near-net-shape in the electronics, automotive, and defense industries. In freeze casting, the ceramic slurry is normally prepared by ball-milling and then casting into a mold at a temperature below its freezing temperature, which results in the production of interconnected pore channels in a tailored manner.

In pore forming inclusion technique, organic particulates that can be pyrolyzed during binder removal step are mixed with the ceramic powder during the green body fabrication
process. After burning off in the binder removal step, they leave behind stable pores that are not removed during the sintering process. This technique offers several advantages, namely direct control of the porous characteristics by adjusting amount, size, and shape of the pore forming agent, and the ability to form open pore networks, because of incorporation of the pyrolyzable pore formers in the green body\textsuperscript{34,35}.

1.2.2.1. Pore Forming Agent

To increase the open porosity, organic additives are mixed with the ceramic powder. These materials, which are called ‘pore forming agent’, are evaporated or burnt out during sintering, and as a result pores are formed. Different types of pore formers have been used in the form of solid and liquid. Starch, carbon black, petroleum coke, melamine, wood dust, charcoal, salicylic acid, ammonium tetrachloride, carbonyl, iodine fluoride, coal, Dextrin (a group of low-molecular-weight carbohydrates produced by the hydrolysis of starch or glycogen), Poly(methyl methacrylate) (PMMA), and liquid paraffin are among the solid and liquid pore formers, which have been utilized to fabricate porous ceramics. The degree of open porosity, pore shape, and pore size of porous materials fabricated by the pore forming method depend on the volume, particle shape, and size of the mixed pore forming agent, respectively. This method is suitable for cost effective preparation of porous materials with relatively large pores and open porosity\textsuperscript{49}.

Using Poly methyl methacrylate (PMMA) to fabricate porous YSZ has been studied previously. Boaro and his co-workers were prepared porous YSZ by both slip-casting of the pyrolyzable pore former (graphite and PMMA) and acid leaching of nickel from a Ni-YSZ cermet. It was found that pore size and shape of the porous YSZ could be controlled by the choice of pore former\textsuperscript{49}.

In another study, Tang and his colleagues fabricated highly porous YSZ via heterocoagulation of template (PMMA) and ceramic particles colloidal processing. In this process, polymer and ceramic particles were modified by allocating opposite charges; therefore, a well-dispersed suspension was obtained because of electrostatic attraction of constituent particles. It was shown that using this method, pore size and porosity could be controlled by varying the
polymer particle size and volume ratio of polymer to ceramic, respectively. Various polymer particle sizes of 0.35 µm, 0.8 µm, 1.3 µm were used to mix with YSZ powders with an average particle size of 30 and 70 nm. Sintering temperature was selected at 1100 °C for 2 h with the heating rate of 1°C/min. Porous YSZ with the porosity of 75.5% was obtained when the volume ratio of YSZ to PMMA was 0.42.

Porous YSZ was fabricated by dry pressing method with different sizes (1.8-20 µm) and amounts of PMMA (2-60 vol%) as the pore former. The optimum particle size and PMMA amount was found to be 5 µm and 20 vol%, respectively, which exhibits the highest flexural strength (106.88 MPa), thermal conductivity, and decent porosity (18.03–21.74%).

Zhou and his co-workers fabricated porous YSZ using tert-butyl alcohol (TBA)-based gel casting with PMMA both as pore forming and lubricant agents. The average pore size decreased from 16.9 to 15.7 µm when the sintering temperature was increased from 1350 to 1550 °C. However, the pore size in this work is measured from the SEM images, which is not accurate because the pore size measured by common techniques, such as mercury intrusion porosimetry, represents the size of the pore channels connecting the big pore rather individual pore diameter. Also, the compressive strength increased from 14.57 to 142.29 MPa when the porosity decreased from 71.6 to 45.1%. It was shown that the main processing factors were controllable using this fabrication technique, particularly in the cases, for which high compressive strength and low thermal conductivity were required simultaneously.

Gain and his colleagues manufactured porous tetragonal-ZrO2 by pressure-less sintering, in which different volume percentages of PMMA with average particles size in the range of 150-200 µm were used as the pore-forming agent. The values of relative density, elastic modulus, bending strength and hardness of the 60 vol% PMMA content sample, sintered at 1550 °C, were determined at 43%, 40 GPa, 170 MPa, and 248 Hv, respectively.

Various types of pore formers including PMMA were utilized to fabricate porous YSZ by Sarikaya et al. Sucrose and flake graphite showed relatively broad size distributions with random shaped particles, while spheroidal graphite, PMMA, and polystyrene showed more spherical particles with narrow size distributions. It was demonstrated that the thermal and
morphological properties of the pore formers have a crucial effect on the features of final microstructures.

In this research, we chose pore forming inclusion technique to fabricate porous YSZ ceramics because it allows tailoring the pore size by adjusting the pore former particle size. Furthermore, controlling the PMMA to YSZ volume ratio enabled the fabrication of high porosity, and consequently high permeability samples, properties that are key for hot gas filtration applications.

1.3. Powder processing

It is often necessary to treat a powder to achieve specific properties that facilitate handling, compaction, and sintering. Below is a summary of these pre-compaction steps.

1) Classification of a powder using screens to remove selective size fractions: to produce high quality products classification is used to remove contaminates and impurities, which tend to be concentrated in the smaller particle size range. Consequently, removal of smaller particles provides enhanced purity. Classification is also used for production of filters, where the particle size determines the pore size and filtration behavior.

2) Mixing and blending: they both combine powders into a homogenous mixture. Blending refers to the combining different size powders of the same chemistry, while mixing refers to combining different powder chemistries. Powders are blended to achieve control over the particle size distribution, especially after transport, which tends to segregate the small and large particles.

3) Attritioning of powders before compaction: this step might be necessary for powders that are bonded together. Attritioning for de-agglomeration is useful when a fine, discrete powder is needed. In contrast, small powders that exhibit a high interparticle friction are granulated into clusters for better flow in automatic forming equipment.

The above listed processes are examples of precompaction powder treatments, and are designed to facilitate subsequent processing. Some of these treatments are performed along with
the powder production. However, steps like mixing and blending are necessary at the site of compaction to ensure homogenous material in the process.  

1.3.1. Mixing and blending  

Mixing and blending are necessary to prepare unique particle size distributions, combine powders to form new alloys during the sintering, add lubricants for compaction, and prepare powder-binder mixture for shaping. A major reason for blending is to remove segregation, typically occurred by vibration in transport, where powder is separate in size, i.e., the smaller particles tend to stay on top. Such segregation by particle size leads to uneven compaction and sintering. Although there are three causes of segregation (difference in particle size, density, and shape), size segregation is the dominant case.

