Constrained sintering of yttria-doped zirconia: the relationship between microstructure and gas flow rate

Gary J Wright

2006

School of Engineering
University of Surrey
Guildford, UK

Rolls-Royce Fuel Cell Systems Ltd
Holywell Park
Loughborough
Leicestershire, UK

Copyright © Gary J Wright 2006
Abstract

The integrated planar solid oxide fuel cell designed by Rolls-Royce plc consists of a fuel electrode and an air electrode separated by an ion-conducting solid electrolyte. The electrolyte must exhibit ionic conductivity and be non-permeable to the cell gases. The other cell components set limits for the firing temperature of the electrolyte, thus restricting its densification. Further, the use of a thin constrained layer, fabricated via screen-printing, makes the separation of the fuel and oxidant much more challenging than in unconstrained planar fuel cell designs. Thus, the aim of this study was to investigate the influence of the screen-printing and sintering processes on the microstructure of the electrolyte and ultimately on the permeability or gas flow rate.

The ceramic material used throughout this study was zirconia doped with 3-mol% yttria formulated into a screen printable ink and deposited onto a pre-sintered substrate. The ink was deposited through mesh sizes ranging in thickness from 50 to 215 μm. The printed layer was then dried and additional layers added up to a maximum of four applications. The resulting laminate was sintered using a conventional sintering scheme. The thickness, relative density and grain size of the sintered electrolyte were recorded. Increasing sintered layer thickness showed an associated reduction in relative density and grain size. The conventional sintering profile was modified by changing the heating rate, sintering temperature and sintering time. From this part of the study a baseline fabrication process was established. This baseline used a 165 mesh size with three print-dry applications, a heating rate of 10°C min⁻¹, a sintering temperature of 1450°C and a sintering time of 10 hours.

The conventional sintering profile was modified to incorporate coarsening, two-step sintering and a combination of these denoted as 'three-step' sintering. Layer thickness, relative density, grain size distribution and pore size distribution were determined. It was possible to achieve full density with all three types of sintering profile. Grain growth could not be avoided in the constrained thick-films but the pore size distribution was narrower for the modified sintering profiles compared with that for conventional sintering.

Gas leakage testing showed that the effect of microstructure on the gas flow through the electrolyte was not a function of a single variable. Rather, it was a combination of at least four parameters (the ratio of grain size to sintered layer thickness, relative density, pore size range and number of pores per unit area). Only if all four parameters were within certain defined boundary conditions was the gas flow minimised. Although the lowest gas flow rate measured was still just outside of the design requirement for an industrial application, the associated sintering schedule used lower temperatures than currently used to densify the electrolyte and there is scope for further optimisation.
Acknowledgements

I would like to express my appreciation to my supervisor, Dr. Julie Yeomans, for her patience and guidance throughout this work. I also wish to thank my industrial supervisors, Dr. Mark Cassidy and Mr. Paul Greaves for their encouragement and support throughout this work.

I wish to express my gratitude to Rolls-Royce Fuel Cell Systems Limited, for funding this work and allowing me the use of materials and equipment, which made this project possible. There has been support from a number of my colleagues who have provided gratefully received assistance, namely, Mr Philip Delaforce, Dr. Jeff Knight and Mr Dave Brown.

I am extremely grateful for the help and support of Dr. Graeme Roberts who supplied the sub-contracted scanning electron microscopy at key stages of this work.

Finally, I would like to thank Eileen, my family and friends for their patience and support.
Table of contents

Abstract................................................................................................................................................... i
Acknowledgements ............................................................................................................................... ii
Table of contents .................................................................................................................................... iii

1 Introduction ......................................................................................................................................... 1
   1.1 Background to the project......................................................................................................... 1
   1.2 Structure of the thesis ............................................................................................................ 3

2 Overview of fuel cell operation ........................................................................................................ 4
   2.1 Introduction ............................................................................................................................ 4
   2.2 Principle of operation ............................................................................................................ 4
   2.3 Fuel cell development and applications ............................................................................. 5
   2.4 Economic and environmental considerations ....................................................................... 8
   2.5 Electrolyte material requirements ....................................................................................... 9
      2.5.1 Overview of requirements ............................................................................................. 9
   2.5.2 YSZ electrolyte .............................................................................................................. 10
   2.6 Concluding remarks ............................................................................................................. 13

3 Literature review ............................................................................................................................. 14
   3.1 Introduction .......................................................................................................................... 14
   3.2 Sintering theory ................................................................................................................... 14
      3.2.1 Overview .......................................................................................................................... 14
      3.2.2 Driving force for sintering ............................................................................................. 15
      3.2.3 Stages of solid state sintering ....................................................................................... 16
         3.2.3.1 Overview .................................................................................................................. 16
         3.2.3.2 Initial stage of sintering ........................................................................................... 17
      3.2.4 Intermediate stage of sintering ..................................................................................... 19
      3.2.5 Final stage of sintering ................................................................................................. 20
   3.3 Constrained sintering ............................................................................................................ 23
      3.3.1 Overview .......................................................................................................................... 23
      3.3.2 Densification mechanisms ............................................................................................ 23
   3.4 Coarsening ............................................................................................................................. 24
      3.4.1 Overview .......................................................................................................................... 24
      3.4.2 Homogenised pore size .................................................................................................. 25
   3.5 Two step sintering technique ............................................................................................... 27
      3.5.1 Sintering profile ............................................................................................................ 27
      3.5.2 Sintering of YSZ ...................................................................................................... 30
   3.6 Concluding remarks .............................................................................................................. 31
# Table of Contents

## 4 Conventional sintering profiles

4.1 Introduction ................................................................. 32
4.2 Fabrication of thick-film layers ........................................ 32
4.2.1 Background to the screen printing process ...................... 32
4.2.2 Experimental procedure ............................................. 34
4.2.3 Mesh sizes ................................................................. 35
4.2.4 Powder supply and ink formulation ................................. 36
4.2.5 Substrate ................................................................. 38
4.2.6 Sample preparation ................................................... 39
4.2.7 Sintering profiles ....................................................... 42
4.2.7.1 Overview ................................................................. 42
4.2.7.2 Sintering profiles: heating rate, temperature and time variations .............................................. 43
4.2.8 Dilatometry ................................................................. 45
4.2.9 Archimedes measurement of density ................................. 46
4.2.10 Sample characterisation - microscopy ............................... 46
4.2.11 Microstructural analysis ............................................. 47
4.2.11.1 Grain size measurement ........................................ 47
4.2.11.2 Layer thickness measurement .................................. 49
4.3 Results and discussion .................................................... 51
4.3.1 Screen thickness and number of print deposits .................. 51
4.3.1.1 Deposition thickness .............................................. 51
4.3.2 Sintering profile - conventional sintering ......................... 58
4.3.2.1 Heating rate ......................................................... 58
4.3.2.2 Microstructural evolution with heating rate ................. 62
4.3.2.3 Sintering temperature ............................................. 64
4.3.2.4 Sintering time ....................................................... 66
4.4 Concluding remarks ....................................................... 69

## 5 Non-conventional sintering profiles

5.1 Introduction ................................................................. 70
5.2 Experimental details ...................................................... 70
5.2.1 Sample preparation ................................................... 70
5.2.2 Coarsening step processing ......................................... 71
5.2.3 Two-step processing .................................................. 74
5.2.4 Three-step processing ............................................... 76
5.3 Results and discussion .................................................... 78
5.3.1 Coarsening step profiles ............................................. 78
5.3.2 Two-step profiles ....................................................... 84
5.3.3 Three-step profiles ..................................................... 91
### Table of Contents

5.3.4 Microstructural influence of non-conventional sintering .........................................95
5.4 Concluding remarks ...........................................................................................................98

6 Influence of microstructure on gas permeance ................................................................................99
6.1 Introduction ...........................................................................................................................99
6.2 Gas flow through a sintered film ....................................................................................99
6.2.1 Permeability ..........................................................................................................................99
6.2.2 Gas permeance ................................................................................................................101
6.3 Experimental procedure ..................................................................................................102
6.3.1 Gas testing procedure .....................................................................................................102
6.3.2 Microstructural characterisation ...................................................................................105
6.4 Results and discussion ...................................................................................................107
6.4.1 Conventional sintering ....................................................................................................107
6.4.1.1 Effect of deposited thickness on gas flow rate .................................................107
6.4.1.2 Relationship between microstructural parameters and gas flow rate for conventionally sintered samples .........................111
6.4.2 Non-conventional sintered samples ............................................................................115
6.4.2.1 Effect of coarsening on gas flow rate .................................................................115
6.4.2.2 Effect of two-step sintering on Gas flow rate .....................................................116
6.4.2.3 Effect of three-step sintering on gas flow rate ..................................................117
6.4.3 Relationship between gas flow rate and microstructural parameters for non-conventionally sintered samples ..............................................................118
6.4.4 Gas permeance suitable for an industrial application .............................................125
6.5 Concluding remarks .........................................................................................................127

7 Concluding remarks ...................................................................................................................128
7.1 Conclusions from current work ....................................................................................128
7.1.1 Overview ..............................................................................................................................128
7.1.2 Deposition thickness and conventional sintering parameters ..............................128
7.1.3 Non-conventional sintering profiles .............................................................................129
7.1.4 Gas testing ..........................................................................................................................130
7.2 Suggestions for further work .........................................................................................131

References ........................................................................................................................................132

Wilcoxon signed-rank test ............................................................................ A1
Gas flow calculations ..................................................................................................................................B1
Gas permeance calculation ..................................................................................................................................B3
Chapter 1: Introduction

1 Introduction

1.1 Background to the project

Ceramic materials have had a considerable impact on technology in the previous century. It is likely that the range and diversity of applications of these materials will increase during the twenty first century. One such application is the use of technical grade ceramics in the energy generation industry. Energy production and distribution has been the subject of much discussion in recent decades. The depletion of the world’s resources and environmental concerns has led to the search for cleaner sources of energy, including technologies not using fossil fuels.

The majority of the world’s energy is generated by derivatives of the heat engine, all of which are based on a combustion process. Heat engines are limited by the Carnot cycle, which means that the maximum efficiency is defined by the differential temperature that can be achieved i.e. the heating stage. Fuel cell devices have been proposed as a cleaner and more efficient method of energy production. These devices convert chemical energy directly to electrical energy and thus are not limited by the Carnot cycle.

Solid oxide fuel cells (SOFCs) operate at temperatures in excess of 600°C and are constructed from technical grade ceramics. They consist of a fuel electrode and an air electrode separated by an ion-conducting solid electrolyte. The principal roles of the electrolyte are to promote the transport of ions to complete the electrical circuit between the electrodes and to separate the fuel and oxidant, thus preventing them from reacting. In the case of a solid oxide fuel cell (SOFC), anions are transported through the solid electrolyte structure, which is typically yttria stabilised zirconia (YSZ), and are liberated at the anode (fuel electrode), producing water as the by-product. The reduction in noxious emissions and the increased potential efficiencies make SOFCs with YSZ electrolytes an attractive alternative to existing power generation technology.

Rolls-Royce Fuel Cell Systems Limited (RRFCS) have been involved with the development of a SOFC system since 1992. The fuel cell technology is based on a low-cost design called the Integrated Planar Solid Oxide Fuel Cell (IP-SOFC). In its simplest form, the fuel cell can be described as series-connected cells fabricated on a porous support tube, as seen in Figure 1.1.
Chapter 1: Introduction

Figure 1.1: Schematic diagram of a cross-section through an IP-SOFC. The individual cell components are screen-printed onto a pre-fired substrate.

The IP-SOFC has been designed around a YSZ electrolyte and this is applied via screen-printing. The final sintered ceramic layer produced from this thick-film technique is of the order of tens of micrometres. However, the use of a thin layer makes the separation of the fuel and oxidant much more challenging. It is imperative that the electrolyte is impermeable to both the fuel and the oxidant.

The electrolyte cannot be sintered freely as it is constrained by the adjacent layers. Constrained sintering can retard the densification of YSZ. If the resulting porosity is open, i.e. interconnected, this would bring the fuel and oxidant into contact. Combustion due to mixing of fuel and oxidant leads to failure of the fuel cell structure. Normally, firing the ceramic at a higher temperature or for a longer time would reduce the porosity. This approach cannot be adopted here, however, as it would lead to problems with the performance of other fuel cell components. Although a satisfactory sintering regime is being used currently there is a need to reduce the peak sintering temperature of the electrolyte while maintaining an impermeable barrier between the fuel and oxidant.

The principal aim of this research was to understand the relationship between processing conditions, microstructure and gas permeability such that processing regimes could be devised that would optimise the fabrication of YSZ thick-films, i.e. produce a gas-impermeable layer under conditions that were compatible with other cell components.
Chapter 1: Introduction

1.2 Structure of the thesis

Following this introduction, Chapter 2 gives an overview of fuel cells. The function of fuel cells and the basis of their operation is presented. This is followed by an overview of the history of the technology, along with a discussion of current and future developments. These future developments are accompanied by a summary of the economic and environmental issues surrounding fuel cells. Chapter 2 concludes with the role of YSZ as the electrolyte material within the IP-SOFC design.

A firing or heating method described as sintering is normally employed to achieve densification of a ceramic material such as YSZ. The theory of sintering, including the difference between free and constrained sintering is covered in Chapter 3. A review of the literature on coarsening and an alternative sintering method called 'two-step sintering' is included.

Chapter 4 covers the fabrication, by screen-printing, and sintering of YSZ layers. The changes made to heating rate, sintering temperature and sintering time for conventional sintering are described and include the resulting changes in sintered layer thickness, relative density and grain size. A baseline fabrication procedure is identified.

Coarsening, two-step and a combination of these approaches called 'three-step' sintering are presented and discussed in Chapter 5. Sintered layer thickness, relative density, grain size and pore size are considered.

Chapter 6 presents the gas testing results for samples sintered using the schemes from Chapters 4 and 5. This chapter brings together conventional sintering and the profile modifications, coarsening, two-step and three-step sintering and relates the gas flow rate to parameters such as sintered layer thickness, relative density, grain size and pore size distribution.

The concluding remarks on the present work are given in Chapter 7 and ways in which the research may be moved forward are also outlined in this chapter.
Chapter 2: Overview of operation

2 Overview of fuel cell operation

2.1 Introduction

The IP-SOFC is designed around the YSZ thick-film electrolyte. This layer forms an ion conducting solid interface between the electrically conducting electrodes and fuel and oxidant gases. In this chapter an overview of SOFC operation is given, which details how the overall reaction converts the fuel and oxidant gases into electrical power. The fundamental principles of fuel cells have been known since 1839 and an overview of the historical development is given along with a description of current and future developments as well as applications of fuel cell technology. Material property requirements are discussed, including the key parameters relating to the IP-SOFC design. The chapter concludes with a description of YSZ as a SOFC electrolyte.

2.2 Principle of operation

The reactions taking place in the fuel cell involve ionisation of either the fuel or oxidant and the giving and receiving of electrons with respect to the external circuit or load. Fuel gas, such as hydrogen, is combined with oxygen from the air, producing a theoretical direct current voltage of 1.1 volts per cell. A schematic diagram of the SOFC is shown in Figure 2.1.

![Schematic diagram of SOFC operation](image)

**Figure 2.1:** Schematic representation of SOFC operation. Hydrogen gas enters at the anode and steam exits, while air enters at the cathode and depleted air exits.
Chapter 2: Overview of operation

The fuel supplied to the anode electrode is oxidised, while the oxygen supplied to the cathode electrode is reduced. This gives the overall reaction:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$$  \hspace{1cm} (2.1)

The overall reaction from the oxygen ions, conducted through the YSZ electrolyte between the two electrodes, provides direct current electricity generated by the corresponding electron flow. Nernst's work on solid oxide electrolyte materials provides a relationship between the electromotive force (emf), generated by the electron flow and the partial pressure of oxygen, expressed as the Nernst equation:

$$emf = \frac{RT}{4F} \ln \left( \frac{P_{O_2}}{P_{O_2}^*} \right)$$  \hspace{1cm} (2.2)

where $R$ is the universal gas constant; $T$ is the absolute temperature; $F$ is the Faraday constant; $P_{O_2}$ is the partial pressure of $O_2$ oxidant; and $P_{O_2}^*$ is the partial pressure of $O_2$ fuel.

2.3 Fuel cell development and applications

Advances in materials have driven the development of the fuel cell. In 1839, Sir William Grove demonstrated that the electrolysis of water in dilute sulphuric acid was nearly reversible (Grove, 1839). At the time Grove recognised the need for intimate contact between the gas, the electrolyte and the solid electrode, known as the "notable surface of action". Establishing this three-phase interface is critical to the operation of the electrodes at high current densities. Grove was mostly interested in the use of hydrogen as a fuel and it was not until 1889 that alternative fuels such as coal were proposed for use with fuel cell devices (Mond and Langer, 1889).

A decade later the 'Nernst Glower' provided solid-oxide electrolytes, the basis for ceramic fuel cells. Nearly one hundred years after Grove's discovery, Bacon worked on the hydrogen oxygen fuel cell. He believed that successful commercialisation could only be accomplished with non-noble metal catalysts capable of reducing oxygen efficiently. By controlling the porosity of the electrode, Bacon optimised the three-phase interfacial area, greatly increasing the available reaction sites on the electrode. In 1959 Allis-Chalmers demonstrated a fuel cell tractor, and the Pratt and Whitney aircraft corporation licensed the right to Bacon's fuel cell in the same year (Fuller, 1997).
The acceleration in fuel cell development came due to defence and space programmes, such as Gemini and Apollo. Fuel cells were selected for space due to weight considerations and because they were the source with the highest energy density (kWh kg⁻¹) and acceptable specific power (kW kg⁻¹) (Fuller, 1997).

Current fuel cell technology can be distinguished by its temperature of operation and the type of electrolyte used. There are five main kinds of fuel cell; proton exchange membrane (PEM) / direct methanol fuel cells (DMFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), solid oxide fuel cell (SOFC). The major applications can be categorised into: space and defence, stationary power generation, transportation and portable power. Table 2.1 shows the applications for the fuel cell types described above.

**Table 2.1: Typical applications for different types of fuel cells**

<table>
<thead>
<tr>
<th>Type of Fuel Cell</th>
<th>Electrolyte</th>
<th>Fuel</th>
<th>Operating temperature (°C)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOFC</td>
<td>Zirconium /yttrium oxide</td>
<td>Methane, hydrogen</td>
<td>800-1000</td>
<td>Large stationary plant</td>
</tr>
<tr>
<td>MCFC</td>
<td>Lithium carbonate/potassium carbonate</td>
<td>Hydrogen</td>
<td>600-700</td>
<td>Large stationary plant</td>
</tr>
<tr>
<td>PAFC</td>
<td>Phosphoric acid (H₃PO₄)</td>
<td>Hydrogen, reformate with &lt; 10 ppm carbon monoxide</td>
<td>190-200</td>
<td>Small stationary plant (with combined heat and power)</td>
</tr>
<tr>
<td>AFC</td>
<td>Potassium hydroxide</td>
<td>Hydrogen, reformate containing no carbon dioxide</td>
<td>60-130</td>
<td>Space, some specialised applications</td>
</tr>
<tr>
<td>PEM</td>
<td>Solid polymer membrane</td>
<td>Hydrogen, reformate with &lt; 10 ppm of carbon monoxide</td>
<td>60-100</td>
<td>Automotive, portable, small stationary plant (with combined heat and power)</td>
</tr>
</tbody>
</table>
Chapter 2: Overview of operation

The team to advance research on gas energy transformation (TARGET) programme in the late 1960s and 70s focussed on the first commercial applications, and were sponsored by both the gas and electricity utilities in the United States. Natural gas supply problems in the early 1970s hampered the development of the phosphoric acid fuel cells (PAFC), associated with the TARGET project. During the mid 1970s the Department of Energy (DOE), the Electric Power Research Institute (EPRI) and the Gas Research Institute (GRI) intensified development of all types of fuel cell power plants, leading to testing of a 4.8 MW unit in the early 1980s and a number of 40 kW power plants in the mid 1980s (Fuller, 1997).

In 1992 the first commercial power plant, the 200 kW PC25™ power plant began operation. The 1990s saw fuel cell development focus on light-duty transportation applications. The first polymer fuel cell had cross-linked polystyrene divinyl benzene sulfonic acid electrolytes. These early polymers were degraded under the oxidising conditions in the fuel cell and had a limited life. Dupont introduced fully fluorinated polymers (Nafion) that have shown good stability up to 100°C. Proton exchange membrane (PEM) fuel cells developed quickly, but it was not until the 1980s that PEM fuel cells received significant research and development. Ballard, a Canadian company, is currently a world leader in the development of PEM fuel cells, based on a solid polymer electrolyte membrane. PEM fuel cells have been under intense development for vehicle applications with several demonstrations in cars and buses. Daimler Benz and Ford in collaboration, General Motors, Toyota, and Mazda are all developing their own fuel cell vehicles. In 1998 a new generation of buses were delivered to Chicago and British Columbia for on-road testing (Fuller, 1997). This type of fuel cell bus is now transporting passengers in many major cities across the world and the first fuel cell powered red London bus was delivered in 2005 (www.fuel-cell-bus-club.com, 2005).

PEM fuel cells are primarily aimed at transportation and portable applications while SOFCs, the only true “solid” electrolyte fuel cells, are being developed for the stationary power market. Westinghouse have developed a tubular cell configuration, demonstrating long term stability that generated power over 69,000 hours (more than 7.5 years). They are now involved with the development of the Delta 9 design which is based around flattened tubular cells (Baker and Adamson, 2006). Kansai Electric Power Company have produced a SOFC unit operating over 10,000 hours at 85% fuel utilisation which endured 100 thermal cycles between 1000°C and ambient temperature (Fuller, 1997). Intensive efforts continue to reduce fabrication costs with commercialisation targeted for ~ 2010.

Within the last few years, SOFC development has increased activities with companies and institutions starting SOFC related work. Demographically these projects are operating in Europe, North America, Asia and Australia. The large stationary applications for SOFC systems still fall behind that of molten carbonate technology. SOFC technology is being developed by the largest number of companies, compared with other fuel cell types, and has
Chapter 2: Overview of operation

a strong Japanese focus. Despite this it has the lowest number of test units in the field. This is associated with no one company resolving all of the challenges in order to send a significant number of systems to market. Gas turbine hybridisation, where the fuel cell is linked to a gas turbine is the approach taken by FuelCell Energy (MCFC), GE Energy (SOFC), Siemens Westinghouse (SOFC) and Rolls-Royce Fuel Cell Systems (SOFC) giving potential efficiency > 40% (Agnew et al., 2005). While many of these hybrid fuel cell systems remain in the modelling and development stage, FuelCell Energy has placed a 250-kW Direct FuelCell® power plant at GK insulators in Japan. This is a combined heat and power application for their ceramic kiln operations, with the goal to reduce carbon dioxide emissions over the next five years, although they do not quantify what the reductions will be (Baker and Adamson, 2006).

Rolls-Royce Fuel Cell Systems Limited are planning to enter the stationary power market with a 1 MW hybrid cycle fuel cell system by 2008. This will be based on a SOFC stack combined with a gas turbine (Rolls-Royce, 2005). They will face direct competition from Siemens Westinghouse and GE Energy (Baker and Adamson, 2006).

2.4 Economic and environmental considerations

Most of the cost of fuel cell stacks can be ascribed to materials used during the fabrication process, for example polymer membranes and precious metal catalysts. Reducing the amount of these materials in the stack is one option in reducing cost. The alternative approach is to reduce costs by improving the performance of the fuel cell (Fuller, 1997). Heat engines have been under development for over 100 years and in that time they have reduced in weight and cost due to a competitive market place. Fuel cell performance, efficiency and prices are at the development stage and competitiveness will take some considerable time to be achieved (Whitworth, 1998). One of the major issues facing fuel cell developers is materials and technology challenges for stacking fuel cells and currently they are still too expensive to be cost competitive for commercial applications. Therefore the marketing of fuel cell systems must be considered on more than simply the unit cost of electricity to allow them into the market place. The cost of fuel cells will be determined by whole life cycle cost, more specifically from the cost of raw material extraction through to the cost of disposal at the end of life (Hoogers, 1998).

It is a remarkable underachievement that despite enormous technological advances in other areas it is still necessary to burn fuel for power. The inefficiency of heat engines means most of the energy from precious carbon-based resources is wasted and the products of combustion are major atmospheric pollutants. Development of alternative methods of power generation which are less polluting is required, and electric power from fuel cells is probably one of the best contenders. Success in developing fuel cell power would have many
economic implications, most of which are not considered in conventional analyses. These are far-reaching. For example, many researchers think that a range of human respiratory complaints such as asthma may be caused in part by atmospheric pollutants from combustion power sources. The use of fuel cell systems might therefore reduce health expenditure on these wide-spread respiratory complaints (Burstein and Barnett, 1998).

A fuel cell system with an efficiency of 60% would emit 35-60% less carbon dioxide from a hydrocarbon fuel and 80% less from hydrogen compared with conventional heat engines. Other emissions such as sulphur dioxide and nitrous oxide would be significantly reduced, compared with the emissions from the current mixture of conventional power stations in the UK. According to estimates from the American DOE, over one year, 1 MW of electricity generated by fuel cells will avoid 45 tonnes of sulphur dioxide and 19 tonnes of nitrous oxide being released into the atmosphere (Whitworth, 1998).

2.5 Electrolyte material requirements

2.5.1 Overview of requirements

In the IP-SOFC the state of the art material used for the electrolyte is YSZ. This material exhibits a number of properties that satisfy the requirements for a SOFC electrolyte. YSZ has an adequate ionic conductivity at SOFC operating temperatures and the electronic conduction is negligible. The ionic transfer number $t_\text{i}$, the ratio of the ionic and electronic conductivities, is typically greater than 0.9 for YSZ (Goodenough and Whittingham, 1976). Any reduction in the ionic transfer number would reduce efficiency by effectively short circuiting the fuel cell through the electrolyte.

The electrolyte needs to be chemically stable over a wide range of oxygen partial pressures. Crystallographic modification is undesirable as volume changes could lead to cracking and delamination. Thermal expansion mismatch between the electrolyte and electrode materials causes stresses in the SOFC structure, which may lead to loss of mechanical integrity; hence, mismatch needs to be minimised. Fundamentally the electrolyte must be impermeable to the fuel and oxidant gases. In the IP-SOFC design the fuel and oxidant must remain separated while the YSZ electrolyte needs to be less than 20 μm thick to limit the ohmic losses (Gardner et al., 2000; Marques and Navarro, 1996).
Chapter 2: Overview of operation

2.5.2 YSZ electrolyte

Pure zirconia has a monoclinic structure at room temperature and above 2370°C a cubic fluorite phase forms, with zirconia melting at 2680°C. In undoped zirconia the monoclinic structure transforms to the tetragonal structure at 1170°C, which has an associated volume change of 3 to 5%. When this phase change occurs on cooling from the sintering temperature the volume expansion can be associated with crack propagation.

With the addition of a few percent of "stabilisers," such as calcia (CaO), magnesia (MgO), or yttria (Y₂O₃), the cubic phase can be preserved to lower temperatures. Stabilising the cubic fluorite structure increases the oxygen ion conduction. The YSZ phase diagram in Figure 2.2 shows the effect of yttria doping on phase stability.

![Yttria-Doped Zirconia Phase Diagram](image)

**Figure 2.2:** The ZrO₂-rich region of the ZrO₂-Y₂O₃ phase diagram. The symbols c, t, m and I denote the cubic, tetragonal, monoclinic and liquid phases, respectively. The shaded areas illustrate uncertainty in the phase boundaries (after Yoshimura, 1988).

Substitution of an yttrium cation for zirconium leads to a charge imbalance. Charge balance is regained by the formation of half an oxygen ion vacancy. This change in the electronic structure occurs because yttrium has a valency of three and zirconium is a group four
element, meaning that there is a difference in valency of one. A simplified two-dimensional representation of the resulting structure is shown in Figure 2.3.

![Diagram of zirconia structure](image-url)

Figure 2.3: Representation of zirconia structure showing (a) pure zirconia and (b) solid solution of YSZ (after Kocache et al., 1984).

Despite this increase in oxygen ion vacancies the conductivity remains very low at room temperature. However, when YSZ is heated to a temperature above 700°C it exhibits adequate oxygen ion conductivity for use within an SOFC (Minh, 1993). This relates to a conductivity of 0.06 S cm⁻¹ for 3-mol% YSZ at a typical SOFC operating temperature of 900°C (Bossell, 1992). Although there are a number of dopants available that provide a higher level of oxygen-ion conductivity, yttria tends to be the most commonly used due to its availability and cost. In the case of YSZ, levels above ~ 8-mol% yttria provide no significant increase in performance (Minh, 1993).

The resistance of a fuel cell is described by the area specific resistance (ASR). This is related to the operating temperature and includes the resistance of the electrolyte, cathode and anode cell components. In the IP-SOFC design a cell voltage of 0.33 volts and a current density of 0.28 A cm⁻² results in an ASR of 1.18 Ω cm². The ASR is divided equally between the electrodes of the cell while the electrolyte value is 0.05 Ω cm² (Rolls-Royce Fuel Cell Systems, 2004). To meet this resistance target for the IP-SOFC operating at 800°C would require an electrolyte with a thickness of 15 μm. This value is in
good agreement with the data from Bossell (1992) and Steele (1996). The effect of electrolyte thickness and operating temperature on ASR is shown in Figure 2.4.

Figure 2.4: The change in resistance of YSZ electrolytes with increasing thickness and operating temperature (after Bossell, 1992)

Changes to the electrolyte thickness to achieve a specific ASR must take into account the need for the layer to remain impermeable to both fuel and oxidant gases. Thickness may influence these layers through changes in microstructure. Potential changes in the gas tightness of the layer can be quantified by gas testing. This approach results in a gas flow rate across the electrolyte and this can be expressed as a percentage of the total flow or as gas permeance. The IP-SOFC design has a gas flow specification based on the sub-systems requirements document (Rolls-Royce Fuel Cell Systems, 2004). The gas flow across the YSZ electrolyte must be ≤ 3% for a commercial product. The gas flow requirements of 3% in the IP-SOFC design relate to a nominal value for gas permeance of $10^{-5}$ mbar l s$^{-1}$ cm$^{-2}$. A specification for the electrolyte used within the IP-SOFC is given in Table 2.2.
Chapter 2: Overview of operation

Table 2.2: Requirements for the electrolyte specified for the IP-SOFC

<table>
<thead>
<tr>
<th>Material</th>
<th>Sintered thickness (µm)</th>
<th>System leakage (%)</th>
<th>Gas permeance (mbar l s⁻¹ cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-mol% YSZ</td>
<td>15 ± 5</td>
<td>3</td>
<td>10⁻⁵</td>
</tr>
</tbody>
</table>

2.6 Concluding remarks

SOFCs have been identified as the technology of choice for stationary power applications. The entry of fuel cells into the market place relies on further materials development as well as addressing the economic and environmental challenges. The electrolyte in SOFCs, which is based on zirconia doped with yttria, provides adequate ionic conductivity. It has been shown that a change in thickness of the electrolyte alters the ASR of the fuel cell and thus the electrolyte must be as thin as possible to avoid losses in cell performance. However, the electrolyte must also be impermeable to the fuel and oxidant gases. Thus, there are considerable demands on the fabrication process.
Chapter 3: Literature review

3 Literature review

3.1 Introduction

The following review begins with an outline of the theory of the sintering of ceramic powders, covering the evolution of sintering and densification and including the sintering mechanisms for YSZ. The theories behind the sintering of constrained thick-film layers are introduced with an overview of how these compare with free sintering. Additional techniques are also discussed, including the application of a coarsening step and two-stage sintering profiles.

3.2 Sintering theory

3.2.1 Overview

The process of firing and consolidation of powder particles is described as sintering. The sintering of ceramics has been carried out for many hundreds of years, but it is only in the last century that there has been any scientific understanding of the processes involved. Sintering is a thermal treatment for bonding particles together into a coherent, solid structure via mass transport events that occur largely at the atomic level. The main aim of sintering is usually to achieve complete densification; however, another competing process, grain growth, occurs simultaneously. Generally, densification needs to be balanced against grain growth to achieve the desired final properties. Densification can occur in the presence of a liquid at the sintering temperature. Significant amounts of liquid can exist if minerals decompose or react on heating and these aid in bonding the particles together; the liquid then solidifies on cooling, usually as a glass. This method is known as viscous phase sintering and is suitable for some materials but not in the case of advanced ceramics such as YSZ where mechanical or functional properties are critical.

When a smaller amount of liquid phase is formed that is not sufficient to fill the pores between the ceramic particles, it can still aid sintering by providing a rapid diffusion path. Again a second phase is present at the grain boundaries in the final microstructure. This process is known as liquid phase sintering. Liquid phase sintering is used to produce advanced ceramics but is not relevant to YSZ. Therefore the detailed mechanisms of viscous and liquid phase sintering will not be considered within this review. In solid state sintering all matter is redistributed by solid or gaseous diffusion and no liquid is formed. Solid state sintering is appropriate for most oxides and is considered in more detail below.
3.2.2 Driving force for sintering

Powder particles have a high surface area to volume ratio and the driving force for sintering is to lower the total free energy. Atoms on a surface have a high free energy, so the lowest energy state is that of the minimum surface area. When exposed to high temperature, particles join together to reduce the surface area and hence the amount of surface free energy.

At the microscopic level material is transferred from regions of high chemical potential to regions where the chemical potential is lower. The chemical potential change is due to the pressure difference across a spherical surface, which is defined as:

$$\Delta P = \frac{2\gamma}{r}$$  \hspace{1cm} (3.1)

where $\Delta P$ is the pressure difference, $\gamma$ is the surface energy and $r$ is the radius of curvature.

The pressure difference results in a change in solubility or vapour pressure compared with a flat surface. A concave surface has a lower vapour pressure than a planar surface, while a convex surface has the highest equilibrium vapour pressure. The work done in transferring one mole of material from a flat surface to a curved surface is equal to the change in chemical potential. When temperature, external pressure and composition are constant, this can be expressed in the form:

$$\Delta \mu = (RT \ln c - RT \ln c_o) \text{ or } \Delta \mu = (RT \ln P - RT \ln P_o)$$  \hspace{1cm} (3.2)

where $\Delta \mu$ is the change in chemical potential, $c$ is the solubility, $P$ is the vapour pressure and $c_o$ and $P_o$ are the equilibrium solubility and vapour pressure, over a flat surface, respectively.

If work is done reversibly, this is equal to the change in surface energy, $\gamma da$, such that:

$$RT \ln \frac{c}{c_o} = RT \ln \frac{P}{P_o} = \gamma da$$  \hspace{1cm} (3.3)

For a spherical surface $dA = 8\pi r dr$. Since $dV = 4\pi r^2 dr$, the radius change for one mole transfer is $dr = V_m / 4\pi r^2$ (where $V_m$ is the molar volume).
Chapter 3: Literature review

For non-spherical surfaces, the solubility is:

\[ c = c_0 \exp\left[\frac{\gamma V_m}{RT} \left(\frac{1}{r_1} + \frac{1}{r_2}\right)\right] \quad (3.4) \]

This is the Thompson-Freundlich equation and as the argument exponent term is typically small, the change in vapour pressure is approximately inversely proportional to \( r \). Therefore the excess surface energy of a powder particle of radius \( r \) is expressed by \( 3 \gamma/r \). YSZ has a density of 6.01 g cm\(^{-3}\) and a typical surface energy = 0.3 J m\(^{-2}\). Therefore the excess energy is approximately 4 J g\(^{-1}\) for a particle radius of 0.1 \( \mu \)m and this becomes 0.004 J g\(^{-1}\) when \( r \) increases to 10 \( \mu \)m.

3.2.3 Stages of solid state sintering

3.2.3.1 Overview

Solid state sintering is broken down into three discrete stages: initial, intermediate and final. This segregation is for convenience, as no clear demarcation exists between these stages; in practice sintering occurs as one continuous process. Powder particles are rarely spherical but using a simplified representation of spheres in point contact allows the basic features of sintering to be considered. A path can be followed from point contacts to the initial, intermediate and final stages of sintering, as shown in Figure 3.1.

![Schematic diagram of pore structure changes during sintering](after German, 1996)
Chapter 3: Literature review

3.2.3.2 Initial stage of sintering

Prior to the initial stage of sintering the loose randomly orientated particles form contacts with each other. These contacts occur due to weak forces such as Van der Waals forces and agglomeration caused by the presence of moisture. The bonds between particles form spontaneously at the beginning of the sintering process.

The growth of the bonds between powder particles is described as the initial stage of sintering. At this stage of the process particles rearrange themselves to achieve the highest number of points of contact. At the points of contact where the surface energy is highest the particles bond together by material diffusion, forming a neck. Neighbouring necks form independently as initially neck formation is small (Kingery et al., 1955). There are a number of competing mechanisms for material transport. Figure 3.2 shows the six possible paths by which atoms can move to the neck region.

![Diagram of sintering process](image)

**Figure 3.2:** Alternative paths for matter transport during the initial stages of sintering (after Ashby, 1974)

These transport mechanisms lead either to densification or to coarsening and the basic approach is to try to promote those mechanisms that lead to densification. Coarsening is generally undesirable as the particle centres do not approach each other. Surface energy
Chapter 3: Literature review

reduction is achieved through material transport from the particle surface to the neck region by vapour or surface diffusion coarsening mechanisms. Densification is not promoted by paths 1-3 as no mass is removed from the plane between the particles.

Densification mechanisms are those in which the grain boundary plane or bulk serves as the “source” for diffusional transport. The neck formed between particles acts as the “sink” for atoms. This kind of transport can take place either along the grain boundary or through the lattice, as shown in paths 4-6. Most ceramics have more than one species that needs to diffuse to maintain stoichiometry, and the rate-limiting step is the transport rate of the slowest species along its fastest path. Densification of zirconia doped with yttria may in principle be rate-limited by any one of the six diffusion mechanisms for any of the three species, zirconium ions, yttrium ions and oxygen ions. This does not mean that any particular rate-limiting process stays constant throughout sintering; however for a fixed temperature and composition, the rate equations for densification and coarsening are in the form:

$$\left( \frac{x}{r} \right)^n = \frac{K}{r^p} t$$  \hspace{1cm} (3.5)

where $K$ is a constant containing the surface tension and the relevant diffusion coefficient, $x$ is the contact radius, $r$ is the radius of the particles, $t$ is the time and $n$ and $p$ are constants which depend on the specific transport path. For example, the rate of neck growth for volume diffusion from the grain boundary to the neck surface is defined given by:

$$\left( \frac{x}{r} \right)^5 = \left( \frac{80\gamma\Omega D_i}{KT} \right) \frac{t}{r^3}$$  \hspace{1cm} (3.6)

where $D_i$ is the lattice self-diffusion coefficient for the rate limiting ion and $\Omega$ is the volume of a vacancy.

For a particular mechanism, the time to reach a particular shape change, $x/r$ ratio, for two particle sizes $r_1$ and $r_2$ is given by equation 3.7 as:

$$\frac{t(r_2)}{t(r_1)} = \left( \frac{r_2}{r_1} \right)^p$$  \hspace{1cm} (3.7)

This relationship is known as Herring's scale law, and shows that finer particles promote faster sintering.
3.2.4 Intermediate stage of sintering

Densification is only minor during the initial stage of sintering. The majority of densification takes place during the intermediate stage, which is characterised by simultaneous pore rounding, densification, and grain growth. Elimination of the remaining surface energy is the driving force and the key focus for the intermediate stage of sintering is the pore structure surrounding the necks.

The pore geometry is assumed to be one of cylindrical pores located at grain edges. The grain shape is described as a truncated octahedron or tetrakaidecahedron. These cylindrical pores are interconnected in three dimensions, by three grain edges, suggesting that grain boundary energy is low compared with the surface energy. This arrangement of pores shrinks but remains connected throughout the intermediate stage (Coble, 1961a).

Densification is achieved through vacancy annihilation where pores located on grain boundaries disappear by volume and grain boundary diffusion. Transport on the grain boundaries leads to pore coarsening creating larger pores and eliminating smaller pores. During grain growth surface transport is evident through pore rounding and pore migration.

Rapid heating at this stage increases vacancy diffusion and densification by maintaining relatively fine microstructures at high sintering densities (Chu et al., 1991). At lower temperatures surface diffusion is significant and the speed of heating should be as rapid as possible to minimise the extent of coarsening (Brook, 1982). At higher temperatures lattice/boundary diffusion mechanisms dominate and the relationship between these diffusion mechanisms is shown in Figure 3.3.