The mechanisms of powder mixing are diffusion, convention, and shear. Figure 6 illustrates these mechanisms, i.e., diffusional mixing in a rotating chamber, convective mixing in a screw mixer, and shear mixing in a blade mixer. Diffusional mixing occurs by the motion of the individual particles into the powder mixture. Continuous rotation provides fresh powders and fresh shear planes that facilitate intermixing of the particles. Convective mixing is defined as a transfer of adjacent powder groups from one location to another. The screw cuts off a small group of particles and transport them elsewhere in the batch. Shear mixing occurs by continual division and flow of powder over the slip planes.  

1.3.2. Powder compaction

In this process, powders are densified by applying pressure, initially by particles sliding past one another and then by particle deformation at higher pressure. The increase in density is rapid initially at low pressures, but the powder resists as the density increases and the pores collapse. A simplified illustration of die compaction is shown in Figure 7. The powder starts at the apparent density of 4 to 6 contacting neighbors for each particle, for which they do not have any bonding strength. As pressure increases, the particles rearrange, deform, and bond. Continuously, more pressure is required to continue compaction because the deformation hardens the particles. Depending on the powder and tool material, the peak compaction pressure ranges up to 1000 MPa.

The compacted powder is termed a green body, so the density after pressing is the green density and the strength after pressing is the green strength. After pressing, the green compact is mechanically locked into the die. The force required to push the compact out of the die is called the ejection force. Here the effect of lubricant is of importance; both ejection force and die wear decrease with increasing of lubricant.

Many die compaction options exist, including hard and soft tooling, heating the die and powder, lubricating the powder, and the tooling only. In full density techniques, both pressure and temperature are applied simultaneously.
1.3.3. Sintering

Sintering facilitates contacting particles to bond together at high temperature. It can occur at temperatures below the melting point by solid-state atomic transport, which involves the formation of a liquid phases in many cases. From a microstructural scale, the bonding becomes evident as necks grow between the touching particles. Such neck growth increases the strength over the green strength and results in many beneficial property changes.

Sintering is a result of the motion of atoms, which occurs at high temperature and the reduction in the surface energy associated with the small particles. It is worth noting that powder fabrication is mainly related to putting energy into the material to create surface area or surface energy, after which in sintering, that energy is eliminated. Surface energy per unit volume depends on the inverse of the particle size. Therefore, smaller particles with high specific areas have more energy and sinter more quickly. For a crystalline solid, nearly every particle contact will evolve a grain boundary energy. Thus as neck growth removes surface energy, adding grain boundary. Obviously, this only occurs when the decrease in surface energy is greater than the increase in grain boundary energy.
The driving force or sintering stresses come from the curvatures in the microstructure. Sintering mechanisms are usually diffusion processes over the surfaces, along the grain boundaries, or through the crystalline lattice. The stages of sintering help describe the driving force and kinetics, and are used to mathematically model the process.

1.3.3.1. Stages of sintering

Sintering normally occurs in three sequential stages, namely the initial stage, the intermediate stage and the final stage. It is also believed that there is an extra stage, considered as stage zero, which describes the initial contact between the particles when they are first brought together, due to elastic deformation in response to reduction in surface energy at the interface. Figure 8 presents the idealized models for the three stages of sintering. The initial stage consists of fast inter-particle neck growth by diffusion, vapor transport, plastic flow, or viscous flow. The large initial differences in surface curvature are removed in this stage, and shrinkage (or densification) accompanies neck growth for the densifying mechanisms. For spherical powder particles, the initial stage is presented in Figure 8(a) and 8(b). This stage lasts until the radius of the neck between the particles reaches a value between 0.40 - 0.50 of the particle radius. For a powder system with an initial relative density of 0.50 - 0.60, this associated with a linear shrinkage of 3% - 5%, or an increase in relative density to 0.65, when the densifying mechanisms dominate.
To predict the rate of the sintering requires assembly of several mathematical models, out of which, the model for monosized spheres under idealized conditions is presented here. The change in number of vacancies between convex and concave surfaces results in a vacancy concentration gradient. Fick’s first law is used to relate the vacancy concentration gradient to the mass flux. Knowing the volume of the neck and its relationship to the neck size and area over which diffusion occurs allows integration to calculate the total neck size as a function of time, temperature, and particle size. The resulting models of initial stage of isothermal sintering gives the neck size ratio \((X/D)\) as follows:

\[
(X/D)^n = \frac{Bt}{D^m}
\]
where \( X \) is the neck diameter, \( D \) is the particle diameter, \( t \) is the isothermal sintering time. The values of \( n \), \( m \), and \( B \) depend on the mechanism of mass transport. Effect of temperature enters in an exponential form,

\[
B = B_0 \exp \left( -\frac{Q}{RT} \right) \quad (2)
\]

Where \( B_0 \) is a collection of material, temperature, and geometric constants, \( R \) is the universal gas content, \( T \) is the absolute temperature, and \( Q \) is an activation energy associated with atomic transport process. This equation is valid for a neck size ratio \((X/D)\) below 0.3\(^{17}\).

Most of the property development in sintering occurs in the intermediate stage, which begins when the pores have reached their equilibrium shapes, as governed by the surface and interfacial tensions. The pore phase is still continuous in this stage. The structure is usually idealized in terms of spaghetti like array of porosity, sitting along the grain boundaries, as depicted in Figure 2(c). Densification is thought to occur by pore shrinkage to reduce their cross section. Eventually, the pores become unstable and pinch off, leaving isolated pores, which is the beginning of the final stage. The intermediate stage normally covers the major part of the sintering process, and it comes to an end when the density is approximately 0.90 of the theoretical density\(^{55}\).

During the intermediate stage, the rate of density increase, i.e., \( d\rho/dt \) is determined by the flux of vacancies and atoms, which depend on the pore size and temperature, the diffusion distance, which depends on the grain size, and the number of pores per volume leading to the following equation:

\[
\rho_S = \rho_I + B_I \ln \left( \frac{t}{t_I} \right) \quad (3)
\]

Where \( \rho_S \) is the fractional sintered density, \( \rho_I \) is the fractional density at the beginning of this stage, \( B_I \) follows the form of equation (2), \( t_I \) is the time corresponding to the onset of the intermediate stage, and \( t \) is the isothermal sintering time (greater than \( t_I \)).

Lastly, during the final stage, the microstructure can develop in a variety of ways. In the simplest description, the final stage begins when the pores pinch off and become isolated at the
grain corners, as shown by the idealized structure depicted in figure 8(d). The pores are assumed to shrink continuously, and they may disappear altogether. As full densification is approached, grain growth accelerates, because there are fewer pores to avoid grain boundary motion. Pores are barriers to grain growth only where there is considerable porosity.\(^5\)

The rate of the pore elimination in the final stage depends on the balance between the surface energy and the pore gas pressure \(P_G\). The densification rate equation is given as follows:

\[
\frac{dp}{dt} = \frac{12D_V\Omega}{kTg^2} \left( \frac{Y}{dp} - P_G \right)
\]

(4)

where \(p\) is the fractional density, \(t\) is the hold time, \(\Omega\) is the atomic value, \(D_V\) is the volume diffusivity, \(k\) is the Boltzmann’s constant, \(T\) is the absolute temperature, \(g\) is the grain size, \(Y\) is the solid-vapor surface energy, \(dp\) is the pore radius, and \(P_G\) is the gas pressure in the pore.