Each diffusion mechanism is activated by temperature with surface diffusion tending to dominate at lower temperatures, and grain boundary and lattice diffusion becoming more prominent at higher sintering temperatures. Since densification and coarsening mechanisms scale differently with grain size as described by Herring (1950), modifications to the sintering profile can be qualified by the identification of the dominant diffusion mechanism. The mechanisms can be estimated and the diffusion coefficient, D, for YSZ can be expressed by the Arrhenius-type equation, that is:

\[ D = D_0 \exp \left( -\frac{Q}{RT} \right) \]  

where Q is the activation energy, T is the absolute temperature, R is the gas constant and \( D_0 \) is a material constant.
3.2.5 Final stage of sintering

During the final stage of sintering, the size of the grains continues to increase and most of the remaining pores are removed by vacancy diffusion along grain boundaries. The final stage of sintering is evident when tubular pores, present during the intermediate stage, become unstable and close.

The primary driving force for growth of strain free grains is reduction in the interfacial energy per unit volume. In normal grain growth the distribution of grain size is relatively unchanged except that it shifts to larger sizes. Final stage sintering is slow compared with the first two stages and there are simultaneous coarsening events, which impede densification.
Chapter 3: Literature review

Effective final stage sintering occurs when the pore size to grain size ratio is small, giving faster pore shrinkage and higher pore mobility, thereby allowing the pores to remain attached to the moving grain boundaries. It should be recognised that particle size and shape play an important role in promoting faster sintering. Generally, the smaller the particle size the faster the sintering mechanisms. There is a continual effort towards improving the performance of advanced ceramics, including the reduction of powder particle size, however, practical ceramics are far more complex than the simple compositions treated by sintering theory.

The drive towards narrower particle size distributions has important implications for the relationship between grain boundary migration and the presence of pores. There are three routes where pore separation will occur for ratios of grain size to pore size. When the grain size is fine and the pore size is large, pores exert enough boundary drag to remain attached thus slowing down the boundary. Where pores are small relative to the grain size they remain attached to the boundaries but do not exert much drag. In both these cases the pores remain attached to the grain boundaries. Between these two ratios there is a region where pore separation occurs and the boundary migrates unimpeded by pores. The pores that separate from the boundary become a critical issue for continued densification and typically the diffusion is too low for effective annihilation of pores trapped within grains. Impurity content and the pore volume fraction can also influence grain boundary migration and whether pore separation occurs (Chiang et al., 1997).

The feasibility of densification without grain growth relies on the suppression of grain-boundary migration while keeping grain-boundary diffusion active. The driving force for grain growth decreases with grain size, so the temperature required to activate the higher-energy process increases with grain size. It is possible that a similar process, in which grain junctions as well as grain boundary / pore junctions impede grain boundary migration, may explain the apparent suppression of grain growth at lower temperatures (Chen and Wang, 2000).

There have now been numerous studies to obtain the diffusion coefficients in zirconia. Despite many values being quoted for YSZ there is still some debate on the rate controlling mechanism. Table 3.1 summarises published activation energies and diffusion coefficients for YSZ and calcia-doped zirconia (CSZ).
Table 3.1: Published activation energy and diffusion coefficient data for YSZ and CSZ

<table>
<thead>
<tr>
<th>Material</th>
<th>Diffusion coefficient (m² s⁻¹)</th>
<th>Activation energy (kJ mol⁻¹)</th>
<th>Temperature range (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>16-mol% CSZ (Reactive Metals Inc, Ohio, US)</td>
<td>2.2 x 10⁻¹³ (2198 K)</td>
<td>387</td>
<td>1700-2150</td>
<td>Rhodes and Carter, 1966</td>
</tr>
<tr>
<td>YSZ (Zyttrite, Ohio, US)</td>
<td>8.8 x 10⁻¹⁷ (1548 K)</td>
<td>377</td>
<td>1125-1460</td>
<td>Young and Cutler, 1970</td>
</tr>
<tr>
<td>3-mol% YSZ (MEL chemicals, Manchester, UK)</td>
<td>6.8 x 10⁻¹⁶ (1623 K)</td>
<td>352</td>
<td>1300-1400</td>
<td>Luo et al., 1998</td>
</tr>
<tr>
<td>3-mol% YSZ (screen printed constrained thick-film)</td>
<td>1.4 x 10⁻²¹ (1546 K)</td>
<td>696</td>
<td>1273</td>
<td>Kanters et al., 2001</td>
</tr>
</tbody>
</table>

The values taken from the literature show activation energy ranging from 352 to 696 kJ mol⁻¹. The activation energy quoted by Kanters et al., (2001) was for samples fabricated using screen-printing and sintered under constraint. These literature values are difficult to compare as the processing conditions and particle sizes are different in each case, but they do indicate the range of diffusion coefficients that have been reported for YSZ. The diffusion coefficient for Zr⁺⁺ is quoted as being between 2.2 x 10⁻¹³ (Rhodes and Carter, 1966) and 1.4 x 10⁻²¹ m² s⁻¹ (Kanters et al., 2001). Lee (2004) showed that YSZ reached full density when sintered, with a constant heating rate, to 1500°C for 30 minutes and suggested that sintering of YSZ is rate limited by cation diffusion in either the lattice or grain boundary.

It has also been suggested that in YSZ the cation, Zr⁺⁺, controls the process of grain growth. Luo et al., (1998) showed that the energy barrier for grain growth, 352 kJ mol⁻¹, was close to the value of 387 kJ mol⁻¹ quoted by Rhodes and Carter (1966). The diffusion coefficients for these activation energies were 6.8 x 10⁻¹⁶ (1350°C) and 2.2 x 10⁻¹³ m² s⁻¹ (1925°C), respectively. The changes in activation energy and diffusion coefficient may be due to sample density (Matsuda et al., 1998).
3.3 Constrained sintering

3.3.1 Overview

Constrained sintering is the term used to describe any sintering process in which the sintering body is not able to move freely in all three dimensions. Constrained sintering of adherent films and multilayers is important in several technologies, including microelectronic circuit packaging, and thick films for conductors, resistors and dielectrics. The design of many SOFCs requires the sintering of three different ceramic materials (anode, cathode and solid electrolyte). The individual layers will, in general, sinter at different rates. This difference in the unconstrained densification rates between the layers leads to the generation of transient stresses that affect the densification of each layer and can lead to the development and propagation of microstructural flaws (e.g. cracking and delamination) as well as to anisotropic shrinkage (Choe et al., 1995).

Conventional unconstrained sintering allows free movement in all directions. During constrained sintering, a low density layer on a dense substrate is restricted from shrinking in the substrate plane (i.e. in the x and y directions) and densifies mainly by shrinking normal to the substrate, in the z plane. The densification rate of a constrained film is substantially lower than that of an unconstrained film. The initial rate of densification can be a factor of ten lower in constrained films (Choe et al., 1995). Modelling of constrained sintering remains a controversial area, as many of the assumptions are incorrect. An example of this is the model proposed by Carroll and Rahaman (1994) in which it is assumed that the volumetric shrinkage of a constrained thin film is equal to the linear shrinkage for free sintering as the constrained film only shrinks in one plane. In fact Garino and Bowen (1990), Carroll and Rahaman (1994) and Choe et al. (1995) showed that volumetric shrinkage of constrained films ranged from slightly more than the linear shrinkage to 50% more than the linear shrinkage for free sintering. This resulted in a ten-fold retardation in the rate of densification for the constrained film.

3.3.2 Densification mechanisms

It has been suggested that the retardation of the densification rate observed in constrained sintering of films is a result of a change in the dominating densification mechanism from faster grain boundary diffusion to that of slower lattice diffusion (Choe et al., 1995). However, the interaction between densification and grain growth in an inhomogeneous powder compact could also cause retardation of densification kinetics (Choe et al., 1995). It has already been established that in an unconstrained film, atoms flow along the grain boundaries into the neck regions, causing the pores to shrink, with the counter flow of vacancies out of the pores along the grain boundaries to all the free film surfaces (German, 1996).
In a constrained film the powder particles are physically restricted from coming together in the substrate plane. Thus, the flow of vacancies along the grain boundaries in the substrate plane is restricted. Vacancies can only flow out in the direction normal to the substrate. This leads to the diffusion of atoms through the bulk into pore regions, making lattice diffusion the rate-limiting step for densification in constrained sintering (Bordia and Scherer, 1988). Their models showed that the densification rate of constrained thin films is highly dependent on the dihedral angle of the material and on grain growth. Grain growth reduces the sintering pressure and increases the distance required for atomic diffusion, which further slows the densification rate (Carroll and Rahaman, 1994). Constrained films were more porous and the grain size was smaller compared with the free sintered case (Lin and Jean, 2004).

In-plane tensile stresses are generated in the constrained layer as a result of shrinkage prevention in the substrate plane, the x and y directions. These stresses increase rapidly with temperature and reach a maximum at the isothermal sintering temperature (Choe et al., 1995). Generation of these stresses is only in plane and it can be assumed there is no stress along the film thickness, or z direction. The level of stress in a constrained film is not large enough to account for the ten-fold rate-retardation in densification, previously stated by Garino and Bowen (1990) and therefore means that this approach is not sufficient to model constrained sintering. Choe et al., (1995) and Lin and Jean (2004) showed that tensile stresses generate internal flaws simply by the diffusive growth of pores. It has been speculated that the reduction in the densification rate could be a result of subtle interactions between the densifying and coarsening mechanisms in an inhomogeneous powder compact (Bordia and Scherer, 1988). Thus, the next section considers coarsening in more detail.

3.4 Coarsening

3.4.1 Overview

Coarsening, or Ostwald ripening, occurs when smaller particles shrink and larger particles grow. For solid-state sintering, the basic thermodynamic and kinetic factors are well understood. Conventional sintering theory highlights coarsening as a retarding mechanism for densification and processes to avoid coarsening are based on the principle of fast firing. This rapid heating can bypass the coarsening regime and densification can be promoted. Firing at lower temperatures results in coarsening without significant densification and can be used to fabricate porous materials.
Chapter 3: Literature review

3.4.2 Homogenised pore size

The rate retardation shown in constrained films has been linked to an increase in pore size and defects within the film. It has been suggested that the opportunity for inhomogeneous pore distribution is increased. Coarsening can be used to manipulate the pore network to homogenise these defects and pores in the fabrication of porous bodies. This type of matter transport would be dominated by surface diffusion (Lin et al., 1997). This is achieved by an isothermal hold at a temperature lower than the sintering temperature, where the coarsening process is dominant.

This homogenisation due to rearrangement of the pore network is suggested to be much more active at lower green densities because of the much lower rigidity of the particle network. As homogenisation proceeds, the density or number of particles and the particle-particle connectivity will tend towards the mean. At the same time particles with either uncharacteristically low connectivity or that are agglomerated will be progressively incorporated into neighbouring particles and will join the particle network. This evolution towards a steady state regardless of the initial state is a consequence of capillary action, which drives grain growth and causes pore size distribution to homogenise over time (Chen and Chen, 1996).

Materials that are produced using a coarsening step in the sintering profile generally have a slightly higher density, a smaller average grain size and a narrower grain-size distribution when compared with similar materials that have been produced by conventional sintering. A typical coarsening temperature for YSZ is 1100°C with a dwell time of several hours, dependent upon the desired microstructure (Wolff et al., 2003).

The mechanism proposed by Chen and Chen (1996) is based on an extension of a packing model, which incorporates particle coarsening. Specifically they assume that mass is locally preserved and that particle contacts are maintained while packing evolves from particle coarsening. Coarsening of particles under these assumptions leads to a decrease of pore volume and an increase in packing density. This involves a coordinated inward movement of coarsened particles on a “ring”, towards the central pore, to maintain particle contacts, as shown in Figure 3.5.
Coarsening \rightarrow \text{Re-packing} \rightarrow \text{Densification}

Figure 3.5: Particle coarsening and repacking. Particle contacts are maintained and mass is conserved, as pore space decreases and packing factor increases (after Chen and Chen, 1997).

As the extra pore space is displaced to the exterior of the ring, a compact full of such particle rings shrinks macroscopically. This packing mechanism fundamentally differs from the conventional densification mechanism in solid-state sintering in that vacancy transport out of pores via grain boundary or lattice diffusion is not explicitly required. However, in reality, some rotation or interparticle sliding is likely to be involved in the repacking process envisioned in Figure 3.5. Grain-boundary migration following surface diffusion is likely to be involved in the coarsening process and some grain-boundary diffusion is probably necessary (Chen and Chen, 1997).

The overall density in the initial stage of firing is not expected to increase significantly, however some very large pores disappear and this is related to the coarsening-motivated repacking mechanism where particle relocation leads to pore-volume redistribution. The cause of particle relocation, after the initial firing, is also related to coarsening, because interparticle contacts must be repeatedly perturbed by surface diffusion and movement of the grain boundary, leaving non-central interparticle forces to motivate particle sliding and rotation. Eventually the particle network approaches homogeneity with a narrower pore-size distribution, as shown in Figure 3.6 (Chen and Chen, 1997).

Figure 3.6: Schematic diagram showing particle relocation leading to pore-volume redistribution through to densification (pores are shaded in the final two stages) (after Chen and Chen, 1997).
This approach is contrary to the conventional wisdom in the field of sintering theory as described previously. Chen and Chen (1997) propose that coarsening is beneficial and is a central element of the homogenisation process as well as being a prelude to densification. Re-examination of the normalised pore size data for ceria and yttria by Chen and Chen (1997) reveals an important discrepancy between their data and the conventional theory of solid-state sintering proposed by Kingery and Francois (1967). If all the pores are initially supercritical within the particle network then theoretically they should shrink and the overall density of the compact should increase. Chen and Chen (1997) showed that supercritical pores did not shrink in the compacts of fine (10-200 nm) powders, irrespective of their thermodynamic disadvantage. Pan et al. (1998) have shown that the rate of shrinkage between particles is not significantly affected by their size difference as long as this difference is not greater than 50%. Further, Kucherenko et al. (2000) showed that pore-boundary separation can be prevented if the grain-boundary diffusion is as fast as the surface diffusion, allowing pores to disappear. Thus combining this work on particle size and pore size shows the limitations to the original theory proposed by Kingery and Francois (1967).

3.5 Two step sintering technique

3.5.1 Sintering profile

The normal sintering practice used to sinter a powder compact is heating at a constant rate and then holding at the highest temperature until the maximum density is reached. Typically the grain size increases continuously with density. Chen (2000) proposed a two-step sintering cycle in which the first step is rapid heating to a high temperature, \( T_1 \), to achieve an intermediate density. The second step is then a rapid cool down and isothermal hold at \( T_2 \) until full density is achieved. An example of the two-step sintering profile is shown in the inset in Figure 3.7. This approach is designed to suppress grain growth normally associated with increasing density and takes advantage of the coarsening-motivated repacking mechanism for pore homogenisation, proposed by Chen and Chen (1997).

It has been suggested that a sintered density of 99% or better can be achieved regardless of green density (Chen and Chen, 1996). This appears to be counter to normal practice where high green densities are preferred prior to the sintering stage. Only Chen and Chen (1996) have pursued low green densities for use with two-step sintering. More recently two-step sintering has been applied to BaTiO\(_3\) samples with a high green density, ~ 61%, which achieved the 70% target for density at temperatures lower than \( T_1 \) (Wang et al., 2006b). This work on BaTiO\(_3\) did not compare samples with a lower green density sintered using the same
values for the peak and dwell temperatures, $T_1$ and $T_2$, respectively. Therefore it is difficult to assess the change due to the higher green density.

The example of two-step sintering of yttria shown in Figure 3.7 shows two possible temperatures for $T_1$, each achieving a different density above the critical value of 70%. Once $T_1$ (1250°C or 1310°C) is reached the temperature is then reduced to $T_2$ (1150°C) where the isothermal hold occurs. At $T_2$ the density increases while the grain size remains relatively constant. Normal or conventional sintering of yttria would be at a temperature of typically 1500°C, where the grain size continues to increase with density (Chen 2000), as shown in Figure 3.7.

Figure 3.7: A density-grain size trajectory for yttria. The two-step sintering profiles indicate that after temperature, $T_1$, is reached the density continues to increase without significant grain growth (after Chen, 2000).

In two-step sintering the particle network is frozen in the second step and therefore pores can only be filled as long as grain boundary diffusion is sufficient (Laberty et al., 2003). Sintering in a frozen microstructure is an exhaustion process that dramatically slows with increasing density (Chen and Wang, 2000). Consequently the isothermal hold in two-step sintering presented by Chen and Chen (1997), Laberty et al., (2003) and Wolff et al., (2003) is typically 20 hours compared with only 1 hour or less for conventional sintering. This two-step profile has been described as slowing or restricting grain growth and this is shown in comparison with normal or conventional sintering in Figure 3.7.
Chen (2000) indicates that two-step sintering can be used to achieve a density of 98% by exploiting the 'kinetic window' that separates grain-boundary diffusion and grain-boundary migration. To succeed in two-step sintering, a sufficiently high density of 70% needs to be achieved at $T_1$ (Laberty et al., 2003). However, a density of 70% would appear to conflict with the intermediate density required for the coarsening motivated repacking mechanism originally presented by Chen and Chen (1997). Once this critical density is reached a lower temperature, $T_2$, used for the isothermal hold will be sufficient to achieve full density and place samples within the 'kinetic window', as shown in Figure 3.8 (Wang et al., 2006a). When conditions for two-step sintering fall below the 'kinetic window' a density $\geq$ 96% cannot be achieved (open circles) even if a starting density of 70% is achieved at $T_1$. Below the 'kinetic window' grain growth may still be suppressed but densification will be exhausted. Above the 'kinetic window' grain growth (open circles with arrows) is likely to occur (Wang et al., 2006a). These data appear to conflict with the basis of two-step sintering as increasing grain size would place samples (open circles with arrows) within the 'kinetic window'.

![Figure 3.8: Temperature ($T_2$) used for second-step sintering of yttria oxide ($Y_2O_3$) as a function of grain size ($D_1$, grain size at $T_1$). Within the 'Kinetic window' (solid circles) full density was achieved without grain growth. Those samples outside the window (open circles) achieve full density with grain growth (above window) or did not achieve full density without grain growth (below window) (after Wang et al., 2006a).](image)
When this idea was proposed no data were supplied to support this theory but recently Wang et al., (2006a, 2006b) have provided data on kinetic windows for yttria, barium titanate and nickel-copper-zinc ferrite. Although a small amount of data has been published for two-step sintering of YSZ a 'kinetic window' for YSZ constrained or unconstrained has not been proposed.

3.5.2 Sintering of YSZ

It is reported that the grain growth of YSZ can be retarded and full density can be achieved by using a two-step sintering profile with $T_1 = 1500^\circ C$ followed by $1450^\circ C \ (T_2)$ for 20 h (Laberty et al., 2003). The initial powder size was < 0.5 µm and this increased to ~ 1 µm and 5 µm for conventional and two-step sintering, respectively. Heating the sample to $1500^\circ C$ achieved a density of 90% compared with > 98% when the second step at $T_2$ was added. The critical density for YSZ at $T_1$ was indicated to be > 80%, which is a higher value than the 70% quoted by Chen (2000) for yttria.

A two-step sintering method was applied to micrometre-sized 3-mol% YSZ (Lee, 2004). This commercially available YSZ powder was injection-moulded into pellets and then sintered using normal continuous sintering and two-step sintering schedules. For normal sintering, the samples were sintered at 1500°C for 30 minutes. Samples were heated at a rate of 10°C min$^{-1}$ to 1600°C ($T_1$), held for 5 min, and then rapidly cooled down and held at the lower temperature of 1300°C ($T_2$) for 10 h in a two-step sintering cycle (Lee, 2004). The final bulk density of the two-step sample was 99% compared with 97% for the conventional sintered sample. Average grain sizes increased from 0.27 µm to 0.59 µm and 1.05 µm for two-step and conventional sintering cycles, respectively (Lee, 2004).

A further study also investigated the use of two-step sintering with 3-mol% and 8-mol% YSZ powders. The 3-mol% YSZ powder had a particle size of 12 nm and consisted of the tetragonal phase and the 8-mol% YSZ powder had a size of 0.5 µm with a cubic phase. Dilatometry measurements of the green bodies showed the maximum shrinkage rate was at 1100°C for the 3-mol% and 1360°C for 8-mol% YSZ (Wolff et al., 2003). The maximum shrinkage rates were used for the two-step sintering profile, where an isothermal hold at 1100°C ($T_2$) was used for the 3-mol% YSZ material. An initial grain size of 60 nm at $T_1$ increased to < 300 nm at a density of 93% (Wolff et al., 2003).

Luo et al., (1998) analysed data from the sintering of 3-mol% YSZ pressed powders to obtain the rate of change in relative density against temperature (dp/dt) with peak positions corresponding to 1150 and 1330°C. This is in good agreement with the temperature for the two-step sintering profiles used by Wolff et al., (2003) for 3-mol% YSZ. When sintering the 3-mol% YSZ powder under conventional conditions a maximum density of 94% was achieved.
Chapter 3: Literature review

after firing at 1300°C for 1 hour. A density of 95% was reached by sintering in two-steps at 1400°C and 1200°C for 10 hours. The grain size for the conventional and two-step sintered samples were 300 nm and 200 nm, respectively from a starting particle size of 12 nm (Wolff et al., 2003). This indicates that grain growth could not be avoided by two-step sintering of YSZ.

3.6 Concluding remarks

The fundamental approach to sintering theory for constrained and unconstrained ceramic powders has been considered. This has included the methods used to achieve full density in unconstrained sintering. While conventional sintering theory is reasonably well understood, the mechanisms which retard densification in constrained sintering are not well defined.

Coarsening and repacking of particles during unconstrained sintering has been shown to improve the pore distribution. Two-stage sintering claims to restrict grain growth while still achieving high density. While grain growth suppression has been claimed in the work by Chen (2000) on yttria, two-step sintering of YSZ has achieved high density but the grain growth normally associated with conventional sintering could not be avoided (Wolff et al., 2003; Lee, 2004). Both coarsening and two-step methods are controversial and remain on the fringe of sintering theory. Neither method has been applied to constrained sintering in any published work to date.
4 Conventional sintering profiles

4.1 Introduction

Screen-printing is a popular technique employed in many industrial applications to produce consistent thick films of material. YSZ used within the IP-SOFC design is processed in powder form, and then mixed with a dispersant, lubricant and binder to produce ink suitable for the screen-printing process. The ink deposited onto a pre-sintered support forms a porous green body, which is subsequently sintered at elevated temperatures. Each of these aforementioned factors are considered in the following chapter. The chapter begins with an overview of the fabrication of screen-printed layers including the process parameters and this is followed by a description of the experimental procedures for investigation of these layers.

Screen-printing mesh screens were used to provide increasing printed layer thickness by increasing the wire diameter of the mesh. Deposition thickness was also increased by repeating the printing operation to create a laminate. Layer thickness, relative density and grain size have been determined as a function of mesh size and number of print deposits to enable optimisation of the green body fabrication process. Additionally these microstructural parameters have been used to assess the effect of individual elements of a sintering cycle i.e. heating rate, sintering temperature and sintering time. This has provided a means of optimising the fabrication and sintering cycle for conventionally sintered YSZ thick-films and defines a baseline for further studies.

4.2 Fabrication of thick-film layers

4.2.1 Background to the screen printing process

Screen-printing is the deposition technique used for fabrication of individual green layers in the IP-SOFC design. The use of thick-film technology holds out the prospect of manufacturing devices, such as sensors and fuel cells, at particularly low unit cost (Maskell, 2000). This unit cost is based on the cycle time of screen-printing being capable of ~ 10 seconds per printing application. While this process has been described as low cost it also provides layers with low densities. This is not a significant problem with many sensor applications where electrodes are screen-printed and the porosity is a key element in their operation. Mochizuki et al., (2001) and Debeda-Hickel et al., (2005) have described sensors for which screen-printing of YSZ is used to produce the solid oxide electrolyte element of the device. The low densities have resulted in porosity in the YSZ screen-printed layer, which induces diffusion of gaseous oxygen in the electrolyte as well as a lower ionic conductivity.
Chapter 4: Conventional sintering profiles

However, all of these factors would be detrimental to the operation and long-term performance of a SOFC.

A potential solution to these problems was suggested by Gouverneur et al., (1993). When a mechanical pressure was applied to an oven dried layer it resulted in a reduction of 30% of the layer thickness, roughly equal to the organic solvent removed during the drying process. The improved densification of the layer reduced the diffusion of gaseous oxygen in the electrolyte as well as improving the ionic conductivity.

Thick layers of some tens to hundreds of micrometres are obtained by the transfer of the screen-printing ink through a mesh screen onto a substrate. The final thickness of the layer depends on the screen (mesh size), the settings of the screen-printing machine and the ink viscosity (Debeda-Hickel et al., 2005). The principal steps in the process are described in Figure 4.1, where the ink is deposited through a mesh screen onto the substrate forming a thick film layer.

Figure 4.1: Schematic diagrams outlining the screen-printing process, a) Components required for the screen-printing operation, b) Squeegee pressure applied to the screen, c) Squeegee travels across the screen and deposits ink through the screen, d) Squeegee pressure is released and a defined thickness of ink has been deposited onto the substrate (after Agnew et al., 2003).
4.2.2 Experimental procedure

The required deposition thickness of a YSZ thick-film for the IP-SOFC electrolyte can be achieved in one of two ways. One approach is to perform a single printing operation, which provides the optimum thickness of 10 to 20 μm when sintered. Alternatively, the more cautious approach is to perform multiple printing operations with a drying stage between each print operation creating a laminate which can then be sintered. Application of a second layer would cover any potential defects from the previous print operation and avoid the problems described by Mochizuki et al., (2001) and Debeda-Hickel et al., (2005), such as printing defects, pin holes and micro porosity. The first option may provide an optimum thickness for electrochemical performance, but does not guarantee the mechanical integrity of the layer, while the latter option is more time consuming and will increase the unit cost. Therefore the approach taken in this study was to establish the optimum screen thickness and number of print deposits for the YSZ ink.

Using a Smtech Benchmark 90 screen-printing machine supplied by Reprint Services (Dorset, UK) the thick film layers were deposited using a range of different mesh screens. Screen-printing can be influenced by many parameters and therefore it is important to keep as many parameters fixed as possible. The printing operation used to deposit the ink through the mesh screen was described in Figure 4.1, which shows the squeegee in contact with the ink. The squeegee is a rubber blade that is used to move the ink across the surface of the screen. There are a range of squeegee blades for screen-printing which are characterised by their colour and shore hardness (A°). The pressure applied to the blade during the printing operation is based on the hardness of the rubber. This pressure also influences how much the screen deforms. As the mesh is only expected to ‘kiss’ the substrate when the pressure is applied the gap between the substrate and the screen can be set accordingly. This print gap should be sufficient to allow the screen to snap away from the substrate as the squeegee blade passes across the screen. The ‘snap-off’ can also be controlled via the printing speed. This is the speed at which the squeegee blade passes across the screen when the pressure is applied. The printing setup used in this study is detailed in Table 4.1.


Chapter 4: Conventional sintering profiles

Table 4.1: Screen-printing parameters for the screen-printing machine

<table>
<thead>
<tr>
<th>Print mode</th>
<th>Squeegee type (Shore hardness A°)</th>
<th>Squeegee pressure (kgf)</th>
<th>Print speed (mm s⁻¹)</th>
<th>Print gap (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Print</td>
<td>65-70</td>
<td>4.5</td>
<td>45</td>
<td>2.0</td>
</tr>
</tbody>
</table>

4.2.3 Mesh sizes

The mesh sizes used for printing are made from stainless steel wire positioned at 45° relative to the support frame and stretched to put the mesh in tension. The mask embedded into the mesh has an area of 50 mm x 50 mm through which the ink can pass. Emulsion is used to form the mask and prevents ink passing through the remaining mesh area. Screen thickness is defined by the wire diameter with two wires crossing at an angle 90° to each other. A cross-section and plan view of the weave of the mesh is shown in Figure 4.2.

![Screen mesh cross-section](attachment:image1.png)

![Screen mesh plan view](attachment:image2.png)

**Figure 4.2:** Screen mesh a) in cross-section, illustrating how the mesh achieves its overall thickness and b) intertwined wires forming the mesh; the thickness is a function of the intertwining and the diameter of the wire (after Hobby, 2001).

Mesh thickness is one of the variables within the screen-printing process. The mesh size controls the overall thickness of the print application and increasing the wire diameter increases the quantity of ink deposited through the screen. Typical screen-printing screen specifications are shown in Table 4.2.
Table 4.2: Specifications for mesh sizes typically used in screen-printing processes
(data supplied by MCI (Cambridge) Ltd)

<table>
<thead>
<tr>
<th>Mesh size (count per inch)</th>
<th>Open area (%)</th>
<th>Wire diameter (mm)</th>
<th>Screen thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>48</td>
<td>0.1</td>
<td>215 ± 5</td>
</tr>
<tr>
<td>105</td>
<td>48</td>
<td>0.075</td>
<td>162 ± 4</td>
</tr>
<tr>
<td>165</td>
<td>44</td>
<td>0.06</td>
<td>110 ± 2.5</td>
</tr>
<tr>
<td>200</td>
<td>48</td>
<td>0.04</td>
<td>90 ± 2.5</td>
</tr>
<tr>
<td>325</td>
<td>39</td>
<td>0.03</td>
<td>60 ± 1.5</td>
</tr>
<tr>
<td>325 Ultra-Thin (UT)</td>
<td>47</td>
<td>0.024</td>
<td>50 ± 1.5</td>
</tr>
</tbody>
</table>

The smaller the mesh size or counts per inch the thicker the mesh or screen thickness. This increasing screen thickness allows a greater volume of ink to be deposited. The mesh sizes of 325UT through to 80 provide screen-printing screens, of thickness 50 µm to 215 µm through which ink can be deposited.

4.2.4 Powder supply and ink formulation

The powder used in this study was a 3-mol% YSZ supplied by MEL Chemicals (Manchester, UK). This powder is a commercial product, Melox 3Y XZ07078/14, available from the supplier in tonne quantities. The powder was taken from a 20 kg batch, 02/298/01M, and its chemical composition was measured using X-ray fluorescence (XRF) at Ceram (Stoke, UK), with results shown in Table 4.3.
Table 4.3: XRF analysis of Melox 3Y XZ07078/14, batch number 02/298/01M

<table>
<thead>
<tr>
<th>Description of compound</th>
<th>Compound</th>
<th>Percentage (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconia</td>
<td>ZrO₂</td>
<td>91.7</td>
</tr>
<tr>
<td>Yttria</td>
<td>Y₂O₃</td>
<td>5.31</td>
</tr>
<tr>
<td>Hafnia</td>
<td>HfO₂</td>
<td>2.08</td>
</tr>
<tr>
<td>Lime</td>
<td>CaO</td>
<td>0.08</td>
</tr>
<tr>
<td>Soda</td>
<td>Na₂O</td>
<td>0.54</td>
</tr>
<tr>
<td>Alumina</td>
<td>Al₂O₃</td>
<td>0.29</td>
</tr>
<tr>
<td>Silica</td>
<td>SiO₂</td>
<td>&lt;0.02</td>
</tr>
</tbody>
</table>

Results are accurate to 3 significant figures or the number of figures given, whichever is the lesser.

The screen-printable ink formulated for this study used YSZ powder with an organic dispersant and binder system. Prior to the formulation of the ink the 3-mol% YSZ powder was milled with a dispersant and solvent to deagglomerate the powder. The particle size distribution of the as-supplied powder was compared with the final particle size distribution of the suspension as shown in Figure 4.3.

![Particle size distribution](image)

**Figure 4.3:** Particle size distribution of the as-supplied powder and the 3-mol % YSZ suspension after milling.

The particle size was measured using the laser diffraction method (Mastersizer 2000, Malvern Instruments Ltd, Worcester, UK). Ultrasound prior to the measurement aided the solvent dispersion of the ceramic powder. Once the milling was complete the binder system was added to the dispersed powder and then mixed to provide a screen printable ink.
Chapter 4: Conventional sintering profiles

The ink viscosity with this binder system is defined by the ratio of powder to binder, known as the solids content. A fixed solids content of 35 wt% was used and a Brookfield programmable HBDV III rheometer (Brookfield, Middleboro, US) was used to measure the viscosity. Ink viscosity was measured prior to printing, using the cone and plate method (spindle CP52) with a 0.125 mm gap at a constant speed of 80 revolutions per minute (rpm) and a constant temperature of 25°C. The viscosity for the 3-mol % YSZ ink was 3000 ± 500 mPa s.

4.2.5 Substrate

The substrate used for supporting the screen-printed layers was the standard porous support tube used in the IP-SOFC design, with a pre-fired priming layer applied to the surface. It is described as a flat tube with multiple open channels running along its length. The tube is fabricated using ceramic extrusion and the final sintered component has two flat parallel sides suitable for screen-printing, as shown in Figure 4.4.

![Figure 4.4](image_url)

Figure 4.4: a) Substrate with substrate priming layer and screen printed thick-film electrolyte applied and b) cross-sectional view showing the dimensions of the substrate.

The substrate material is a magnesia-rich spinel, and the components were supplied by Advanced Ceramics Limited (Stafford, Staffordshire, UK). Two substrates were used during this investigation and are designated substrate A and substrate B. While the composition of the base material for substrate A and B is the same, the particle size of the starting powder of the substrate is slightly different as shown in Table 4.4.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Composition</th>
<th>Particle size of starting powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Magnesia rich spinel</td>
<td>Sieved through 325 mesh</td>
</tr>
<tr>
<td>B</td>
<td>Magnesia rich spinel</td>
<td>Sieved through 425 mesh</td>
</tr>
</tbody>
</table>
Chapter 4: Conventional sintering profiles

A priming layer consisting of YSZ was deposited onto the substrate at a thickness of \( \sim 30 \mu m \). The priming layer was pre-fired prior to the application of the electrolyte layer and was the same for samples printed on both substrate A and B. This priming layer was used to reduce the surface roughness of the sintered substrate, as shown in Figure 4.5.

![SEM of a cross-section through a pre-fired substrate priming layer on a substrate.](image)

**Figure 4.5:** SEM of a cross-section through a pre-fired substrate priming layer on a substrate.

### 4.2.6 Sample preparation

Each batch of samples was designated a code which provides the parameters used for that batch. Due to the nature of this study, in any one test there were a number of variables that were fixed and one that was varied. The parameters are detailed in the batch sample index; an example of this is given below in Table 4.5.

<table>
<thead>
<tr>
<th>Substrate type</th>
<th>Mesh size</th>
<th>No. of deposits</th>
<th>Heating rate ( (°C \text{ min}^{-1}) )</th>
<th>Sintering temperature ( (°C) )</th>
<th>Sintering time ( (h) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>325</td>
<td>1</td>
<td>3</td>
<td>1450</td>
<td>1</td>
</tr>
</tbody>
</table>

A batch sample code of A-325-1-3-1450-1 indicates the construction and sintering parameters of this particular batch of samples. The preparation of samples initially used one screen mesh size (325UT). A thin mesh size was chosen based on advice from Imperial College who were partners in the Multifunctional SOFC European program (Framework V) where it was discussed that thinner layers would be preferable to thicker layers as the stresses would be lower in the thinner layers (Atkinson, 2003). Subsequently the screen thickness trials
Chapter 4: Conventional sintering profiles

eliminated the 325UT mesh screen and concentrated on the mesh sizes between 325 and 80 with increasing screen thickness of between 60 μm and 215 μm as shown in Table 4.6.

Table 4.6: Details of samples printed using increasing screen thickness

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Mesh size</th>
<th>Screen thickness (μm)</th>
<th>Drying temp. (°C)</th>
<th>Sintering temp. (°C)</th>
<th>Sintering time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-325-1-3-1450-1</td>
<td>325</td>
<td>60</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-200-1-3-1450-1</td>
<td>200</td>
<td>90</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-165-1-3-1450-1</td>
<td>165</td>
<td>110</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-105-1-3-1450-1</td>
<td>105</td>
<td>162</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-80-1-3-1450-1</td>
<td>80</td>
<td>215</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
</tbody>
</table>

Single screen-printing applications were difficult to differentiate from the substrate priming layer when viewing the sintered cross-section. The addition of more screen-printing applications, creating a laminate structure, was expected to further increase the sintered thickness. The number of deposits was increased from one to two, three and then four prints. This type of print application where the layer is printed and dried prior to the application of the next print is described as a print-dry operation. The laminate is created from multiple print-dry operations as shown in Figure 4.6.

Figure 4.6: Schematic diagram showing a cross-section through the laminate created with four print-dry applications to the pre-fired substrate priming layer.

Samples prepared using this method were all sintered to a standard scheme, with multiple print-dry applications being co-fired. The range of mesh sizes from 325 to 80 was used, with two, three or four print-dry operations, to create the laminate, detailed in Table 4.7.
Chapter 4: Conventional sintering profiles

Table 4.7: Details of samples printed using increasing screen thickness and additional print-dry operations using the same mesh size

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>No. of prints</th>
<th>Mesh size (μm)</th>
<th>Screen thickness (μm)</th>
<th>Drying temp. (°C)</th>
<th>Sintering temp. (°C)</th>
<th>Sintering time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-325-2-3-1450-1</td>
<td>2</td>
<td>325</td>
<td>60</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-325-3-3-1450-1</td>
<td>3</td>
<td>325</td>
<td>60</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-325-4-3-1450-1</td>
<td>4</td>
<td>325</td>
<td>60</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-200-2-3-1450-1</td>
<td>2</td>
<td>200</td>
<td>90</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-200-3-3-1450-1</td>
<td>3</td>
<td>200</td>
<td>90</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-200-4-3-1450-1</td>
<td>4</td>
<td>200</td>
<td>90</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-165-2-3-1450-1</td>
<td>2</td>
<td>165</td>
<td>110</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-165-3-3-1450-1</td>
<td>3</td>
<td>165</td>
<td>110</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-165-4-3-1450-1</td>
<td>4</td>
<td>165</td>
<td>110</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-105-2-3-1450-1</td>
<td>2</td>
<td>105</td>
<td>162</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-105-3-3-1450-1</td>
<td>3</td>
<td>105</td>
<td>162</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-105-4-3-1450-1</td>
<td>4</td>
<td>105</td>
<td>162</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-80-2-3-1450-1</td>
<td>2</td>
<td>80</td>
<td>215</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-80-3-3-1450-1</td>
<td>3</td>
<td>80</td>
<td>215</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-80-4-3-1450-1</td>
<td>4</td>
<td>80</td>
<td>215</td>
<td>80</td>
<td>1450</td>
<td>1</td>
</tr>
</tbody>
</table>

Drying of the printed layers was performed in an oven supplied by Elite Thermal Systems Ltd (Market Harborough, Leistershire, UK) for 30 minutes, at 80°C in air. The dried layers were then sintered in an electric furnace supplied by Elite Thermal Systems Ltd.
Chapter 4: Conventional sintering profiles

4.2.7 Sintering profiles

4.2.7.1 Overview

The screen-printed layers were heated using conventional sintering with a constant heating rate to the target temperature, an isothermal hold at the sintering temperature and a cool down to room temperature, as shown in Figure 4.7. Changes made to the conventional sintering profile included faster heating rates, different target temperatures and longer dwell times. The firing of each batch of samples was controlled using a furnace fitted with a 2408 Eurotherm controller supplied by Elite Thermal Systems Ltd (Market Harborough, UK). The furnace calibration was UKAS accredited and conducted by Roxspur (Sheffield, UK). For a set point of 1450°C an average value of 1453 ± 16°C was measured across the furnace hearth.

![Figure 4.7: Schematic diagram of a conventional sintering cycle used for thick-film fabrication. The variable parameters are heating rate, sintering temperature and sintering time.](image)

Data logging software (Scitek consultants, Derby, UK) was used to monitor the output from the control thermocouple throughout the sintering profile. Temperature and time data were logged at one minute intervals allowing a comparison of the errors associated with the set
Chapter 4: Conventional sintering profiles

point and the thermocouple within the furnace chamber. The typical errors associated with a conventional sintering profile are shown in Figure 4.8.

Figure 4.8: Differential temperature between the sintering furnace set point and the control thermocouple. The variation occurs at lower temperatures where the furnace tends to be less controllable and when changes occur in the heating rate.

4.2.7.2 Sintering profiles: heating rate, temperature and time variations

The 3-mol% YSZ powder was pressed into pellets which were sintered at a range of heating rates. These pressed pellets were used to assess the effects of heating rate without the constraint of the pre-fired substrate. The sample details are given in Table 4.8, with the sample index shortened for the pressed pellets such that only the heating rate, sintering temperature and dwell time is given. The ‘C’ denotes that this is a conventional sintering profile.
Chapter 4: Conventional sintering profiles

Table 4.8: Details of pressed powder samples sintered with different heating rates

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Heating rate (°C min⁻¹)</th>
<th>Sintering temp. (°C)</th>
<th>Sintering time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1250-0-C</td>
<td>1</td>
<td>1250</td>
<td>0</td>
</tr>
<tr>
<td>3-1250-0-C</td>
<td>3</td>
<td>1250</td>
<td>0</td>
</tr>
<tr>
<td>5-1250-0-C</td>
<td>5</td>
<td>1250</td>
<td>0</td>
</tr>
<tr>
<td>7-1250-0-C</td>
<td>7</td>
<td>1250</td>
<td>0</td>
</tr>
<tr>
<td>10-1250-0-C</td>
<td>10</td>
<td>1250</td>
<td>0</td>
</tr>
</tbody>
</table>

Changes applied to the conventional sintering profile for pressed pellets were then applied to the screen-printed layers. A screen thickness of 110 µm (165 mesh) with three print-dry applications was used to prepare samples to assess the influence of changes to the heating rate. Sintering temperature and sintering time changes were assessed using samples prepared using a screen thickness of 50 µm (325UT mesh) with a single print-dry application. The variations made to the conventional sintering profile are shown in Table 4.9.