The equation shows that when gas is trapped in the pore, the densification rate reaches zero before all porosity is eliminated. Thus, full densification is achieved only under vacuum or atmosphere that dissolved into the solid.\(^5\)
Figure 9. SEM images taken during (a) initial, (b) intermediate, (c) final stages of sintering.

1.3.3.2. Heating schedule

Heating schedule can be simple, as in isothermal sintering or constant heating rate sintering of single-phase powders in the laboratory-scale experiments, or they can have more complex heating patterns, as in the sintering of ceramics for industrial application, which consists four main stages, i.e., binder burnout, heat up to the sintering temperature, isothermal sintering, and cool-down to the room temperature.

Prior to sintering, in the binder burn out stage, the polymers used as the binder or lubricants are removed. Polymer burnout occurs as the powder compact heats up to the temperature at which the polymer becomes unstable and decomposes into constituents that evaporate. Heat first melts the polymer, and then breaks down its molecular bonds, forming small molecules that evaporate out of the compact. Furthermore, the removal of volatile
materials, such as adsorbed water and the conversion of additives, such as metal organic compounds or organic binders take place. The heating rate is often slow and carefully controlled, often < 2 °C/min, because rapid heating may cause boiling and evaporation of organic additives, leading to swelling and even cracking of the specimen. Typically the hold temperature in this stage is at most 400-500 °C. Examples of polymer loss versus temperature are given in Table 1.

Table 1. Polymer decomposition temperatures (temperatures for 50% polymer evaporation during heating in nitrogen)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin wax</td>
<td>295</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>414</td>
</tr>
<tr>
<td>Poly(ethylene oxide)</td>
<td>345</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>387</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>364</td>
</tr>
<tr>
<td>Poly (methyl methacrylate)</td>
<td>237</td>
</tr>
<tr>
<td>Poly(vinyl acetate)</td>
<td>269</td>
</tr>
<tr>
<td>Poly(vinyl carbon)</td>
<td>274</td>
</tr>
</tbody>
</table>

The next stage involves heat up to the isothermal sintering temperature. The heating rate is limited by the sample size and the thermal characteristics of the furnace. For large samples, heating duration can prolong for many hours to avoid temperature gradients that could lead to cracking or to avoid the formation of a dense outer layer on an incompletely densified core, which could result from the inhomogeneous densification. In laboratory-scale experiments with small samples, it is often observed that a faster heating rate in this stage enhances the densification in the subsequent isothermal sintering stage.

The isothermal sintering temperature is chosen to be as low as possible and at the same time compatible with the requirement that densification could be achieved within a reasonable time (typically less than 24 hours). Higher sintering temperatures lead to faster densification, but the coarsening rate also increases, which may results in grain growth, where pores are trapped inside
large grains. Although the densification occurs faster, the final density may be limited, as shown in Figure 10.

**Figure 10.** Relative density as a function of sintering time to illustrate the selection of optimum isothermal sintering temperature.

The cooling rate to the room temperature can be fairly fast for relatively small particles, but it should be much slower for larger particles to prevent large temperature gradient that can lead to cracking. When compositional or microstructural modification is achieved, the cooling rate needs to be controlled carefully. 
1.3. Research Objective

The main objective of this research is to fabricate porous YSZ ceramics that could potentially utilized for hot gas filtration. One potential application for such a material is in steelmaking industry. The off gas from blast furnace is hot, more than 1000 °C and sometimes close to 1700 °C and contains a large volume of mixed gases, including CO, CO₂, H₂, H₂O, O₂, and N₂ along with particulate matters of variable composition and size. Online analysis of the off-gas stream requires continuous sampling, which is sent to the gas analyzer. It is imperative to filter the off gas prior to sending to the analyzer; otherwise, the metals oxide particles and particulate matters will clog the instrument. To the best of our knowledge, currently there is no filter material suitable for harsh environment application. In the current practice, the off gas sample is cooled and then filtered by a porous metallic filter membrane and then sent to the analyzer. Replacing the metallic filter with a porous ceramic membrane would be beneficial, as the ceramic filter can withstand high temperature, eliminating the need for costly water-cooling facility, thus resulting in saving the costs and complexity of the process.

This research aims to design and fabricate porous YSZ ceramic to be used in the blast furnace off gas sampling probe. The target specifications for this industrial setting are permeability higher than $4 \times 10^{-15}$ m$^2$, pore size in the range of 0.4-0.5 µm, and porosity of 40 %. Here, we used a simple pore forming technique to fabricate these ceramics, using poly methyl methacrylate (PMMA) as the pore former, which percolated during the binder removal step, resulting in stable open pores in the sintered ceramic product.

The research project was divided into three concurrent Project Segments:

- Project Segment (I) was focused on developing a recipe to fabricate the pellets. Here, we investigated the effect of three processing parameters, namely sintering temperature, PMMA particle size, and PMMA-to-YSZ ratio, on the pore size, porosity, gas permeability, and hardness of the final product.

- Project Segment (II) was focused on the characterization of the fabricated YSZ ceramics in terms of porosity, pore size, permeability, and hardness.
• Project Segment (III) was focused on the performance testing of the fabricated ceramics to examine their capability to be used as the membrane for desired application. We performed high temperature exposure and cyclic heating/cooling experiments and demonstrated that the fabricated porous ceramic can sustain these conditions.

1.4. Thesis Overview

The present thesis is composed of five chapters, which are structured as follows:

• Chapter 1 presents an introduction to the research project.
• Chapter 2 presents the materials and experimental procedure utilized in this work.
• Chapter 3 focuses on the results and discussions.
• Chapter 4 summarizes the major conclusions drawn from this work.
• Chapter 5 outlines the recommendations for future work

The thesis was prepared on the basis of the following manuscript, which will be submitted shortly. The result of this work has been presented in COM2016 (Conference of Metallurgists).

Publication

Conference Presentation
Shahini, S., Tam, J., Azimi, G., “Rare earths containing ceramic membranes for high temperature gas filtration,” Presented In: COM2016 (Conference of Metallurgists), Symposium: Rare Earth Elements, Quebec City, QC, Sep. 11–15, 2016.
2. CHAPTER TWO - MATERIALS AND EXPERIMENTAL PROCEDURES

This chapter describes materials characterization, experimental procedures, and analytical techniques used in this work.

2.1. Materials

To fabricate porous YSZ ceramics, mono dispersed PMMA powders were obtained from Soken Chemical and Engineering, Japan with the purity of 99%. Also, yttria-stabilized zirconia (8 mol% yttria) was obtained from Stanford Advanced materials, US with the purity of 99.9%. Deionize water (0.055 μS/cm (18 MΩ·cm), Millipore) was used as the medium to mix the powders.