Table 4.9: Details of samples sintered with different heating rates, sintering temperatures and sintering times

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Mesh size</th>
<th>Heating rate (°C min⁻¹)</th>
<th>Sintering temp. (°C)</th>
<th>Sintering time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-165-3-1-1450-1</td>
<td>165</td>
<td>1</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>B-165-3-5-1450-1</td>
<td>165</td>
<td>5</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>B-165-3-10-1450-1</td>
<td>165</td>
<td>10</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>B-165-3-20-1450-1</td>
<td>165</td>
<td>20</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-325UT-1-3-1300-1</td>
<td>325UT</td>
<td>3</td>
<td>1300</td>
<td>1</td>
</tr>
<tr>
<td>A-325UT-1-3-1350-1</td>
<td>325UT</td>
<td>3</td>
<td>1350</td>
<td>1</td>
</tr>
<tr>
<td>A-325UT-1-3-1400-1</td>
<td>325UT</td>
<td>3</td>
<td>1400</td>
<td>1</td>
</tr>
<tr>
<td>A-325UT-1-3-1425-1</td>
<td>325UT</td>
<td>3</td>
<td>1425</td>
<td>1</td>
</tr>
<tr>
<td>A-325UT-1-3-1450-1</td>
<td>325UT</td>
<td>3</td>
<td>1450</td>
<td>1</td>
</tr>
<tr>
<td>A-325UT-1-3-1400-1</td>
<td>325UT</td>
<td>3</td>
<td>1400</td>
<td>1</td>
</tr>
<tr>
<td>A-325UT-1-3-1400-4</td>
<td>325UT</td>
<td>3</td>
<td>1400</td>
<td>4</td>
</tr>
<tr>
<td>A-325UT-1-3-1400-6</td>
<td>325UT</td>
<td>3</td>
<td>1400</td>
<td>6</td>
</tr>
<tr>
<td>A-325UT-1-3-1400-10</td>
<td>325UT</td>
<td>3</td>
<td>1400</td>
<td>10</td>
</tr>
</tbody>
</table>
4.2.8 **Dilatometry**

Dilatometry is a technique in which the dimensions of a substance are measured as a function of temperature while the ceramic body is subjected to a controlled temperature programme under negligible load. This technique was used to assess the characteristics of the as-supplied powder without the constraint of the pre-fired substrate. The as supplied 3-mol% YSZ powder was pressed into 4 mm cubes using a Rondol pellet press, (Stone, Staffordshire, UK). Pellets were pressed at 14 MPa for 60 seconds before the pressure was released and the pellet could be removed from the die. Each pellet was weighed prior to heating using a Sartorius CP324S balance, (Germany). The weighing scales were accurate to four decimal places, allowing the addition of 0.3 wt% binder, (corn oil, Co-op, UK), to the 0.3 g of powder to provide a small amount of green strength. Measurements of the green and sintered bodies were conducted using a micrometer, (Mitutoyo, UK) with a precision to ± 0.01 mm.

Dilatometry of the pressed pellets was conducted using a Netzsch, DIL 402 PC (1250°C max. temperature version), (Wittelsbacherstraße, Germany) dilatometer. The push rod movement resulting from the change in length of the sample was detected by a linear variable displacement transducer. Tube and rod-type sample holders of alumina were used for temperatures up to 1250°C. Samples are manually loaded into the sample holder and the push rod placed in contact with the sample, as shown in Figure 4.9.

![Figure 4.9: Schematic diagram of a dilatometer sample holder and push rod, showing how a pressed sample is loaded prior to the measurement (after Netzsch, 2005).](image-url)
During operation the dilatometer was purged with argon. The sample temperature was measured by the sample thermocouple, type S (platinum-platinum/rhodium), mounted in the sample holder next to the sample. The measured length change includes both the sample holder expansion and the length change of the sample itself. The required correction was accomplished by measuring the alumina standard reference material under identical conditions (temperature program, heating rate, gas atmosphere) as the sample and comparing the measured values with the tabulated reference data via the machine software.

4.2.9 Archimedes measurement of density

The densities of the sintered pellets were measured using an Archimedes balance, Sartorius CP224S (Germany). The Archimedes method may be used to determine the density of a ceramic body larger than approximately 1 cm³ to a precision of ± 0.0002 Mg m⁻³ (Reed, 1995). The method used water as the penetrating and suspending fluid. A measurement of the dry weight of the sintered pellet was taken prior to immersion. The pellets were immersed in water and the air was evacuated from the samples using a desiccator and Edwards vacuum pump (Derby, UK). After 15 minutes the samples were removed and the suspended weight was measured after the removal of the excess water; a thermometer monitored the water temperature. The third measurement taken was the dry surface weight after impregnation. These data were then used to estimate the density and closed porosity of the sintered pressed pellets.

4.2.10 Sample characterisation - microscopy

A number of the 50 mm x 50 mm squares were cut (using a Struers Accutom-5) down the centre of the printed sample. This was achieved using a 130 mm diameter metal bond-cutting disc. The samples were clamped in place and coolant water was added prior to the cutting operation. The cut samples were then washed and dried with half of the sample used for the surface analysis and the remainder used for cross-sectional analysis.

The cut sample was fitted with a mounting clip and then was placed in a moulding cup. Struers Epofix resin was mixed and poured slowly into the moulding cup at one edge. Once the sample was sufficiently covered it was left for 12 hours to cure prior to polishing. Polishing of the samples was conducted using the following Struers grit papers and pastes on a Struers Rotopoll-11, as shown in Table 4.10.
Table 4.10: Polishing schedule for mounted cross-sections of screen-printed layers

<table>
<thead>
<tr>
<th>Grit paper or paste</th>
<th>Elapsed time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P180 SiC</td>
<td>1</td>
</tr>
<tr>
<td>P320 SiC</td>
<td>5</td>
</tr>
<tr>
<td>P1200 SiC</td>
<td>5</td>
</tr>
<tr>
<td>P2400 SiC</td>
<td>5</td>
</tr>
<tr>
<td>6 μm (yellow diamond paste)</td>
<td>1</td>
</tr>
<tr>
<td>1 μm (blue diamond paste)</td>
<td>1</td>
</tr>
</tbody>
</table>

The samples were washed with detergent and alcohol and dried between each stage. Samples were then coated with a thin carbon layer, applied to the polished surface prior to examination. A Cambridge Instruments (Stereoscan 240) scanning electron microscope (SEM) was used to investigate the morphology and microstructure of the samples. An acceleration voltage of 20 kV was selected for these samples. This high voltage was chosen to provide good penetration of the sample and optimised resolution. The working distance was set at 15 mm for both the surface and cross-sectional analyses. Sintered layer thickness, grain size and pore structure were studied. A number of the samples were examined by MCS (Roslin, Midlothian, UK).

4.2.11 Microstructural analysis

4.2.11.1 Grain size measurement

There are a number of standards that can be used for determining grain size such as the ASTM and BS standards. Intercept procedures are convenient to use and are recommended for all structures that depart from the uniform equiaxed form. The linear-intercept method devised by Heyn in 1903 is described below and is taken from ASTM E112. The method determines the mean grain size from the number of grains (intercepts) or grain boundary (intersections) that intersect one or more lines of a known length superimposed on a micrograph. This method requires lines oriented in several random directions for nonequiaxed microstructures. The grain diameter and intercept count can be correlated using:
Chapter 4: Conventional sintering profiles

\[ d = \frac{L \cdot A_i}{M \cdot N} \]  

(4.1)

where \( d \) is the equivalent grain diameter, \( L \) is the length of superimposed line(s), \( A_i \) is the shape correction factor, normally 1.00, \( M \) is the magnification (dimensionless) and \( N \) is the number of intercepts or intersections (ASTM standard E112-96, 1999).

The method used in this study for grain size measurement was the linear intercept method, British Standard BS EN 623-3:2001 (method B), which uses the following equation:

\[ g_{\text{lin}} = \frac{\sum L_i \cdot 10^2}{N_{(g)} \cdot M} \]  

(4.2)

where \( g_{\text{lin}} \) is the mean linear intercept distance in mm, \( L_i \) is the individual intercept length in mm, \( N_{(g)} \) is the number of discrete phase regions or pores counted and \( M \) is the calibrated magnification of the micrograph.

The British standard requires at least five randomly positioned and randomly orientated lines across the micrograph such that at least 100 discrete phase regions or pores of the type to be assessed are intersected. Grains touching the edge of the micrograph are ignored and each measurement is taken to the nearest 0.5 mm with a calibrated rule. In this study six lines per micrograph and five micrographs per sample were used to ensure that the 100 discrete phase regions were maintained despite the variation in grain size due to sintering parameters. This method was also used to measure the defect size and relative density from images of the planar surfaces taken using an SEM. The defect size can be determined by using the linear intercept method described above, with the pores measured instead of the grains.

The Wilcoxon signed-rank test was used to determine if repeated measurements of the same sample or a range of different samples were statistically different. This is a modification of the sign test and can be used to determine if the median particle size has changed to a significant extent. It can also be used to test the hypothesis that the grain size distribution functions of two different samples are identical (Maca and Simonikova, 2005).

Relative density can be determined by using the pore size measurements and taking the summation of all the lines measured, thus providing the proportion of open area. This open area, \( \sum L_i \), can then be calculated as a percentage of the total distance measured. An alternative method is defined by the standard test method for determining volume fraction by systematic manual point count. An array of points formed by a grid of lines or curves is superimposed upon a magnified image of a metallographic specimen. Then:
where $P_{P(i)}$ is the percentage of grid points in the constituent observed on the $i^{th}$ field, $P_i$ is the point count on the $i^{th}$ field and $P_T$ is the total number of points in the test grid.

The number of points falling within the microstructure constituent of interest is counted and averaged for a selected number of fields. This average number of points expressed as a percentage of the total number of points in an array ($P_T$) is an unbiased statistical estimation of the volume percent of the microstructural constituent of interest (ASTM standard E562-02, 1999). In this study six lines per micrograph and five micrographs per sample were used. This ensured that 3000 mm of discrete phase regions were maintained per sample giving $P_T$, with the pore length given by $P_i$. The result of equation 4.3 is then expressed as percentage porosity in the sample (Loehman, 1993).

### 4.2.11.2 Layer thickness measurement

Variation of the layer thickness was measured using an SEM. In an SEM image, the apparent width of the printed layer can vary, depending on the contrast and brightness settings; an example of the type of sample investigated is shown in Figure 4.10.

![SEM cross-sectional image of screen-printed layer on the pre-fired substrate priming layer and substrate.](image)

Figure 4.10: SEM cross-sectional image of screen-printed layer on the pre-fired substrate priming layer and substrate.
Chapter 4: Conventional sintering profiles

The variation can be as great as 10% without any change in instrument magnification. To minimise the resulting uncertainty an adjustment of the brightness and contrast can be made such that the image contains surface detail of the materials on either side of a boundary or interface (ASTM standard, E766-98, 1999). For critical measurements the mean measurement of the test specimen should be taken and in this study five measurements per image and three images per sample were taken to determine the mean.

The critical factor in studies of this type is the calibration of the SEM. An SEM stage micrometer or other calibration method may be used if it can be demonstrated to be sufficiently accurate for meeting the standard (ASTM standard, B748-90, 2001). MCS (Roslin, Midlothian, UK) were responsible for calibrating the SEM sufficiently to meet the ASTM standard.
4.3 Results and discussion

4.3.1 Screen thickness and number of print deposits

4.3.1.1 Deposition thickness

Screen-printing was investigated to assess the impact of increasing the printed layer thickness on the sintered layer thickness, relative density and grain size. The screen-printing process uses screen thickness (mesh size) and the number of printing applications to change the thickness of the laminate prior to sintering. The printing trials for each screen thickness included print-dry applications of one, two, three and four layers. Once fabricated the samples were sintered once using an identical sintering profile for each batch of samples. A microstructural examination of the cross-sections showed increasing sintered layer thickness for increasing screen thickness and additional print-dry applications.

Single print-dry applications of the thinnest mesh size (325UT) produced very thin sintered layers. Typically these were 1-2 μm thick and were difficult to differentiate from the substrate priming layer. Therefore the 325UT mesh size and single print-dry applications were not considered further in the deposition study. The screen mesh sizes used were 325, 200, 165, 105 and 80, corresponding to screen thicknesses of 60, 90, 110, 162 and 215 μm, respectively. As the ink passes across the screen only the open areas within the mesh are available for the ink to flow through. Therefore the volume of ink deposited through the screen is a function of the screen thickness and open area of the mesh. This reduces the thickness of the printed (wet) and dried layer relative to the screen thickness. The reduction in open area results in a wet layer of around 23 μm and 103 μm for the 325 and 80 mesh sizes, respectively. This printed layer is then dried in an oven to remove the solvent within the ink vehicle. The removal of solvent reduces the single print-dry layer thickness to around 4.1 μm and 17.5 μm for the 325 and 80 mesh sizes, respectively. Once the layer is dry it can be sintered and this resulted in a thickness of 1 μm and 6 μm from a single print of the 325 and 80 mesh sizes, respectively. An additional number of print-dry applications prior to sintering also increase the sintered layer thickness.

The effect of screen thickness on the sintered layer is shown in Figure 4.11. These images show the increasing sintered layer thickness produced from samples with three print-dry applications through the 325, 165, 105 and 80 mesh sizes.
The range of sintered thickness achieved in the deposition study was from $2 \pm 0.4 \, \mu m$ to $23 \pm 0.8 \, \mu m$. As the screen thickness increases the sintered thickness also increases from $3 \pm 0.3 \, \mu m$ for the 325 mesh to $17 \pm 1.2 \, \mu m$ for 80 mesh size (Figure 4.11a and d, respectively). This is in good agreement with Zhang et al., (2006) who showed that the thickness of a screen printed YSZ film ranged from 2 \mu m to 15 \mu m when printing with one to seven print-dry applications. A polymer based mesh with a wire diameter of $\sim 30 \, \mu m$ was used in the study by Zhang et al., (2006) which would be roughly equivalent to a 325 stainless steel mesh used in this study. The change in mesh size dominates the relationship between printed thickness and the sintered thickness. However, the effect of increasing the number of print-dry applications increases with increasing screen thickness.
Chapter 4: Conventional sintering profiles

The change in mesh size and number of print-dry applications is a function of the wire diameter and the open area within the mesh. This deposited thickness then corresponds to a sintered thickness for each mesh size and number of print-dry applications, as shown in Figure 4.12.

![Figure 4.12: Deposited thickness and sintered thickness as a function of screen thickness. Sintered thickness and deposited thickness do not show the same relationship to screen thickness. Error bars represent one standard deviation from the mean.](image)

A 325 mesh size with three print-dry applications has an equivalent screen thickness (180 μm) to a 200 mesh size with two print-dry applications. This screen thickness results in a lower deposited thickness (69 μm) for the 325 mesh size (black square) compared with the 200 mesh size (86 μm) (blue diamond). The change in deposited thickness results in sintered layer thicknesses of 3.0 ± 0.3 μm and 5.1 ± 0.3 μm for the 325 and 200 mesh sizes, respectively.
Although nominally the same thickness could be achieved in two different ways, the application of three thin layers results in a thinner deposit and a thinner sintered layer than the application of two thicker layers. This trend is seen in all of the data in Figure 4.12. This implies that the application of several thin layers should result in a denser body than the application of fewer thicker layers. One possible explanation for this is that the printing application allows 'defects' in the previous layers to be filled.

The sintered layer thickness requirement for an electrolyte film for the IP-SOFC design is \( \sim 10-20 \) \( \mu \text{m} \) (Gardner et al., 2000). This requirement means that only the 165, 105 and 80 mesh sizes would be suitable. Ideally the lowest number of print-dry applications would be preferable as this would reduce the number of processing steps. However, it is not possible to differentiate between sintered layers purely on sintered thickness. There are other factors to consider such as the ionic conductivity, which increases with increasing thickness (Bossell, 1992), and the ability to maintain a physical barrier between the fuel and air within the fuel cell. When considering these requirements other microstructural parameters such as the density and grain size should be considered. The ideal electrolyte would have a low ionic resistance (thin sintered thickness) while maintaining the separation between the fuel and oxidant (impermeable). The 165 mesh with three print-dry applications is potentially the most suitable even though a sintered thickness of \( 9 \pm 0.8 \) \( \mu \text{m} \) is just at the lower end of the design requirements for the IP-SOFC design.
4.3.1.2 Microstructural evolution with deposition thickness

The relative density and grain size of the sintered layer surfaces were measured to assess the effect of printed layer thickness on densification. These data show that increasing the thickness of the printed layer reduces the relative density and the grain size as assessed from observation of the microstructure of the surface. The data show some spread and there is no specific trend with number of print-dry applications, particularly with the thinner layers, indicating that the number of applications does not dominate the relative density or grain size. However, the observed reduction in relative density shows an approximately linear relationship with increasing screen thickness. The grain size data show a less linear response with increasing screen thickness. The results for relative density and grain size are presented in Figure 4.13.

![Figure 4.13: The effect of grain size and relative density as a function of increasing screen thickness and number of print-dry applications on screen-printed layers. Error bars represent one standard deviation from the mean.](image)

As screen thickness increases, due to the increased wire diameter within the mesh, the relative density and grain size of the sintered layer decreases. The 325 mesh size has a screen thickness of 60 µm and sample A-325-3-3-1450-1 had a relative density of 0.94 and a
Chapter 4: Conventional sintering profiles

grain size of 2.2 ± 0.3 μm. For the sample sintered using the same sintering scheme, the relative density and grain size reduced to 0.81 and 0.94 ± 0.1 μm, respectively when the screen thickness was increased to 215 μm (80 mesh).

The change in grain size for the 165, 105 and 80 mesh sizes is small compared with the change between the mesh sizes 325, 200 and 165. This suggests that once the screen thickness is ≥ 110 μm (165 mesh) the grain size remains relatively unchanged with increasing screen thickness or number of print-dry applications. Grain size data for the 165 (A-165-2-3-1450-1, A-165-3-3-1450-1, A-165-4-3-1450-1), 105 (A-105-2-3-1450-1, A-105-3-3-1450-1, A-105-4-3-1450-1) and 80 mesh (A-80-2-3-1450-1, A-80-3-3-1450-1, A-80-4-3-1450-1) samples were assessed using the non-parametric two-selection Wilcoxon signed-rank test (Hinton, 2004). This tests the hypothesis that the grain size distribution functions of the different samples are identical. The data were taken from mean grain size measurements using the linear intercept method, with SEM images printed on the same printer and measured using the same scale. The Wilcoxon signed-rank test showed that the mean grain size was not significantly different for samples fabricated with 165, 105 or 80 mesh sizes or when fabricated with 2, 3 or 4 print-dry applications. This analysis was then used to ensure that grain sizes measured for samples (A-325-2-3-1450-1, A-325-3-3-1450-1, A-325-4-3-1450-1) printed with the 325 mesh size were statistically different from that of the 165, 105 and 80 mesh sizes. The grain sizes of samples printed with the 325 mesh were statistically different to those measured for samples printed with the 165 (A-165-2-3-1450-1, A-165-3-3-1450-1, A-165-4-3-1450-1), 105 (A-105-2-3-1450-1, A-105-3-3-1450-1, A-105-4-3-1450-1) and 80 mesh (A-80-2-3-1450-1, A-80-3-3-1450-1, A-80-4-3-1450-1) with a probability of as much as 99%. Worked examples of these two Wilcoxon signed-rank tests are given in appendix A.