2.2. Fabrication of Porous YSZ

For the fabrication of porous YSZ ceramics, various PMMA particle sizes with different concentrations were used. The effect of processing parameters, namely sintering temperature, PMMA particle size, and PMMA-to-YSZ ratio on pore size, porosity, gas permeability, and hardness of the fabricated pellets were investigated. The detailed experimental matrix for the fabrication is summarized in Table 2.
Table 2. Experimental matrix of pellets fabrication

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>PMMA-to-YSZ Ratio (%, v/v)</th>
<th>PMMA particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.8</td>
</tr>
<tr>
<td>1400</td>
<td>30/70</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>1300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1400</td>
<td>30/70</td>
<td>1.5</td>
</tr>
<tr>
<td>1500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1600</td>
<td></td>
<td></td>
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<tr>
<td>1700</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10/90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20/80</td>
<td></td>
</tr>
<tr>
<td>1400</td>
<td>30/70</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>40/60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td></td>
</tr>
</tbody>
</table>

To make the green pellets, first a uniform distributed mixture of YSZ and PMMA was prepared. A pre-determined amount of PMMA powder with a particular particle size was added to 150 mL of deionized water in a beaker. The slurry was mixed using magnetic stirring (Corning, PC-420D) for 1 h. A Teflon-coated stirring bar was used to suspend the particles and maintain stirring at 600 rpm to ensure solid suspension. Afterwards, a desired amount of YSZ was gently added to the slurry, and let the mixture stir for 5 h. The slurry was then filtered using vacuum filtration. The resultant mixture was dried in an oven at 50 °C for 5 h to remove the remaining water before making the green pellets. The dried solid mixture was crushed to form fine powders, and poured into a metallic mold (28.5 mm in diameter). The powder was dry-pressed into a disk-shaped pellet, using a 50 tons hydraulic shop press under a pressure of 70 MPa. The green bodies were first calcined at 425 °C for 2 h and then sintered in an ambient air environment inside a box furnace (Carbolite HTF 18/4) for 2 h with the heating rate of 1 °C/min. The sintering temperature was set at 1300-1700 °C depending on the case.
2.3. Characterization of the Fabricated Pellets

2.3.1. Scanning Electron Microscopy (SEM)

To gain information about the surface morphology of the sintered pellets, they were characterized using SEM equipped with High angle backscattered electron detector (Hitachi SU8230). Pellets were mounted rigidly on a specimen holder using carbon tape. To obtain cross-section of the pellets, they were cut into the half using a diamond saw and mounted on the stub.

2.3.2. Vickers Hardness

To measure the hardness of the pellets, Vickers microhardness testing was utilized. Because the prepared samples were white, the light was reflected under the light microscope, which was used to measure the square indents. To tackle this challenge, the sample were coated with a thin layer of gold, thin enough not to affect the hardness measurement results. The hardness was measured using a micro indentation Vickers (Buehler Micromet 5103) by applying the load of 0.5 Kg. Because of the porous nature of the samples, the variation in the measured values was fairly high, thus 10 points per sample were measured to compensate for the variation.

2.3.3. Helium Gas Pycnometer

To obtain the true volume of porous pellets and in turn porosity, a helium gas pycnometer (Quantochrome Corp., ultrapycnometer 1000) was utilized. In this equipment, a sealed sample chamber of known volume was pressurized to a target pressure with the displacement gas. Once stabilized, this pressure was recorded. Then, a valve was opened to allow the gas to expand into a reference chamber with a known volume. Once stabilized, the second pressure was recorded. The pressure drop ratio was then compared with the behavior of the system when a known volume of standard undergoes the same process. Then, the volume to pressure relationship (Boyle’s law) was used to calculate the volume and in turn the density, because the mass of the sample was known. After obtaining the skeletal volume from the machine, the apparent volume was measured using a caliper. The porosity was calculated by
subtracting these two values and dividing the result by the apparent volume.

\[
\text{Porosity (\%)} = \frac{V_{\text{apparent}} - V_{\text{skeletal}}}{V_{\text{apparent}}} \times 100
\]  

(5)

where \(V_{\text{apparent}}\) is geometrical volume of the pellets, which is measured using caliper, and \(V_{\text{skeletal}}\) is the true volume, which is measured by the gas pyrometer.

### 2.3.4. Mercury Intrusion Porosimetry (MIP)

The pore size of the fabricated porous YSZ ceramics was measured using mercury porosimeter (Quantochrome Corp., Autoscan porosimeter). In this technique, non-wetting mercury was intruded into the sample’s pores using a porosimeter, and the pore size was determined on the basis of the external pressure versus the opposing force as result of the liquid surface tension. From the extracted data, the Logarithm of differential volume was plotted versus pore diameter, from which the highest peak represents the most frequent pore size in the sample.

### 2.3.5. Gas Permeability

The gas permeability of the porous YSZ ceramics was measured to determine their applicability as gas filters. For gas permeability measurements, we used an apparatus built in the house (Figure 11) and followed the ASTM standard. In this process, the ceramic sample was tightly held by two polyurethane O-rings to expose a nominal with the area of 1.98 cm², and nitrogen gas was passed through the chamber. Pressure of the gas at the inlet and the flow rate of the gas at the outlet were measured by a pressure gauge and a flow meter, respectively. This allowed direct determination of the specific gas permeability via Darcy’s law, base on the following formula:

\[
\frac{\Delta P}{L} = \frac{\mu}{k} \nu
\]  

(6)
where \( \Delta P \) is the pressure drop, \( L \) is the thickness of the material, \( \mu \) is the viscosity of the gas, \( \nu \) is the fluid velocity and \( k \) is the specific gas permeability.

To calculate the fluid velocity we divided the measured flow rate \( Q \) by the cross-sectional area \( A \) of the sample. For compressible fluids (i.e., nitrogen gas) flowing through a solid porous medium, the specific permeability is given by \(^{10,31}\):

\[
\frac{P_i^2 - P_o^2}{2P_o L} = \frac{\mu}{k} \frac{\nu}{k}
\]  

where \( P_i \) and \( P_o \) are the inlet and outlet pressures, respectively. When nitrogen gas is employed as the fluid gas, the dynamic viscosity \( \mu \) is \( 1.75 \times 10^{-5} \text{ Pa.s} \) \(^{32}\).

**Figure 11.** Schematic of the gas permeability measurement setup.
2.3.6. Particle Size Distribution

The average particle size distribution of as-received YSZ powder was determined using the light scattering technique with a particle size analyzer (Horiba Partica LA-950V2). This technique uses a laser diffraction particle size analyzer.
3. CHAPTER THREE - RESULTS AND DISCUSSIONS

3.1. YSZ Powder Characterization

We performed surface and particle size characterization of as-received YSZ ceramic particles by scanning electron microscopy and laser diffraction particle size analysis. Figure 12(a) and 12(b) present a low and medium magnification secondary electron (SE) image of the as-received YSZ powder. There is agglomeration of smaller particles. To investigate the morphology, very high magnification images were taken (Figure 12(c)), which shows that the particles are composed of agglomerated nanometer sub-particles.