Microscopy of the sintered layers showed a variation in the surface structure for increasing screen thickness. The variation in surface microstructure between samples A-325-3-3-1450-1, A-165-3-3-1450-1, A-105-3-3-1450-1, A-80-3-3-1450-1 are presented in Figure 4.14. These surface images show that sample A-325-3-3-1450-1 results in a larger grain size and reduced surface porosity when compared with samples A-165-3-3-1450-1, A-105-3-3-1450-1, A-80-3-3-1450-1. The grain sizes and surface porosity for samples A-165-3-3-1450-1, A-105-3-3-1450-1, A-80-3-3-1450-1 appear similar and this was confirmed by the Wilcoxon signed-rank test.
Figure 4.14: Scanning electron micrographs of the surfaces of the sintered layers with three print-dry applications for a) 325, b) 165, c) 105 and d) 80 mesh sizes.

In each case the samples printed with increasing screen thickness and three print-dry applications were sintered using the same sintering scheme. It is difficult to interpret any significant difference from these images. However, from the microstructural analysis it has been established that sample A-325-3-3-1450-1 printed using a screen thickness of 60 μm (325 mesh) had a relative density of 0.94. The relative density decreases to 0.91, 0.83 and 0.81 as the screen thickness increases to 110 μm (165 mesh), 162 μm (105 mesh) and 215 μm (80 mesh). Subsequently, the 165 mesh size with three print-dry applications is selected as the baseline fabrication.
4.3.2 Sintering profile – conventional sintering

4.3.2.1 Heating rate

This section investigates and separates out the three distinct parts of a conventional sintering schedule; the heating rate, the sintering temperature and the dwell time at temperature. Traditionally, for YSZ, a normal sintering schedule is employed to heat the powder compact at a certain rate, then to hold it at the highest temperature, such as 1500°C, until the maximum density is reached. The heating rate is the constant rate at which the temperature is increased until the sintering temperature is reached. Heating rates of 1, 3, 5, 7 and 10°C min⁻¹ were used to sinter pressed pellets of YSZ without an isothermal hold at the peak temperature. Dilatometry analysis was used to measure the effect of each heating rate. The data for the unconstrained pressed pellets are shown in Figure 4.15.

Figure 4.15: Rate of change of length as a function of temperature for unconstrained 3-mol% YSZ when heated at increasing rates of 1, 3, 5, 7 and 10°C min⁻¹.

These data show that there is a greater change in length with time, associated with increasing the heating rate. The initiation in movement of the sample started at a lower temperature for the higher heating rate samples. At 10°C min⁻¹ the temperature was ~ 988°C, while a reduction in heating rate to 1°C min⁻¹ increased this temperature to ~ 1034°C. The relative
density was calculated from the dimensional changes in the pressed pellet. Relative density ranged from 0.71 to 0.55 for the increase in heating rate from 1 to 10°C min⁻¹. These measured data were compared with the data calculated from the dilatometer displacement and the typical error was ± 2% and ± 4% for 1 and 10°C min⁻¹ heating rates, respectively. The microstructure was assessed using the Archimedes method and the relative density and percentage of open and closed porosity are given in Table 4.11.

Table 4.11: Archimedes measurement of pressed pellets at different heating rates

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Heating rate (°C min⁻¹)</th>
<th>Open porosity (%)</th>
<th>Closed porosity (%)</th>
<th>Relative density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1250-0-C</td>
<td>1</td>
<td>20</td>
<td>1</td>
<td>0.78</td>
</tr>
<tr>
<td>3-1250-0-C</td>
<td>3</td>
<td>32</td>
<td>1</td>
<td>0.67</td>
</tr>
<tr>
<td>5-1250-0-C</td>
<td>5</td>
<td>30</td>
<td>2</td>
<td>0.69</td>
</tr>
<tr>
<td>7-1250-0-C</td>
<td>7</td>
<td>35</td>
<td>2</td>
<td>0.63</td>
</tr>
<tr>
<td>10-1250-0-C</td>
<td>10</td>
<td>44</td>
<td>2</td>
<td>0.54</td>
</tr>
</tbody>
</table>

These data show that estimated relative density values reduce as the open porosity increases with increasing heating rate. Despite the greater shrinkage per unit time measured by the dilatometer the 10°C min⁻¹ sample has a greater level of open porosity and a lower density than any of the other heating rate samples. The data obtained by measuring the change in length show that the physical shrinkage reduces when the heating rate is increased. Interestingly the samples heated at 5, 7 and 10°C min⁻¹ may have a higher level of closed porosity. Sintering theory, previously discussed in chapter 3, suggests that the faster heating rates should produce a finer grain size and pore size. However, the accuracy of the closed porosity data would indicate that above 5°C min⁻¹ the values are effectively the same. The grain and pore size were measured from polished sections for each heating rate sample using the linear intercept method, as shown in Figure 4.16.
These data show that the grain size reduces slightly and pore size also reduces with increased heating rate. A similar grain size was measured for samples heated at 3, 5, 7 and 10°C min⁻¹; the value is close to that measured for the milled powder, i.e. 0.15 μm. Chu et al., (1991) showed that densification of zinc oxide powders was influenced by heating rate. The highest densities were achieved with 0.5 and 5°C min⁻¹ heating rates, while the faster heating rates of 10 and 15°C min⁻¹ gave the lowest densities (Chu et al., 1991). Teng et al., (2002) showed that sintering 3-mol% YSZ powder with an initial grain size of 0.35 μm heated at 2, 5 and 8°C min⁻¹ resulted in decreasing density with increasing heating rate. This is in good agreement with the conventionally sintered pressed pellets measured in this study. The pore size values show a gradual reduction for heating rates from 1 to 5°C min⁻¹. This suggests that the faster heating rates result in a smaller grain size and pore size. If this assumption is correct then the application of faster heating rates (5, 7 and 10°C min⁻¹) to constrained YSZ thick-films should keep the pore size small which may be significant in the later stages of the sintering scheme.
Similarly, a set of screen-printed samples was sintered using a range of heating rates between the initial binder removal and the isothermal hold. Heating rates of 1, 5, 10 and 20°C min\(^{-1}\) were used. A heating rate of 20°C min\(^{-1}\) was not achievable in the dilatometer samples due to technical limitations of the equipment. The samples were fabricated using a 165 mesh size with three print-dry applications. The effect of heating rate on sintered thickness is shown in Figure 4.17.

![Figure 4.17: Sintered thickness as a function of heating rate for a 165 mesh size with three print-dry applications, heated using constant heating rates of 1, 5, 10 and 20°C min\(^{-1}\). Error bars represent one standard deviation from the mean.](image)

Sintered thickness was measured for samples fired to 1450°C for 1 hour. The variation in sintered thickness shows only small changes for an increasing heating rate. The sample prepared at 5°C min\(^{-1}\) shows a slightly thicker layer compared to the other heating rates. This is too small a difference to be considered significant but in good agreement with repeated samples using the same heating rates.
4.3.2.2 Microstructural evolution with heating rate

The relative density and grain size of the sintered surfaces were measured to assess the effect of the heating rate on densification. These data show that an increasing heating rate increases the relative density and the grain size (see Figure 4.18). Density measurements show that there is a discrepancy at 5°C min\(^{-1}\) as the sample sintered at this rate has the lowest relative density and is considerably less dense than the samples heated at 20°C min\(^{-1}\). This relationship is inconsistent with conventional sintering theory but repeat studies gave similar results to those presented in Figure 4.18.

![Figure 4.18: Relative density and grain size as a function of heating rate for samples prepared with a 165 mesh size and three print-dry applications, heated using constant heating rates of 1, 5, 10 and 20°C min\(^{-1}\). Error bars represent one standard deviation from the mean.](image)

Surface analysis of the sintered screen-printed layers showed a general trend of increasing relative density and grain size with increasing heating rate. The exception was the sample heated at 5°C min\(^{-1}\) which showed a distinct visual difference in the surface microstructure. This sample has a smaller grain size and increased number of pores when compared with the samples heated at 1°C min\(^{-1}\) and 10°C min\(^{-1}\). The temperature of the isothermal hold was kept constant in this set of samples, although it was noted that this parameter will affect grain
growth and final density. Examples of the surface analysis for all four samples are shown in Figure 4.19.

The surface microstructures show a change in the grain and pore structure when heated at different rates. It is suggested that as heating rate increases it influences the grain size and the pore size distributions. This can be seen in the error bars associated with each mean grain size. The error bars are quoted as one standard deviation and these increase as the grain size increases. Heating rates of 1, 5, 10 and 20°C min⁻¹ have standard deviations of 1.1, 0.1, 2 and 2.2 μm respectively. This shows that the range of grain sizes is greater at the faster heating rates. The 5°C min⁻¹ heating rate requires further investigation to assess why this particular value appears to retard the grain size and density. Subsequently, a heating rate of 10°C min⁻¹ was selected as the baseline.
4.3.2.3 Sintering temperature

The heating rate in conventional sintering typically ends at what is described as the sintering temperature. This temperature should be high enough to bring the ceramic body to full density. The sintered layer thickness, relative density and grain size of samples held at different sintering temperatures were assessed. Establishing the effect of sintering temperature for a consistent heating rate and dwell time provides microstructural information on how YSZ densifies as a constrained thick-film.

The sample batches were fabricated using a 325UT mesh size and one print-dry application allowing the change in sintered layer thickness with temperature to be measured, as shown in Figure 4.20.

![Scanning electron micrographs of cross-sections through layers sintered for 1 hour at temperatures of a) 1400°C and b) 1450°C.](image)

The samples sintered at 1400°C have a thickness of 4.1 ± 0.3 μm compared with 2.9 ± 0.2 μm for the samples sintered at 1450°C. This change in sintered thickness can be attributed to densification as the temperature increases. The microstructure developed through this temperature range has reached the final stage of sintering where continuous grain growth and pore isolation is expected. The resulting relative density and grain size are shown in Figure 4.21.
An increase in relative density is associated with an increase in the grain size as sintering temperature increases. These grain sizes have been compared with those for unconstrained pressed pellets. The pressed pellet study was conducted by the manufacturer of the 3-mol% YSZ powder, MEL Chemicals (Manchester, UK) where pellets were sintered between 1300 and 1500°C. The dwell time was also varied between 4, 8 and 16 hours for each temperature range (Stone, 2005). Scanning electron micrographs obtained from MEL Chemicals were measured using the linear intercept method to determine the change in grain size as shown in Figure 4.21 above. This analysis showed that unconstrained samples had a higher relative density and smaller grain size than the constrained samples sintered in this study. The MEL Chemicals data for relative density is not shown as the specific values are unreliable due to uncertainty of the phase content. The trends shown between grain size and relative density in this study are in good agreement with Levänen and Mäntylä (2002) who studied unconstrained and constrained multi-layered alumina membranes. From the results in the sintering temperature study a temperature of 1450°C was selected as the baseline.
4.3.2.4 Sintering time

Once the sintering temperature is reached the body can be held at this temperature until full density is achieved and then cooled to room temperature. This isothermal hold or sintering time can influence the extent of grain growth within the final microstructure. The sample batches were investigated for sintered thickness, relative density and grain size. Grain growth occurs as the sintering temperature increases and continues when the isothermal hold begins. In thin film strips it has been shown that the grains continue to grow although the rate of growth will slow as density increases and the grain size approaches the layer thickness (Walton et al., 1992). Examples of this type of microstructural development are shown in Figure 4.22, where the sintered layer thickness is less than the surface grain size.

![Scanning electron micrographs for samples with increasing sintering times](image)

**Figure 4.22:** Scanning electron micrographs for samples with increasing sintering times

a) surface image of 4 hour dwell, b) surface image of 10 hour dwell, c) cross-section of 4 hour dwell and d) cross section of 10 hour dwell.
Samples sintered with increasing dwell times were prepared using a screen thickness of 50 μm (325UT mesh size) with a single print-dry application. The surface images for samples sintered for 4 hours (A-325UT-1-3-1400-4) and 10 hours (A-325UT-1-3-1400-10) show a well developed grain structure. Sintered thickness reduced with increasing sintering time. As a single print-dry application was used for these samples, a sintering time of 10 hours (A-325UT-1-3-1400-10) makes it difficult to differentiate the surface layer from the substrate priming layer. The initial rate of reduction in thickness from 1 hour (A-325UT-1-3-1400-1) to 4 hours (A-325UT-1-3-1400-4) slowed as the length of the isothermal hold was increased, as shown in Figure 4.23. This is in good agreement with Walton et al., (1992).

![Figure 4.23: The change in sintered layer thickness as a function of increasing sintering time. Sintered thickness reduces as the sintering time is increased. Error bars represent one standard deviation from the mean.](image)

Increasing the sintering time resulted in the layer thickness reducing from 4.5 ± 0.3 μm to 2.5 ± 0.4 μm. This change in the sintered thickness occurs after increasing the time of the isothermal hold from one to ten hours. The effects on relative density and grain size were measured across this range of sintering times and are shown in Figure 4.24.
Chapter 4: Conventional sintering profiles

Figure 4.24: Grain size and relative density as a function of sintering time for constrained layers and pressed pellets. The increase in grain size is related to an increase in relative density in the constrained layers, although after 4 hours the pressed pellets are fully dense. Error bars represent one standard deviation from the mean.

Increasing the sintering time shows an associated increase in the relative density and grain size. The initial reduction in sintered thickness is associated with an increase in grain size from 1.6 ± 0.2 μm to 8.3 ± 2.4 μm for an isothermal hold of 1 hour (A-325UT-1-3-1400-1) and 4 hours (A-325UT-1-3-1400-4), respectively. Increasing the dwell time to 10 hours increases the grain size to 10 ± 3.6 μm (A-325UT-1-3-1400-10). The relative density also increases with increasing sintering time from 0.91 to 0.96 for an isothermal hold of 1 hour (A-325UT-1-3-1400-1) and 4 hours (A-325UT-1-3-1400-4), respectively. Increasing the sintering time beyond 4 hours increased the relative density towards 0.97. The increase is not linear with respect to time and shows that the relative increase in density and grain size reduces as time proceeds, as would be expected. The pressed pellets have a higher starting density than that of the constrained samples and hence full density should be reached after a shorter time with the pressed pellets as can be seen. From these results a sintering time of 10 hours was selected as the baseline.
4.4 Concluding remarks

This chapter has considered fabrication and conventional sintering of YSZ thick-films. The final microstructure of a thick-film is a function of the deposition process and sintering scheme. Therefore changes to the fabrication of the green layer can influence the sintered microstructure. Sintered thickness can be controlled by the screen thickness (mesh size) and number of print-dry applications. An electrolyte thickness of between 10 and 20 μm is required for the IP-SOFC design. The sintered thickness of 9 ± 0.8 μm obtained from a screen thickness of 110 μm (165 mesh) with three print-dry applications is at the bottom limit of this requirement. Increasing the screen thickness beyond 110 μm increases the sintered thickness beyond 9 μm. However, this leads to a reduction in relative density and grain size. The change in sintered thickness due to additional print-dry applications has a minor effect compared with increasing the mesh size. Therefore it can be concluded that the mesh size is the major factor influencing the relative density and grain size of sintered YSZ layers.

Using a stable fabrication process allowed the examination of the individual elements of the conventional sintering profile. It was shown that heating rate, sintering temperature and sintering time all influence the final microstructure. A heating rate of 20°C min⁻¹ showed the highest relative density and grain size with little change in the sintered thickness compared with slower heating rates. The IP-SOFC design cannot tolerate a heating rate greater than 10°C min⁻¹ due to cell components other than the electrolyte. Up to a sintering temperature of 1450°C the grain size change was small with respect to changes in the heating rate and sintering time. A dwell time of 10 hours resulted in the highest density and grain size.

Therefore a heating rate faster than 10°C min⁻¹, a peak sintering temperature of 1450°C and a sintering time of 10 hours have been assumed as the optimised parameters. However, the baseline values for heating rate (10°C min⁻¹), sintering temperature (1450°C) and sintering time (10 hours) are concessions on the optimal microstructure due to limitations in the IP-SOFC design. This simple approach to a complex system of variables has established baseline processing parameters for green state fabrication and sintering for the YSZ screen-printed layers. This provides a starting point from which modifications to a conventional sintering profile can be investigated to further optimise the microstructure.
Chapter 5: Non-conventional sintering profiles

5 Non-conventional sintering profiles

5.1 Introduction

A conventional sintering profile for a ceramic is designed to apply a constant heating rate to the sample up to a temperature at which it is held for a period of time prior to being cooled to room temperature. The choice of heating rate, sintering temperature and sintering time is dependent on a variety of factors. These include the particle size of the starting powder, component geometry and material properties. Using these factors a conventional sintering profile to densify a ceramic body to a relative density of > 0.98 can be designed.

Modifications to conventional sintering are classified herein as non-conventional sintering. Non-conventional sintering profiles can include coarsening, two-step and three-step sintering techniques. Coarsening adds an isothermal hold at a temperature below that of the sintering temperature. Two-step sintering is described as an initial rise to a peak temperature, followed by a rapid reduction to a lower temperature at which an isothermal hold is performed. Three-step sintering combines the lower temperature coarsening step with two-step sintering. Within this chapter the results of applying these non-conventional sintering profiles to YSZ screen-printed thick-films are described.

5.2 Experimental details

5.2.1 Sample preparation

Each sample was prepared using the same batch of YSZ powder, ink and substrate. These samples were screen-printed using the same parameters defined for the mesh study described in Chapter 4. The possibility of results being influenced by processing conditions were minimised by randomly selecting the print-dry samples prior to the sintering stage. Each screen-printed batch contained approximately one hundred samples from which a sample batch consisted of five samples. The sample batches were prepared using the baseline parameters outlined in Chapter 4.

Each batch of samples was designated a code that was unique to that set of samples. As the construction of the samples was constant throughout, the sample batch parameters such as substrate type, mesh size and number of print-dry applications could be excluded in this case. The sample batch parameters were based on the elements of the sintering profile. An example of each type of sintering profile is given below in Table 5.1. A sample batch code of 10-1450-1100-10-2 indicates the sintering parameters for a two-step sintering profile (line 3 in Table 5.1).
Table 5.1: Non-conventional sintering profile sample identification index

<table>
<thead>
<tr>
<th>Heating rate (°C min⁻¹)</th>
<th>Sintering temperature (°C)</th>
<th>Coarsening time (h)</th>
<th>Sintering temperature (°C)</th>
<th>Sintering temperature (°C)</th>
<th>Sintering time (h)</th>
<th>Sintering profile type</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1450</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>C</td>
</tr>
<tr>
<td>10</td>
<td>1100</td>
<td>2</td>
<td>1450</td>
<td>-</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>1450</td>
<td>-</td>
<td>1100</td>
<td>-</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>1100</td>
<td>2</td>
<td>1450</td>
<td>1150</td>
<td>10</td>
<td>3</td>
</tr>
</tbody>
</table>

C = conventional sintering, 1 = coarsening, 2 = two-step sintering, 3 = three-step sintering

5.2.2 Coarsening step processing

Coarsening of ceramics has been considered previously in Chapter 3, where it is described as a process that occurs at a temperature below that at which the majority of the densification takes place. Each sample batch was sintered in an Elite Thermal Systems 1700°C sintering furnace, (Market Harborough, Leicestershire, UK). A sintering profile which includes a coarsening step is shown in Figure 5.1.
Figure 5.1: Schematic illustration of a sintering profile with an isothermal hold at a lower temperature than the sintering temperature. This portion of the sintering profile can be described as the coarsening step.

Luo et al., (1998) indicated that the coarsening temperature for 3-mol% YSZ could be as high as 1150°C. In other research the coarsening temperature has been quoted as being between 900 and 1100°C (Wolff et al., 2003). Despite the range of temperatures quoted by Wolff et al., (2003) they also sintered samples at 1150°C, although these were not included in the original experimental work.

In the current study, temperatures of 1050°C, 1100°C and 1150°C were used as the basis for the experimentation on coarsening. Initial work focussed on the effect of just the coarsening step on pressed powders. This allowed dilatometry to be used and Table 5.2 gives details of the sintering parameters used for this study.
Chapter 5: Non-conventional sintering profiles

Table 5.2: Coarsening profiles for pressed pellets of 3-mol% YSZ

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Heating rate (°C min⁻¹)</th>
<th>Coarsening temperature (°C)</th>
<th>Coarsening time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1050-2-C</td>
<td>3</td>
<td>1050</td>
<td>2</td>
</tr>
<tr>
<td>3-1100-2-C</td>
<td>3</td>
<td>1100</td>
<td>2</td>
</tr>
<tr>
<td>3-1150-2-C</td>
<td>3</td>
<td>1150</td>
<td>2</td>
</tr>
</tbody>
</table>

The samples shown above were heated to the coarsening temperature and then cooled to room temperature after the isothermal hold. These sintering profiles were then applied to the constrained screen-printed layers. The coarsening step was used in isolation and heating to the sintering temperature was added to complete the sintering profile. The sintering profiles for screen-printed layers are given in Table 5.3.

Table 5.3: Coarsening profiles for screen-printed thick-films of 3-mol% YSZ

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Heating rate (°C min⁻¹)</th>
<th>Coarsening temperature (°C)</th>
<th>Sintering time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1100-0-C</td>
<td>3</td>
<td>1100</td>
<td>0</td>
</tr>
<tr>
<td>3-1100-2-C</td>
<td>3</td>
<td>1100</td>
<td>2</td>
</tr>
<tr>
<td>10-1400-10-C</td>
<td>10</td>
<td>n/a</td>
<td>0</td>
</tr>
<tr>
<td>10-1100-2-1400-10-1</td>
<td>10</td>
<td>1100</td>
<td>2</td>
</tr>
</tbody>
</table>
5.2.3 Two-step processing

Two-step sintering profiles can be defined by two temperatures, the peak temperature $T_1$ and the dwell temperature $T_2$. This allows the process to be separated into two sections, A and B, as shown in Figure 5.2.

Creating two discrete sections allows the two-step process to be separated into its component parts. The two-step sintering profiles used in this study are given in Table 5.4. In the literature these two-step sintering profiles have only been applied to pressed powder compacts and not constrained YSZ thick-films.
Thus, the sample index for sample 10-1400-1200-10-2, indicates that the sintering profile comprises an initial ramp to remove binders, followed by heating at 10°C min⁻¹ to 1400°C, and a hold for 0.083 hours (5 minutes) (section A). This is then followed by section B where the temperature is reduced to 1200°C and held for 10 hours before the sample is cooled to room temperature.
5.2.4 Three-step processing

Three-step sintering combines a coarsening step with two-step sintering. This is intended to take advantage of the re-packing mechanism associated with coarsening and suppression of grain growth in two-step sintering (outlined in Chapter 3). Constrained sintering slows densification and the addition of a third step is designed to aid the homogenisation and subsequent densification of constrained thick-films. An example of a three-step sintering profile is given in Figure 5.3. The actual schedules used are given in Table 5.5.

![Three-step Sintering Profile Schematic](image_url)

Figure 5.3: Schematic illustrating a three-step sintering profile. The heating regime is shown as three discrete parts; a coarsening step followed by sections A and B from two-step sintering.
Chapter 5: Non-conventional sintering profiles

Table 5.5: Three-step sintering profiles, combining the coarsening and two-step sintering profiles

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Coarsening temperature (°C)</th>
<th>Peak temperature, $T_1$ (°C)</th>
<th>Isothermal hold temperature, $T_2$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-1100-2-1330-1100-10-3</td>
<td>1100</td>
<td>1330</td>
<td>1100</td>
</tr>
<tr>
<td>10-1100-2-1330-1150-10-3</td>
<td>1100</td>
<td>1330</td>
<td>1150</td>
</tr>
<tr>
<td>10-1100-2-1367-1300-10-3</td>
<td>1100</td>
<td>1367</td>
<td>1300</td>
</tr>
<tr>
<td>10-1100-2-1400-1200-10-3</td>
<td>1100</td>
<td>1400</td>
<td>1200</td>
</tr>
<tr>
<td>10-1100-2-1450-1400-10-3</td>
<td>1100</td>
<td>1450</td>
<td>1400</td>
</tr>
<tr>
<td>10-1100-2-1500-1300-10-3</td>
<td>1100</td>
<td>1500</td>
<td>1300</td>
</tr>
<tr>
<td>10-1100-2-1600-1150-10-3</td>
<td>1100</td>
<td>1600</td>
<td>1150</td>
</tr>
</tbody>
</table>

Thus, the sample index for 10-1100-2-1400-1200-10-3, indicates that the sintering profile can be defined as an initial ramp to remove binders, then a heating rate of $10^\circ\text{C}\text{ min}^{-1}$ to $1100^\circ\text{C}$ with an isothermal hold of 2 hours (coarsening step), then heating to $1400^\circ\text{C}$ at $10^\circ\text{C}\text{ min}^{-1}$ with a 0.083 hours (5 minutes) hold, then ramp down to $1200^\circ\text{C}$ with an isothermal hold of 10 hours, followed by cooling to room temperature. In every case the duration of the isothermal hold at $T_1$ was 5 minutes, this was conducted to stabilise the furnace before the reduction in temperature to $T_2$. 

77
Chapter 5: Non-conventional sintering profiles

5.3 Results and discussion

5.3.1 Coarsening step profiles

The pressed pellets were sintered to three different temperatures, 1050, 1100 and 1150°C, and held for 2 hours before being cooled to room temperature. Dilatometry was used to assess the effect of an additional coarsening step on the densification of pressed pellets. The data for these unconstrained sintering profiles are shown in Figure 5.4.

![Figure 5.4](image)

Figure 5.4: The densification behaviour of pellets of 3-mol% YSZ when heated to three different coarsening temperatures: 1050, 1100 and 1150°C.

Relative density ranged from 0.35 to 0.5 for the increase in coarsening temperature from 1050 to 1150°C. These data were compared with estimates of final densities from geometrical measurements and were found to be comparable with the typical error being ± 0.01. After dilatometry, the relative density of each sample was measured using the Archimedes method and the percentage of open and closed porosity was calculated, as shown in Table 5.6.
Table 5.6: Density values for the coarsened pressed pellets

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Coarsening temperature (°C)</th>
<th>Open porosity (%)</th>
<th>Closed porosity (%)</th>
<th>Relative density</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1050-2-C</td>
<td>1050</td>
<td>58.0</td>
<td>2.0</td>
<td>0.40</td>
</tr>
<tr>
<td>3-1100-2-C</td>
<td>1100</td>
<td>46.5</td>
<td>2.5</td>
<td>0.51</td>
</tr>
<tr>
<td>3-1150-2-C</td>
<td>1150</td>
<td>40.0</td>
<td>2.0</td>
<td>0.58</td>
</tr>
</tbody>
</table>

These data show that the relative density increases while the closed porosity does not change with increasing coarsening temperature. However, the values are higher than those taken from either the dilatometer displacement or the micrometer measurements, where the nominal values for relative density were estimated to be 0.35, 0.47 and 0.5 for samples heated to 1050, 1100 and 1150°C, respectively i.e. the geometric measurements are overestimating the volume which is not unreasonable for such low density bodies. The amount of closed porosity is small compared with the open porosity and is essentially constant.

The coarsening step was also applied to the screen-printed thick-film layers. Samples were sintered to the coarsening temperature with and without an isothermal hold. The samples were heated using conventional heating profiles 3-1100-0-C and 3-1100-2-C. A 2 hour dwell time was added to one profile in an attempt to initiate the coarsening process. These samples were analysed for microstructural changes caused by the addition of an isothermal hold or coarsening-step. Layer thickness, relative density and grain size were measured for each sample batch. The layer thickness and relative density showed no change with increased time at the coarsening temperature. Visual inspection of the SEM images showed that the microstructures resulting from both the sintering profiles had a very porous structure and showed that the coarsened sample had a larger mean grain size; however, the mean pore diameter was the same in both samples. The median grain size and pore size was also constant and the pore size range was calculated from the difference between the largest and smallest pore size values as shown in Figure 5.5.
The mean grain size and pore size range for samples sintered to the coarsening temperature. The sample sintered for 2 hours at the coarsening temperature showed an increase in the mean grain size while the pore size range was reduced. Error bars represent one standard deviation from the mean.

The grain size (grey column) is larger for the coarsened sample (3-1100-2-C) compared with the sample without the isothermal hold (3-1100-0-C). However the pore size range reduces from 0.8 μm to 0.6 μm after an isothermal hold of two hours at the coarsening temperature. This is in good agreement with the work by Lin et al., (1997) on alumina where the pore size distribution became more uniform after coarsening at 800°C. The grain size and pore size range can be represented as a distribution. These are shown in Figure 5.6.
Chapter 5: Non-conventional sintering profiles

Figure 5.6: The grain and pore size distributions for samples sintered to a coarsening temperature of 1100°C and then cooled or held at temperature for 2 hours. The grain size and pore size values are denoted as g.s and p.s, respectively.

The grain size of the sample with a coarsening step shows a small increase in the mean value compared with the profile with no dwell. The pore size values show a similar distribution and this was confirmed by the mean, median, first and third quartile values all being equal. A difference was seen in the range of the values (pore size range) and the population of pores. The coarsened sample (3-1100-2-C) had a smaller pore size range (0.6 μm), but had a greater population of pores per unit area (0.0025 m²) compared to the sample with no dwell time (3-1100-0-C).

A coarsening step was also added to a conventionally sintered screen-printed sample. These samples were heated with and without the coarsening step at 1100°C (10-1400-10-C and 10-1100-2-1400-10-1), with an isothermal hold of 2 hours then heated to the sintering temperature to complete the sintering process. Relative density and layer thickness for these samples are given in Figure 5.7.
Figure 5.7: The change in sintered layer thickness and relative density for thick-film YSZ layers sintered conventionally and with the addition of a coarsening step. Error bars represent one standard deviation from the mean.

The values for sintered layer thickness for the coarsened samples are close to those of the conventionally sintered samples. These data are presented as mean values from five samples within each batch, suggesting that the coarsened samples have a very slightly larger layer thickness. It has already been established that the grain and pore sizes change when coarsening is used on unconstrained samples. Therefore the small increase in layer thickness could be due to changes in the grain and pore structure of the thick-film. Relative density is 0.98 compared with 0.96 for the conventionally sintered sample and this increase is unexpected as it is not associated with a reduction in the layer thickness. A thicker layer would be expected to be less dense, as described previously in Chapter 4. However, density is estimated from the surface microstructure and it is possible that this is not adequate to describe the bulk density in coarsened samples. Hence, further microstructural examination was undertaken.

Polished cross-sections were used to assess pore location: pores at the grain boundaries (intergranular) and pores within the grains (intragranular). Samples were chemically etched in 40 vol.% hydrofluoric acid for 15 minutes to reveal the grain structure. The heating profile
without the coarsening step showed that intragranular pores dominate the microstructure with only 25% of pores being present as intergranular porosity. This value increases to 43% for the coarsened sample indicating that there are fewer pores within the grains. The relative changes in grain size and pore size range with the addition of a coarsening step are shown in Figure 5.8.

![Figure 5.8: The grain size and pore size range for YSZ thick-film layers sintered using conventional and coarsening profiles. The grain size increases and the pore size range is reduced with the addition of an isothermal hold. Error bars represent one standard deviation from the mean.](image)

After sintering to 1100°C the mean grain sizes were 0.58 µm and 0.47 µm for the samples with and without the isothermal hold, respectively. Raising the temperature to 1400°C further increased the grain size in both samples from 0.58 to 21.6 µm for the coarsened sample and from 0.47 to 13.6 µm for the conventionally sintered sample. The pore size range reduced from 0.8 µm for samples without an isothermal hold at 1100°C to 0.6 µm with the addition of the 2 hour isothermal hold. Increasing the temperature from 1100°C to 1400°C resulted in an increase in pore size range to 12 µm and 5.1 µm for the samples without and with an isothermal hold of 2 hours, respectively. While the mean pore sizes were within one standard deviation in samples heated to either 1100 or 1400°C, the pore size range or distribution has been shown to narrow with the addition of a coarsening step.
Chapter 5: Non-conventional sintering profiles

Conventional sintering theory suggests that pore size is independent of grain growth. For both conventionally sintered and coarsened microstructures the sintered layer thickness has been shown to be similar in both cases, while there is a slight increase in relative density for the coarsened sample. This increase in relative density is associated with a narrowing of the pore size distribution and therefore coarsening is applicable to constrained YSZ thick-films. However, there is a large increase in grain size when a sample is coarsening and this could mean that the layer is more susceptible to cracking. If the grain growth could be suppressed this would reduce the risk of film fracture and subsequent mixing of fuel and oxidant gases within the fuel cell.

5.3.2 Two-step profiles

The two-step sintering schedule is based around two temperatures: a peak temperature and a dwell temperature. The peak temperature is selected with the intention of taking the sample to a sufficiently high relative density, > 0.7, such that it can reach full density when held at the lower dwell temperature. The peak temperature has been stated to be as high as 1600°C (Wolff et al., 2003) and as low as 1367°C (Leite et al., 2003) for YSZ. Accordingly, dwell temperatures of between 1300°C (Leite et al., 2003) and 1100°C have been quoted (Wolff et al., 2003) for use with YSZ. Application of this type of sintering profile has to date only been applied to unconstrained pressed pellets of YSZ. Here, these types of profile have been used to assess whether high densities can be achieved while grain growth is suppressed when sintering constrained YSZ thick-films.

By using an identical fabrication route for each sample it is possible to establish the extent to which the sintered layers are influenced by the choice of peak and dwell temperatures. Each part of the sintering profile has a role to play in achieving the desired microstructure. Components of the conventional sintering profile have been shown to influence the final microstructure whether through the heating rate, sintering temperature or sintering time. The two-step sintering profile has been broken down into two parts to establish the microstructure after the peak temperature (section A) and the dwell time at lower temperature (section B). Sample batches were sintered using the initial ramp to the peak temperature and then cooled to room temperature in an attempt to simulate section A. It should be noted that due to the cooling to room temperature a true representation of microstructure at T₂ cannot be achieved.
Chapter 5: Non-conventional sintering profiles

Sintered layer thickness, taken from SEM analysis of cross-sections, and relative density achieved for two-step sintering profiles are given in Table 5.7.

Table 5.7: Sintered layer thickness and relative density for samples sintered using two-step sintering profiles. The errors represent one standard deviation from the mean

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Temperature, $T_1$ ($^\circ$C)</th>
<th>Temperature, $T_2$ ($^\circ$C) (Dwell time at $T_2 = 10$ h)</th>
<th>Sintered layer thickness ($\mu$m)</th>
<th>Relative density</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-1330-1100-10-2</td>
<td>1330</td>
<td>1100</td>
<td>9.1 ± 1.1</td>
<td>0.80</td>
</tr>
<tr>
<td>10-1330-1150-10-2</td>
<td>1330</td>
<td>1150</td>
<td>10.2 ± 0.6</td>
<td>0.79</td>
</tr>
<tr>
<td>10-1367-1300-10-2</td>
<td>1367</td>
<td>1300</td>
<td>6.9 ± 0.4</td>
<td>0.87</td>
</tr>
<tr>
<td>10-1400-1200-10-2</td>
<td>1400</td>
<td>1200</td>
<td>8.3 ± 0.6</td>
<td>0.90</td>
</tr>
<tr>
<td>10-1450-1400-10-2</td>
<td>1450</td>
<td>1400</td>
<td>7.0 ± 0.3</td>
<td>0.91</td>
</tr>
<tr>
<td>10-1500-1300-10-2</td>
<td>1500</td>
<td>1300</td>
<td>7.2 ± 0.8</td>
<td>0.92</td>
</tr>
<tr>
<td>10-1600-1150-10-2</td>
<td>1600</td>
<td>1150</td>
<td>7.4 ± 0.4</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Sintering a YSZ layer conventionally to 1450°C for 1 hour produced a 9 ± 0.8 $\mu$m thick layer which is equivalent to the sample sintered to a peak temperature of 1330°C, 10-1330-1100-10-2. While this sample has a similar sintered layer thickness it has a relative density of 0.8 which is lower than that of the conventionally sintered sample at 0.92.

Whilst there is no consistent trend, the higher peak temperatures tend to produce thinner layers with higher densities. In the samples sintered with $T_2 = 1150^\circ$C, for 10-1330-1150-10-2, the layer thickness is larger (10.2 ± 0.6 $\mu$m) while its relative density (0.79) is lower than that of 10-1600-1150-10-2 where layer thickness and relative density are 7.4 ± 0.4 $\mu$m and 0.97, respectively. This suggests that the increased density associated with an isothermal hold at $T_2$ (1150°C) is influenced by the density achieved at $T_1$. When $T_2$ was reduced to 1100°C, 10-1330-1100-10-2, the layer thickness reduced to 9.1 ± 1.1 $\mu$m and relative density increased slightly to 0.8. This indicates that the isothermal hold at 1100°C is more effective than the one at 1150°C. This was also seen in the pressed pellet sample, 3-1100-2-C, where this sample had the highest level of closed porosity. If the isothermal hold at $T_2$ influences the level of porosity then this should be reflected in the relative grain and pore sizes measured for each sample; these are given in Table 5.8.
Table 5.8: Mean grain size, mean pore size and pore size range values for samples sintered using two-step sintering profiles. The errors represent one standard deviation from the mean.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Temperature, ( T_1 ) (°C)</th>
<th>Temperature, ( T_2 ) (°C) (Dwell time at ( T_2 = 10 ) h)</th>
<th>Mean grain size (µm)</th>
<th>Mean pore size (µm)</th>
<th>Pore size range (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-1330-1100-10-2</td>
<td>1330</td>
<td>1100</td>
<td>0.6 ± 0.2</td>
<td>0.5 ± 0.1</td>
<td>1.4</td>
</tr>
<tr>
<td>10-1330-1150-10-2</td>
<td>1330</td>
<td>1150</td>
<td>0.6 ± 0.1</td>
<td>0.5 ± 0.1</td>
<td>1.2</td>
</tr>
<tr>
<td>10-1367-1300-10-2</td>
<td>1367</td>
<td>1300</td>
<td>0.7 ± 0.1</td>
<td>0.7 ± 0.3</td>
<td>1.5</td>
</tr>
<tr>
<td>10-1400-1200-10-2</td>
<td>1400</td>
<td>1200</td>
<td>1.4 ± 0.1</td>
<td>0.8 ± 0.2</td>
<td>2.4</td>
</tr>
<tr>
<td>10-1450-1400-10-2</td>
<td>1450</td>
<td>1400</td>
<td>1.4 ± 0.2</td>
<td>0.8 ± 0.2</td>
<td>2.2</td>
</tr>
<tr>
<td>10-1500-1300-10-2</td>
<td>1500</td>
<td>1300</td>
<td>2.8 ± 1.9</td>
<td>0.8 ± 0.4</td>
<td>2.7</td>
</tr>
<tr>
<td>10-1600-1150-10-2</td>
<td>1600</td>
<td>1150</td>
<td>9.6 ± 1.6</td>
<td>1.4 ± 0.6</td>
<td>3.4</td>
</tr>
</tbody>
</table>

These data show an increasing grain and pore size with increasing temperature \( T_1 \) of the two-step sintering profile, suggesting that the final grain size is dependent on the peak temperature \( T_1 \). In order to investigate this further, the section A part of the final schedules 10-1450-1400-10-2 and 10-1600-1150-10-2 was investigated separately.

A significant amount of grain growth was observed on the surface of these samples. This type of grain growth was present in both sections A and A + B of the sintering profile, as shown in Figure 5.9.
Figure 5.9: Scanning electron micrographs of the surfaces of two-step sintered samples
a) section A: 1600°C, no dwell and b) section A + B: 1600°C peak, 1150°C dwell for 10 hours.

The sample sintered using section A + B of the two-step sintering profile represents the largest differential between $T_1$ and $T_2$, 1600 and 1150°C, respectively. Results of the microstructural examination of section A and the complete sintering profile, sections A + B, are presented in Table 5.9.

Table 5.9: Microstructural data for section A and sections A + B of a two-step sintering schedule with a peak temperature of 1600°C. The errors represent one standard deviation from the mean

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Sintered layer thickness (µm)</th>
<th>Relative density</th>
<th>Mean grain size (µm)</th>
<th>Mean pore size (µm)</th>
<th>Pore size range (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-1600-0-C</td>
<td>7.6 ± 0.7</td>
<td>0.98</td>
<td>8.8 ± 1.5</td>
<td>2.4 ± 1.4</td>
<td>5.5</td>
</tr>
<tr>
<td>10-1600-1150-10-2</td>
<td>7.4 ± 0.4</td>
<td>0.97</td>
<td>9.6 ± 1.6</td>
<td>1.4 ± 0.6</td>
<td>3.4</td>
</tr>
</tbody>
</table>

These data show that the sintered layer thickness and relative density are not statistically different. The sample batch sintered with the addition of section B, the 10 hour dwell at 1150°C, results in a slight increase in grain size and reduction in pore size. However, as the relative density value of 0.98 is achieved without section B this would suggest that the 1150°C isothermal hold is unnecessary at this stage. If the majority of the final microstructure evolves during the ramp to the peak temperature (section A) then section B at 1150°C is acting purely as a coarsening stage. Coarsening tends to be performed at a lower
temperature hold prior to reaching the sintering temperature. Section B could be performed before section A effectively reversing the two-step sintering profile, as shown in Figure 5.10.