![Images of YSZ powder characterization](image)

**Figure 12.** (a) Low magnification, (b) medium magnification, (c) high magnification SE images of as-received YSZ powder.
The ceramic particle size distribution is presented in Figure 13. As shown in the histogram, the particles are in a fairly narrow and monomodal distribution, for which the most frequent particle size, is 2.11 µm. The average particle size of the as-received YSZ is 2.45 µm, which is close to the dominant particle size, indicative of the narrow distribution, which is crucial due to the fact that higher the difference in particle sizes leads to faster motion of grain boundaries; consequently, it results in bigger grains and coarse structure.

![Figure 13. Particle size distribution of the as-received YSZ.](image)

3.2. YSZ Pellet Without PMMA - the Benchmark

We fabricated a pellet without adding PMMA as the pore former to set a benchmark for comparison. The pellet was sintered for 2 h at 1400 °C, which was determined to be the optimum sintering temperature later on in this project. Secondary electron images of the surface of the pellet are shown in figure 14. As can be seen, the structure is fairly dense and majority of the pores pinch off, indicating the sintering process reached the final stage. The measured permeability was low, $0.6 \times 10^{-15}$ m² (design criteria was set at higher than $4 \times 10^{-15}$ m²), which is in agreement with the observation through the SEM images.
Figure 14. Surface SEM micrographs of pure YSZ pellets sintered at 1400°C without adding PMMA as the pore former.

3.3. Powder Sonication in the Fabrication Process

To investigate the effect of sonication in the fabrication process, the powders were sonicated in a water bath for half an hour to make a suspension of powders in water to prevent agglomeration in the precursor powder suspension, and the rest of the fabrication process was conducted on the same conditions as what explained before in section 2.2. This could result in the uniform distribution of pore former and matrix powders.

To test the hypothesis, the pellets with and without sonication treatment were fabricated using the following conditions: sintering temperature of 1400 °C, PMMA-to-YSZ ratio of 30/70 (%v/v), and polymer particle size of 3 µm, which is determined to be the optimum fabrication condition later on this project. Figure 15 presents the SEM micrographs of the
pellets fabricated with and without the sonication. As can be seen, sonication decreases the agglomeration of particles, resulting smaller particle size of YSZ in the sonicated sample close to the particle size of as-received YSZ. Although there was a small change in the microstructure, the permeability measurement showed consistent results between the two samples. This observation suggests that sonication does not have a significant effect on the performance of the fabricated sample; therefore, this process was not utilized in this study to reduce the fabrication cost.

![Figure 15. Surface SEM micrographs of the fabricated pellets at 1400 °C, PMMA-to-YSZ ratio of 30/70 (%v/%v), PMMA particle size of 3 µm: (a) with sonication, (b) without sonication.](image)

### 3.4. Sintering Temperature

In this study, the effect of sintering temperature on porosity, Vickers microhardness, gas permeability, and pore size was investigated. Various sintering temperatures, namely 1300, 1400, 1500, 1600, 1700 °C were investigated, for which the PMMA particle size and YSZ-to-PMMA ratio were kept at 1.5 µm and 70/30 (%/v/v), respectively. The result for each of the properties is discussed below in detail.

#### 3.4.1. Microstructure

Figure 16 presents the secondary electron images of the polished cross section of the pellets fabricated at various sintering temperatures. As can be seen, the grains enlarged as the sintering temperature increased. Furthermore, the densification process is also apparent by
comparing the images as the sintering temperature increases, which is consistent with the results of pore size measurement. The pore shrinkage was observed at higher sintering temperatures. Also, the formation of well-developed necks between the YSZ particles occurred dominantly as the sintering temperature increased, which explains the increasing trend in the Vickers hardness.

Sintering at 1300 °C only led to the first stage of sintering, where the quick inter-particle neck growth started to develop gradually. Increasing sintering temperature to 1400°C, moved the sintering process to the second stage, in which the structure was idealized in terms of a spaghetti-like array of porosity. This stage dominated at the sintering temperature of 1500 °C and finished after 2 h of sintering at this temperature. The third stage of sintering started at 1600 °C, when the pores pinch off and became isolated at grain corner and the connection of porosity chain became disconnected. This stage was ongoing at the temperature of 1700 °C, and finished after the sintering duration of 2 h, when the pores shrunk and pinched off nearly completely and the structure became close to the full density.

Figure 16. Secondary electron images of the polished cross sections at various sintering temperatures: (a) 1300, (b) 1400, (c) 1500, (d) 1600, (e) 1700 °C.
3.4.2. Effect of Sintering Temperature on Porosity

Figure 17 illustrates the porosity of the sintered porous YSZ ceramics as a function of sintering temperature. As can be seen, the porosity decreases linearly with increasing the sintering temperature. The primary reason for this phenomenon is the densification process, which is driven by the tendency of the system to lower its surface free energy through the replacement of solid-vapor interfaces.

![Figure 17. Effect of sintering temperature on the porosity of the sintered YSZ pellets.](image)

To investigate the density change during the sintering process, we measured the density of the green pellet to be at 2.4 g/cm³ when PMMA-to-YSZ ratio of 30/70 (%w/%w), and polymer particle size of 3 µm was used. Figure 18 presents the density of the sintered pellets at various sintering temperatures. As can be seen, density increases with increasing the sintering temperature, i.e., higher degree of densification, which is consistent with the porosity decrease with increasing sintering temperature.
3.4.3. Effect of Sintering Temperature on Vickers Hardness

Mechanical tensile strength and hardness are important properties of porous ceramics, because porosity hinders the mechanical properties. Here, we measured Vickers micro hardness of sintered porous YSZ ceramics, which is defined as the resistance of a material to deformation, scratching, and erosion. Since the porous YSZ ceramic used in this application is constantly collided by the high velocity off gas as well as particulates carried by the stream, the surface has to have sufficient resistance to deformation as well as erosion, which was evaluated by the hardness measurement. Because of the porous nature of the samples, it is expected the micro hardness to vary depending on the site where the indent hits, which results in the low and high value for pore and dense YSZ, respectively.

As it is shown in Figure 19, the Vickers micro hardness increases with increasing the sintering temperature. At 1500 °C, the measured micro hardness is 234 Hv, which is comparable to the hardness of tetragonal-ZrO₂, reported to be at 248 Hv ⁴. The increasing trend is because of the formation of well-developed necks during the sintering process, whose number increases with increasing the sintering temperature, resulting in a large value of 621 Hv at the sintering temperature of 1700 °C.
In many applications, high mechanical strength and high porosity are both desirable, and the relationship between these two parameters has been studied before, and an inverse proportionality has been proposed. Figure 20 presents the relationship between the porosity and hardness obtained in this study.

**Figure 19.** Effect of sintering temperature on the Vickers micro hardness of the sintered YSZ pellets.

**Figure 20.** Relationship between porosity and hardness of the sintered YSZ pellets.
Mechanical properties of porous ceramics are highly dependent on the porosity and pore shape. Pores reduce the effective cross-sectional area and negatively affect the mechanical properties. Several models have been suggested for the strength variation with the fractional density. Table 3 outlines several models developed to account for the change in Young’s modulus \(E\) with porosity \(P\), where the constants \(a\) and \(b\) are often determined empirically, and \(E\) is the Young’s modulus of the dense material.

**Table 3. Relationship between Young’s modulus and porosity**

<table>
<thead>
<tr>
<th>Expression</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E = E_0(1 - aP))</td>
<td>Linear decrease in Young’s modulus with porosity when (P) is small (a \approx 4)</td>
</tr>
<tr>
<td>(E = E_0(1 - aP + bP^2))</td>
<td>For low concentration of spherical pores ((a \approx 1.9, b \approx 0.9))</td>
</tr>
<tr>
<td>(E = E_0(1 - aP)^b)</td>
<td>For solid foams with high porosity (P &gt; 0.7) ((a \approx 1, b \approx 2))</td>
</tr>
<tr>
<td>(E = E_0[(1 - P)^2/(1 + (a - 1)P)])</td>
<td>A is a shape factor with values depending on porosity: (1/a = 0.4) for interconnected porosity, (1/a = 0.3 - 0.7) for porosity that resembles ribbons, (1/a = 0.6 - 1) for isolated pores. (1/a) is known as the Nielson shape factor.</td>
</tr>
<tr>
<td>(E = E_0 \exp(-aP))</td>
<td>Empirical for oxides with porosity in the range 0-40% ((a \approx 4))</td>
</tr>
</tbody>
</table>

Pore shape is another key factor. Sintered materials lose strength if the pore shape is irregular; thus spherical pores are preferred. Irregular pore act as stress concentration site, which is defined by stress intensity factor, \(K_I\), which is a combination of flaw size (in this case, pore is considered as the flaw \(c\)) and applied stress \(\sigma\);

\[
K_I = \sigma Y \sqrt{c}
\]  

(8)

where \(Y\) is a dimensionless parameter that depends on the loading geometries.\(^6\)

---

6. This reference is not provided in the image, but typically, such parameters are determined from experimental data.
3.4.4. Effect of Sintering Temperature on Pore Size

To investigate the effect of sintering temperature on the pore size, two different PMMA particle sizes of 1.5 μm and 3 μm at a constant ceramic to polymer ratio of 70/30 (%v/v) were used to fabricate the sintered porous YSZ ceramics. As can be seen in Figure 21, for both cases, pore size increases with increasing the sintering temperature from 1300 to 1400 °C, and then decreases with increasing the sintering temperature up to 1700 °C. The reason behind the initial increase is because of the enlargement of grains with increasing the sintering temperature, which results in coalescence of small pores and in turn forming of bigger pores. Similar behavior has been reported previously. Migration of the boundaries leads to coalescence of the pores, so the average pore size increases as presented schematically in Figure 22(a) and a real example in Figure 22(b). The subsequent decrease in the pore size is because of the densification process, which is a result of minimization of surface free energy, resulting in pore shrinkage.

![Figure 21](Image_url)

**Figure 21.** Effect of sintering temperature on the pore size of the sintered YSZ pellets.
3.4.5. Pore evolution during sintering

Thermodynamically, whether a pore shrinks or not depends on the free energy change associated with the change in pore size. This can be explained using the two-dimensional schematic shown in Figure 23 for a circular pore of radius \( r \) surrounded by \( N \) grains, where \( N \) is often considered as the pore coordination number. If pore slightly shrinks, the radius of the pore is reduced by \( \delta r \), and the total change in free energy is given by:

\[
\delta E = N\delta r \gamma_{gb} - 2\pi \delta r \gamma_{sv}
\]

(9)

where \( \gamma_{sv} \) and \( \gamma_{gb} \) are the surface and grain boundary energies.
Figure 23. Circular pore surrounded by four grains.

The pore will shrink if $\delta E < 0$. If too many grains surround the pore, the increase in free energy because of the extension of the grain boundaries in the pores is greater than the decrease in the free energy due to the reduction of the pore surface area, so the pore should grow instead of shrinking. The argument can be made to a pore with an equilibrium shape governed by the dihedral angle $\Psi$ defined by:

$$\cos\left(\frac{\Psi}{2}\right) = \frac{\gamma_{gb}}{2\gamma_{sv}}$$

where $(\gamma_{sv})$ and $(\gamma_{gb})$ are the surface and grain boundary energies.

Figure 24 presents an example in which a pore with a dihedral angle of $\Psi = 120^\circ$ is surrounded by $N$ grains. The pore has straight side if $N=6$, convex sides for $N < 6$, and concave sides for $N > 6$. The surface of the pore will move towards its center of curvature, so the pore with $N < 6$ will shrink, whereas the one with $N > 6$ will grow. The pore is metastable for $N = 6$, and this number is called the critical pore coordination number, $N_c$. Generally $N_c$ decreases with increasing the dihedral angle. The two parameters are connected by a simple geometrical relationship given by:

$$\Psi = \frac{180N_c-360}{N_c}$$

(11)
Figure 24. Pore stability in two dimensions for dihedral angle of 120°.

The geometrical considerations can be explained in three dimensions, when the pore is polyhedron. The analysis has been carried out by Kingery and Francois. Taking $r_s$ as the radius of curvature of sphere around the a polyhedral pore surrounded by grains, the ratio of the radius of curvature of the pore $r$ to $r_s$ depends on both on the dihedral angle and the pore coordination number, as shown in Figure 25.
Figure 25. Conditions for pore stability in three dimensions as a function of pore coordination.

The surface ($\gamma_{sv}$) and grain boundary ($\gamma_{gb}$) energies of polycrystalline YSZ (8 mol% Y₂O₃) in the range of 1573-1873 K (1300-1600 °C) have been calculated using the multiphase equilibration technique as follows:

\[
\gamma_{SV} (Jm^{-2}) = 1.927 - 0.428 \times 10^{-3} T \\
\gamma_{gb} (Jm^{-2}) = 1.215 - 0.358 \times 10^{-3} T
\] (12)

At a given temperature, e.g., 1600 °C (1873 K), and using the equation 10, the dihedral angle is calculated to be 152°. Using the equation 11, $Nc$ is determined to be 12, suggesting that the pores are likely to shrink instead of growing, because the pore coordination number is very high. In other words, the number of grains surrounding the pore is highly lower than 12, making pores to shrink, which is in agreement with the observation in this study.

3.4.6. Effect of Sintering Temperature on Permeability

Figure 26 presents the gas permeability as a function of sintering temperature. As can be seen, the permeability shows a linear decrease with increasing temperature. This is because of
the fact that as sintering temperature increases, both pore size and porosity decrease, and because gas permeability depends on both these parameters, it also decreases.

Figure 26. Effect of sintering temperature on the gas permeability of the sintered YSZ pellets.

3.5. Polymer Particle Size

To investigate the effect of PMMA particle size, various sizes of 0.8, 1.5, 3, and 10 µm were used to fabricate the pellets. The sintered samples were characterized in terms of gas permeability, porosity, and pore size. For this set of experiments, the ceramic to polymer ratio and sintering temperature remain constant at 70/30 (%v/v) and 1400 °C, respectively.

3.5.1. Effect of Polymer Particle Size on Pore Size

Figure 27 illustrates the average pore size of the sintered porous YSZ ceramics measured by mercury prosimeter as a function of polymer (PMMA) particles size at a constant ceramic to polymer ratio of 70/30 (%v/v) and sintering temperature of 1400 °C. As can be seen, the pore size increases with increasing the PMMA particle size. There is a discrepancy between the value measured by MIP and the value calculated using the scale of the SEM images, which is found to
be because of the fact that measured pore size by mercury porosimetry is the diameter of the channel connecting the larger pores than the individual pores, which is observed from the SEM images. Furthermore, the measured pore size using mercury porosimetry is found to be much smaller as compared to the polymer size, which is in agreement with what has been reported previously in the case of mullite, where She et al. used 5 µm graphite as the pore former, and they obtained the pore size of about 0.5 µm.

![Graph showing effect of polymer particle size on pore size of sintered YSZ pellets](image)

**Figure 27.** Effect of polymer particle size on the pore size of the sintered YSZ pellets
3.5.2. Effect of Polymer Particle Size on Porosity

Figure 28 presents the effect of polymer (PMMA) particle size on the porosity at constant sintering temperature (1400 °C) and ceramic to polymer ratio (70/30 (%v/v)). As can been, the effect of PMMA particle size on the porosity is minimal, and the porosity remains unchanged at about 40%.

![Graph showing the effect of polymer particle size on porosity](image)

**Figure 28.** Effect of polymer particle size on the porosity of the sintered YSZ pellets.

3.5.3. Effect of Polymer Particle Size on Permeability

Figure 29 presents the gas permeability values as a function of polymer particles size at constant sintering temperature (1400 °C) and ceramic to polymer ratio of 70/30 (%v/v). Permeability increases with increasing the PMMA particle size, which follows the same trend as that of pore size versus permeability. Permeability depends on two key factors, pore size and porosity. Because porosity remains unchanged with the polymer particle size, consequently permeability is governed by pore size, and it decreases.
Figure 29. Effect of polymer particle size on the permeability of the sintered YSZ pellets.

3.6. Polymer to Ceramic Ratio

Various polymer volume ratios of 10, 20, 30, 40 and 50 % were tested to investigate the effect of YSZ to PMMA ratio. The prepared pellets were characterized to investigate the effect on the permeability and porosity. For this set of experiments, the polymer particle size and sintering temperature were kept constant at 3 µm and 1400 °C, respectively.

3.6.1. Microstructure

Figure 30 presents the back-scattered electron (BSE) images of various PMMA-to-YSZ ratios. As can be seen, the pore volume, which is represented by black regions in the images, increases with an increase in the polymer content. The reason is because of presence of larger number of polymer particles with the increase in the ratio, which results in higher pore volume after the calcination process, in which the polymer is burnt off, leaving behind the porous structure. This result is consistent with the porosity measurement, where it is shown that the
porosity decreases with increasing temperature. Furthermore, in extreme cases, the highest and lowest amount of the polymer content, the distribution is not uniform as it is apparent.

![BSE images of various PMMA-to-YSZ (%v/v): (a) 50/50, (b) 40/60, (c) 30/70, (d) 20/80, (e) 10/90, (f) 0/100.](image)

**Figure 30.** BSE images of various PMMA-to-YSZ (%v/v): (a) 50/50, (b) 40/60, (c) 30/70, (d) 20/80, (e) 10/90, (f) 0/100.

### 3.6.2. Effect of Polymer to Ceramic Ratio on Porosity

Figure 31 presents the YSZ ceramic porosity as a function of polymer to ceramic ratio at a constant polymer particle size of 3μm and sintering temperature of 1400 °C. As shown, there is a linear relationship between the porosity and the polymer to ceramic ratio, because as the polymer content increases, the population of pyrolyzable pore formers increases, leading to a higher degree of porosity. This indicates that while porosity does not vary with changing the PMMA particle size at a constant polymer to ceramic ratio, it strongly depends on the polymer to ceramic ratio and increases by a factor of 2 when changing the ratio from 10/90 (%v/v) to 50/50 (%v/v).
3.6.3. Effect of Polymer to Ceramic Ratio on Permeability

Figure 32 presents the gas permeability as a function of polymer to ceramic ratio. As can be seen, increasing the polymer content increases the gas permeability, because of the increased number of pores. Furthermore, the interconnectivity of the pores increases with increasing the polymer content, which contributes to increased gas permeability. As shown, the gas permeability reaches the value of $29.4 \times 10^{-15} \text{ (m}^2\text{)}$ with a porosity of 49%, which is comparable with previous literature that reported a permeability of $25 \times 10^{-15} \text{ (m}^2\text{)}$ with a porosity of 71% for porous mullite-alumina ceramic made for hot gas filtration.18

Figure 31. Effect of polymer to ceramic ratio on porosity of the sintered YSZ pellets.
3.7. Robustness Investigation

To highlight the technological potential of the sintered porous YSZ ceramics, we conducted two sets of experiments. 1) Cyclic heating/cooling experiments: the samples went through the cycles, in which pellets were first heated up to 1400 °C, and then cooled down to 150 °C. 2) High temperature exposure: The prepared pellets were heated at 1700 °C for various durations to investigate how long the fabricated pellets can sustain their properties. For this set of experiments, the porous YSZ ceramic pellets were prepared at a sintering temperature of 1400 °C with 3 µm PMMA particles in size and a polymer to ceramic ratio of 30/70 (%v/v).

3.7.1. Cyclic Heating/Cooling Experiments

To simulate an industrial setting, in which high temperature gas filters go through cyclic heating and cooling, we designed an experiment where we heated the as-sintered porous YSZ ceramic to 1400 °C with a dwelling time of 1 h, then we cooled the sample to 150 °C with a
dwellling time of 30 min. This whole process is considered one cycle, and we investigated up to six cycles.

3.7.1.1. Porosity and Gas Permeability

Figure 33(a) presents the porosity of the pellet as a function of cycle number. As can be seen, the porosity drops from 40% to 29% during the first cycle and then remains constant. Figure 33(b) presents the gas permeability of the pellet after each cycle. As can be seen, unlike the porosity, permeability decreases slightly by only 2% during the first cycle, and then a decrease of 15% after cycle three, and after that it remains constant. Because the observed decrease in porosity does not affect the permeability, it indicates that the fabricated pellets sustain the cyclic heating/cooling without destroying the properties.

![Figure 33](image)

**Figure 33.** (a) Effect heating (1400 °C-1h)/cooling (150 °C, 30 min) number of cycles on porosity. (b) Effect heating (1400 °C-1h)/cooling (150 °C, 30 min) number of cycles on porosity.

3.7.2. High Temperature (1700 °C) Exposure Experiment

After performing the cyclic heating/cooling experiments, we took a step further and tested the sintered pellets at an extreme condition, where the pellets were exposed to 1700 °C,
which is away from the industrial setting condition. Afterwards, gas permeability as well as porosity was measured, and the results were compared with the as-sintered pellets.

3.7.2.1. Microstructure

The samples were exposed to the high temperature for various dwelling times, and then their surface was observed using scanning electron microscopy. The secondary electron (SE) images are presented in Figure 34. As can be seen, pore shrinkage occurs as the dwelling time progresses. Furthermore, the grains enlarge with increasing the dwelling time.

![SEM images of the porous YSZ ceramics after exposure to 1700 °C for: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h.](image)

**Figure 34.** SEM images of the porous YSZ ceramics after exposure to 1700 °C for: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h.

3.7.2.2. Gas Permeability and Pore Size

Porosity measurements indicated that after 1 h of exposure to 1700 °C, the amount of open porosity decreased from 39% to 17%. This is the result of the same process that is
responsible for solid-state sintering and densification. The decrease in open porosity was likely occurred due to grain growth and pore rounding, which led to the closure of some surface-connected porosity. Exposure for longer periods of time (2, 3, or 4 h) did not cause any further reduction in the amount of open porosity (Figure 35(a)). This suggests the remaining open porosity has become more thermodynamically stable and the kinetics controlling further densification have become slow. The results show that porous YSZ ceramics can maintain a network of open porosity after limited exposure at 1700 °C.

We evaluated the gas permeability of porous YSZ ceramics to quantify the effects of high temperature exposure on their performance in hot gas filtration. Figure 33(b) presents the gas permeability after exposure to 1700 °C in air for 1 to 4 h. The gas permeability initially followed a similar trend to open porosity and decreased by a similar proportion to the open porosity after 1 h. However, while the open porosity remained constant with exposure beyond 1 h, we observed a continuous decrease in the gas permeability (Figure 31(b)). Since the amount of surface-connected open porosity was not observed to change much (Figure 30), the decrease in gas permeability was probably due to the closure of pores and pore channels deep within the porous YSZ ceramics. The results show that the porous YSZ ceramics can sustain limited exposure at 1700 °C, but some degradation in their performance occurs.

![Figure 35](image-url)  
**Figure 35.** Effect of high temperature exposure dwelling time on the (a) permeability, (b) porosity of the sintered YSZ pellets.
Upon continued exposure, a number of changes were observed: the grain size continuously increased, the number of pore openings decreased to some extent, and existing pores became more rounded. The results confirmed that gas permeability decreased as a result of the densification mechanisms, which occur during solid-state sintering; namely grain growth, pore rounding, and pore closure. While the same mechanisms decreased the gas permeability, they increase the mechanical integrity of the porous YSZ ceramics.
4. CHAPTER FOUR – CONCLUSIONS

In the present work, porous YSZ ceramics for hot gas filtration were fabricated, using pore-forming procedure, in which PMMA was used as the pore-forming agent. The effect of sintering temperature, polymer particles size, and ceramic to polymer ratio on the porosity, pore size, gas permeability, and Vickers micro hardness of the sintered pellets were investigated. YSZ is the potential candidate for hot gas filtration application. The present study was focused on three thrusts: 1) Fabrication of porous YSZ using pore forming procedure, 2) Characterization of the sintered pellets in terms of various properties, including porosity, pore size, gas permeability, and Vickers hardness, and 3) Robustness investigation of the fabricated pellets through designing two experiments that simulate an industrial setting: 1) cyclic heating/cooling, and 2) High temperature exposure. The following conclusions were drawn on the basis of the results obtained from this study:

1) Porous YSZ structure was obtained, using PMMA as the pore former, within which the pore were distributed uniformly, as the SEM images indicated. Furthermore, the fabricated pellets were hard for all sintering temperatures.

2) It was found that both porosity and permeability decrease with increasing the sintering temperature. However, pore size showed an abnormal behavior, for which pore size first increased from 1300 to 1400 °C and then decreased above 1400 up to 1700 °C. Also, hardness increased with increasing the sintering temperature.

3) The investigation of the effect of polymer particle size indicated that it has no effect on the porosity; however, unlike the porosity, pore size and in turn permeability increase with increasing the PMMA particle size.

4) It is shown that porosity increases as the PMMA-to-YSZ ratio increases, and because the permeability is governed by the porosity, it also increases. Moreover, it was found that hardness is inversely proportional to the porosity.

5) The optimum fabrication condition was determined, for which the sintering temperature and PMMA-to-YSZ are found to be 1400 °C and 30/70 (v%/v%), respectively. Also, the
polymer particle size in the range of 0.8 – 3 µm is optimal depending on the particulate size demanded for filtration.

6) The results of cyclic heating/cooling experiments showed that porosity drops after going through one cycles and then remains unchanged up to 6 cycles. On the other hand, permeability decreases slightly after 3 cycles and then remains constant regardless of the number of cycles.

7) It was found that exposing the sintered pellets to 1700 ºC results in a decrease in the porosity after 1 hour, and after that it remains unchanged up to 4 hours. However, permeability decreases linearly as the dwelling time progresses.

The result of this work provides a procedure to fabricate porous YSZ filters for hot gas filtration. Investigation on the effect of various variables provides an insight into the amount and size of the required pore former to satisfy the requirement of particulates to be filtered in terms of composition and size. The robustness experiments demonstrate that the fabricated filters have the potential to be utilized for hot gas filtration application in industrial conditions.
5. CHAPTER FIVE - RECOMMENDATION FOR FUTURE WORK

Upon completion of this work, a number of prospective extensions to the project have been determined:

1. The mathematical model can be developed in form of an expression to correlate various parameters to the variables, namely sintering temperature, polymer particle size, and ceramic to polymer ratio. Therefore, depending on the application, in which the porous ceramic would be used, all the processing variables could be selected on the basis of the developed expression.

2. The effect of sintering duration could be investigated to determine if it has a significant impact on the sintered pellets. Because all the prepared pellets were solid enough at various sintering temperatures, it is proposed to sinter the pellets for a shorter period of time to determine if it affects the porosity results.

3. The cost benefit analysis is required to be conducted to determine the feasibility of pellets fabrication at large scale.

4. To investigate the effect of other types of pore former and compare the result with the result of this work.
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