Figure 5.10: Schematic illustration of the two-step sintering profile in reverse. Section B, the lower temperature isothermal hold at $T_2$, comes before the peak temperature, $T_1$.

The two-step sintering profile is shown in reverse with the initial part of the profile being the lower temperature dwell, or extended coarsening step, and the second part being the ramp to the peak temperature with no dwell. The resulting microstructure parameters from the 'normal' two-step sintering profile, section A + B, are compared with the 'reverse' two-step sintering profile, 10-1150-10-1600-2, in Table 5.10.
Table 5.10: Microstructural data for 'normal' two-step and 'reverse' two-step sintering schedules with a peak temperature of 1600°C. The errors represent one standard deviation from the mean.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Sintered layer thickness (µm)</th>
<th>Relative density</th>
<th>Mean grain size (µm)</th>
<th>Mean pore size (µm)</th>
<th>Pore size range (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-1600-0-C</td>
<td>7.6 ± 0.7</td>
<td>0.98</td>
<td>8.8 ± 1.5</td>
<td>2.4 ± 1.4</td>
<td>5.5</td>
</tr>
<tr>
<td>10-1600-1150-10-2</td>
<td>7.4 ± 0.4</td>
<td>0.97</td>
<td>9.6 ± 1.6</td>
<td>1.4 ± 0.6</td>
<td>3.4</td>
</tr>
<tr>
<td>10-1150-10-1600-2</td>
<td>7.9 ± 0.6</td>
<td>0.98</td>
<td>8.9 ± 1.8</td>
<td>1.1 ± 0.2</td>
<td>1.5</td>
</tr>
</tbody>
</table>

These data show that the majority of the microstructural development occurs in section A of the two-step sintering profile as shown in the sample heated to 1600°C without an isothermal hold (10-1600-0-C). The addition of section B reduces the pore size and also reduces the pore size range from 5.5 µm (10-1600-0-C) to 3.4 µm (10-1600-1150-10-2) and 1.5 µm (10-1150-1600-2) for the 'normal' and 'reverse' two-step profiles, respectively. A typical example of the surface grain structure is shown in Figure 5.11.

Figure 5.11: Scanning electron micrograph of the surface of a sample sintered using the 'reverse' two-step sintering profile, 10-1150-10-1600-2. The surface grain shape is similar to that seen for the 'normal' two-step sample 10-1600-1150-10-2.
Chapter 5: Non-conventional sintering profiles

The manipulation of the profile from conventional sintering to two-step sintering changes the size distribution of pores within the thick-film. The coarsening study has indicated that the mean pore size does not adequately reflect the effect of the modification of the sintering profile. Pore size range, the difference between the largest and smallest values, appears a more appropriate parameter to represent the effect of these modifications on the porosity. Section A has a pore size range of 5.5 μm compared with a range of 3.4 μm and 1.5 μm for the 'normal' and 'reverse' two-step sintering profiles, respectively. The pore size distribution resulting from sintering samples using section A, 'normal' and 'reverse' two-step sintering schemes are shown in Figure 5.12.

Figure 5.12: The pore size distribution for samples sintered using three different heating profiles: sintered to 1600°C with no dwell (10-1600-0-C); 'normal' two-step sintering profile with peak and dwell temperatures of 1600°C and 1150°C, respectively and an isothermal hold of 10 hours (10-1600-1150-10-2); and 'reverse' two-step sintering with dwell and peak temperatures of 1150°C and 1600°C, respectively (10-1150-10-1600-2).

The pore size range associated with section A shows a broad pore size range (black squares). This pore size distribution narrows for samples sintered using 'normal' two-step sintering (blue diamonds). The pore size distribution sharpens further with coarsening (red circles) at 1150°C for samples sintered using the 'reverse' two-step sintering profile.
Chapter 5: Non-conventional sintering profiles

Wolff et al., (2003) used sub-micrometre powders for two-step sintering of YSZ, although this was conducted on unconstrained pressed pellets. A density of 0.96 was achieved using the sintering scheme, 10-1600-1150-10-2. In this study a slightly higher density of 0.98 was achieved for section A (10-1600-0-C), without section B, which would suggest that in this particular example the addition of the isothermal hold does not influence the relative density in constrained YSZ layers.

The two-step sintering profile with the smallest change between T1 and T2 is 10-1450-1400-10-C. Section A of this profile results in a relative density of 0.90 compared with 0.91 for the sections A + B. The mean grain size increases from 0.8 ± 0.1 μm to 1.4 ± 0.2 μm with the addition of section B. However, taking section B in isolation results in a relative density of 0.96 and a mean grain size of the order of 14 ± 3 μm. This indicates that section B will reach a high density but this is associated with grain growth. The combination of sections A and B suppresses the grain growth but does not bring the sample to full density.

The two-step sintering profile 10-1600-1150-10-2 put forward by Wolff et al., (2003) cannot suppress grain growth as full density is reached at T1 (section A). There is no discernable change in the sintered layer thickness, relative density or grain size for samples sintered using section A, 'normal' two-step or 'reverse' two-step sintering profiles. The sintering profile 10-1600-1150-10-2 taken from the literature results in the largest mean grain size for the two-step sintering profiles observed in this study. However, the additional thermal treatment does reduce the pore size range, which may prove beneficial in some application areas (Lin et al., 1997). The application of two-step sintering using either the 10-1600-1150-10-2 or 10-1450-1400-10-2 profile provides either full density with grain growth or suppression of grain growth without full density being reached. This indicates that these profiles would be outside the 'kinetic window', as described by Wang et al., (2006b), for successful two-step sintering when applied to YSZ thick-films (outlined in Chapter 3).

5.3.3 Three-step profiles

Sintering of YSZ has been investigated using either conventional sintering or two-step sintering profiles. These profiles have shown that by changing the heating rate, sintering temperature and sintering time the final microstructure can be changed. The aim of the sintering process is to achieve high density and limit grain growth. The addition of a coarsening step in combination with two-step sintering is herein designated 'three-step' sintering and is applied to constrained YSZ thick-films.

Each profile was broken into three individual parts as shown in section 5.2.4. A coarsening step forms the first part of the profile, which takes advantage of the re-packing mechanism proposed by Chen and Chen (1996). The coarsening step was described in section 5.3.1 and
the intermediate temperature of 1100°C with a dwell time of 2 hours was selected for consistency. This coarsening step was added to the two-step sintering profiles taken from the literature. The sintered layer thicknesses, taken from SEM micrographs, and relative density measurements are given in Table 5.11.

Table 5.11: Sintered layer thickness and relative density for samples sintered using three-step sintering profiles (two-step sintering data add for comparison). The errors represent one standard deviation from the mean.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Temperature, $T_1$ (°C)</th>
<th>Temperature, $T_2$ (°C) (Dwell time at $T_2 = 10$ h)</th>
<th>Sintered layer thickness (µm)</th>
<th>Relative density</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-1330-1100-10-2</td>
<td>1330</td>
<td>1100</td>
<td>9.1 ± 1.1</td>
<td>0.80</td>
</tr>
<tr>
<td>10-1100-2-1330-1100-10-3</td>
<td>1330</td>
<td>1100</td>
<td>9.2 ± 1</td>
<td>0.80</td>
</tr>
<tr>
<td>10-1330-1150-10-2</td>
<td>1330</td>
<td>1150</td>
<td>10.2 ± 0.6</td>
<td>0.79</td>
</tr>
<tr>
<td>10-1100-2-1330-1150-10-3</td>
<td>1330</td>
<td>1150</td>
<td>10.1 ± 1.3</td>
<td>0.79</td>
</tr>
<tr>
<td>10-1367-1300-10-2</td>
<td>1367</td>
<td>1300</td>
<td>6.9 ± 0.4</td>
<td>0.87</td>
</tr>
<tr>
<td>10-1100-2-1367-1300-10-3</td>
<td>1367</td>
<td>1300</td>
<td>7.3 ± 0.5</td>
<td>0.89</td>
</tr>
<tr>
<td>10-1400-1200-10-2</td>
<td>1400</td>
<td>1200</td>
<td>8.3 ± 0.6</td>
<td>0.90</td>
</tr>
<tr>
<td>10-1100-2-1400-1200-10-3</td>
<td>1400</td>
<td>1200</td>
<td>7.4 ± 0.4</td>
<td>0.82</td>
</tr>
<tr>
<td>10-1450-1400-10-2</td>
<td>1450</td>
<td>1400</td>
<td>7.0 ± 0.3</td>
<td>0.91</td>
</tr>
<tr>
<td>10-1100-2-1450-1400-10-3</td>
<td>1450</td>
<td>1400</td>
<td>7.1 ± 0.3</td>
<td>0.93</td>
</tr>
<tr>
<td>10-1500-1300-10-2</td>
<td>1500</td>
<td>1300</td>
<td>7.2 ± 0.8</td>
<td>0.92</td>
</tr>
<tr>
<td>10-1100-2-1500-1300-10-3</td>
<td>1500</td>
<td>1300</td>
<td>7.0 ± 0.6</td>
<td>0.94</td>
</tr>
<tr>
<td>10-1600-1150-10-2</td>
<td>1600</td>
<td>1150</td>
<td>7.4 ± 0.4</td>
<td>0.97</td>
</tr>
<tr>
<td>10-1100-2-1600-1150-10-3</td>
<td>1600</td>
<td>1150</td>
<td>8.2 ± 0.3</td>
<td>0.98</td>
</tr>
</tbody>
</table>
The addition of an initial coarsening step does not change the sintered layer thickness. A range of 7.0 to 10.1 μm was measured and is comparable with the range of 6.9 to 10.2 μm measured for the samples sintered using the two-step process. This is consistent with the results from the reversed two-step sintering profile where adding a coarsening step of 10 hours showed no significant change in the layer thickness. Three-step sintering achieves the same or increased relative density when compared with two-step or conventional sintering. This was observed in all samples, excluding that sintered to a peak temperature of 1400°C. The grain size, pore size and pore size range for the three-step sintered samples are given in Table 5.12.

### Table 5.12: Mean grain size, mean pore size and pore size range values for samples sintered using three-step sintering profiles (two-step values for comparison).

The errors represent one standard deviation from the mean.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Temp., $T_1$ (°C)</th>
<th>Temp., $T_2$ (°C)</th>
<th>Mean grain size (μm)</th>
<th>Mean pore size (μm)</th>
<th>Pore size range (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-1330-1100-10-2</td>
<td>1330</td>
<td>1100</td>
<td>0.6 ± 0.2</td>
<td>0.5 ± 0.1</td>
<td>1.4</td>
</tr>
<tr>
<td>10-1100-2-1330-1100-10-3</td>
<td>1330</td>
<td>1100</td>
<td>0.6 ± 0.1</td>
<td>0.5 ± 0.2</td>
<td>1.8</td>
</tr>
<tr>
<td>10-1330-1150-10-2</td>
<td>1330</td>
<td>1150</td>
<td>0.6 ± 0.1</td>
<td>0.5 ± 0.1</td>
<td>1.2</td>
</tr>
<tr>
<td>10-1100-2-1330-1150-10-3</td>
<td>1330</td>
<td>1150</td>
<td>0.6 ± 0.1</td>
<td>0.5 ± 0.2</td>
<td>1.6</td>
</tr>
<tr>
<td>10-1367-1300-10-2</td>
<td>1367</td>
<td>1300</td>
<td>0.7 ± 0.1</td>
<td>0.5 ± 0.3</td>
<td>1.5</td>
</tr>
<tr>
<td>10-1100-2-1367-1300-10-3</td>
<td>1367</td>
<td>1300</td>
<td>0.8 ± 0.2</td>
<td>0.6 ± 0.2</td>
<td>1.5</td>
</tr>
<tr>
<td>10-1400-1200-10-2</td>
<td>1400</td>
<td>1200</td>
<td>1.4 ± 0.1</td>
<td>0.8 ± 0.2</td>
<td>2.4</td>
</tr>
<tr>
<td>10-1100-2-1400-1200-10-3</td>
<td>1400</td>
<td>1200</td>
<td>0.9 ± 0.1</td>
<td>0.8 ± 0.3</td>
<td>3.2</td>
</tr>
<tr>
<td>10-1450-1400-10-2</td>
<td>1450</td>
<td>1400</td>
<td>1.4 ± 0.2</td>
<td>0.8 ± 0.2</td>
<td>2.2</td>
</tr>
<tr>
<td>10-1100-2-1450-1400-10-3</td>
<td>1450</td>
<td>1400</td>
<td>1.5 ± 0.1</td>
<td>0.8 ± 0.3</td>
<td>2.0</td>
</tr>
<tr>
<td>10-1500-1300-10-2</td>
<td>1500</td>
<td>1300</td>
<td>2.8 ± 1.9</td>
<td>0.8 ± 0.4</td>
<td>2.7</td>
</tr>
<tr>
<td>10-1100-2-1500-1300-10-3</td>
<td>1500</td>
<td>1300</td>
<td>5.1 ± 1.2</td>
<td>1.0 ± 0.2</td>
<td>2.0</td>
</tr>
<tr>
<td>10-1600-1150-10-2</td>
<td>1600</td>
<td>1150</td>
<td>9.6 ± 1.6</td>
<td>1.4 ± 0.6</td>
<td>3.4</td>
</tr>
<tr>
<td>10-1100-2-1600-1150-10-3</td>
<td>1600</td>
<td>1150</td>
<td>8.6 ± 1.5</td>
<td>1.3 ± 0.9</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Chapter 5: Non-conventional sintering profiles

The three step sintering profile appears to produce similar microstructural trends as those observed in samples fired using a 'normal' two-step profile. In the case of the sample sintered at a peak temperature of 1500°C (10-1100-2-1500-1300-10-3) the grain size increased from 2.8 ± 1.9 µm (achieved by two-step sintering) to 5.1 ± 1.2 µm. The pore size remained constant at 0.8 ± 0.4 µm and 1.0 ± 0.2 µm for the two-step and three-step profiles, respectively. Pore size range was reduced from 2.7 (two-step) to 2 µm (three-step) while the number of pores per unit area (0.0025 m²) remained constant.

The pore size for the sintering profile 10-1600-1150-10-2 remained relatively constant at 1.4 ± 0.9 µm and 1.3 ± 0.6 µm for 'normal' two-step and three-step sintering profiles. However, the 'reverse' two-step sintering profile 10-1150-10-1600-2 showed a reduction in pore size to 1.1 ± 0.2 µm. These small changes in pore size are reflected in the reduction in pore size range from 3.4 to 2 and 1.5 µm for 'normal' two-step, three-step and 'reverse' two-step sintering respectively. However the population of pores is similar for 'normal' and 'reverse' two-step sintering profiles, while three-step has the lowest number of pores per unit area (0.0025 m²). In many of the sintering profiles taken from the literature the addition of a coarsening step has been shown to increase the relative density and this was reflected in the coarsened samples. The microstructural changes for three-step sintering indicate in general a small increase in relative density and a reduction in the pore size range, compared with two-step sintering at the higher temperatures.
5.3.4 Microstructural influence of non-conventional sintering

A grain size-density trajectory for the constrained sintering of micrometre-sized YSZ is shown in Figure 5.13. These data show the comparison between the three main types of sintering profile assessed within this study: 'normal' two-step, three-step and conventional sintering from the mesh study data in Chapter 4.

![Graph showing grain size as a function of relative density for conventional, two-step and three-step sintering profiles. The grain size increases rapidly as the YSZ thick-film approaches full density.](image)

Figure 5.13: Grain size as a function of relative density for conventional, two-step and three-step sintering profiles. The grain size increases rapidly as the YSZ thick-film approaches full density.

In an ideal grain size-density trajectory a ceramic would show no increase in grain size while reaching full density. Two-step sintering has been proposed as a sintering technique to limit grain size while allowing the sample to reach full density. Clearly, the suppression of grain growth with increased density has not been achieved for thick-films formed from sub-micrometre sized 3-mol% YSZ. Neither two-step nor three-step sintering profiles can be described as suppressing grain growth while attaining final density when compared with conventional sintering.
Chen (2000) described two-step sintering as exploiting the 'kinetic window' that separates grain-boundary diffusion and grain-boundary migration. The 'kinetic window' for each material is defined by the temperature $T_2$ as a function of grain size at temperature $T_1$. A 'kinetic window' has not been published for two-step sintering of constrained or unconstrained YSZ. Based on the concept proposed by Chen (2000) (see Chapter 3) an estimate of the position of the 'kinetic window' for 3-mol% YSZ has been proposed and this is given in Figure 5.14.

Figure 5.14: Temperature $T_2$ as a function of grain size for two-step sintering, conventional sintering, section A and section B of the dissected two-step sintering profile.

Section A data represent the thick-film samples sintered to temperature $T_1$ with no isothermal hold. The data from section A (red circles) combined with the conventional data with a 1 hour isothermal hold (blue diamonds) provide an initial grain size from which any increase can be considered as grain growth. None of these samples reached full density and thus are outside the 'kinetic window'. The only exception to this was sample (10-1600-0-C) (red circle) where a relative density of 0.96 was reached at $T_1$. Samples sintered to full density without grain growth would be located within the 'kinetic window' (two black lines) defined in Figure 5.14. Any samples located below the lower boundary of the kinetic window would show no grain
growth, however densification would be exhausted before full density was reached. An example of this type of behaviour is shown by the sample sintered at 1300°C (10-1367-1300-10-2) which has the same grain size as a conventional sintered sample and a density of 0.87 after a 10 hour isothermal hold at $T_2$. The sintering profile (10-1367-1300-10-2) was one that was proposed by Leite et al., (2003) for free-sintered YSZ. Leite et al., (2003) concluded that two-step sintering of the free-body could achieve full density although grain growth in the final stage of sintering could not be avoided. The grain size for nano-sized YSZ increased from 0.014 μm to 1.8 μm and 1.6 μm for conventional and two-step sintering, respectively.

Increasing $T_1$ to 1500°C, while $T_2$ remained constant, resulted in an increase in both grain size and relative density, although relative density of only 0.92 was achieved. It is assumed that under these conditions the densification process is exhausted. This condition has therefore been used to define the lower boundary of the ‘kinetic window’. The sample sintered with a $T_2$ of 1400°C showed an increase in grain size from 0.9 ± 0.1 to 1.4 ± 0.2 μm for conventional and two-step sintering, respectively. Section B sintered at 1400°C reached a relative density of 0.98 after 10 hours but also experienced grain growth bringing the final grain size to where the arrow points to the green cross. The upper boundary was defined from the sample (10-1450-1400-10-2) and it should correspond to full density being reached without grain growth occurring. This could potentially be achieved by an increase in $T_1$ from 1450 to 1500°C to increase the critical density value prior to densification at $T_2$.

It should be noted that the ‘kinetic window’ proposed here is very tentative. Further work is required to define the boundaries and this might mean that the window is impractically narrow such that it is not possible to sinter micrometre-sized YSZ to full density without grain growth. Leite et al., (2003) also concluded that while they could achieve full density in YSZ and CoO doped SnO$_2$ pressed powders, the final stage grain growth could not be avoided. Hence two-step sintering may not be valid for all systems.
5.4 Concluding remarks

This chapter has considered the modification of a conventional sintering profile with the addition of a coarsening step and the application of two-step sintering to constrained thick-films. These have been combined such that three distinct steps are present within the sintering profile, described as ‘three-step sintering’. The following outlines the conclusions taken from this chapter.

The addition of a coarsening step has shown a grain size increase associated with a slight increase in relative density. Although there was no significant change in the mean pore size, the coarsening step reduced the pore size range. Two-step sintering has the potential to achieve high density thick-films. This is shown by the dissection of the two-step sintering profile into sections A and B. Investigation of these two sections individually has shown that the sintered layer thickness, relative density and grain size remain relatively unchanged with the addition of section B to the sintering profile for ‘normal’ two-step sintering. The ‘reverse’ two-step sintering and addition of a coarsening step in three-step profiles yielded a similar result. Grain suppression was observed in sample 10-1367-1300-10-2 but full density was not achieved. This suggests that this profile would be below the lower boundary for the proposed ‘kinetic window’. The upper boundary would be below the datum point for sample 10-1450-1400-10-2 where grain growth was observed. This suggests that the application of two-step sintering to micrometre or sub-micrometre YSZ powders is difficult to justify without further work.

The pore size range was changed by the addition of section B, whether this was before or after the initial ramp to temperature $T_i$, in either two or three-step schemes. This is in agreement with the suggestion in Chen and Chen’s (1996) earlier work that a lower temperature isothermal hold results in re-packing of the microstructure thus homogenising the pore size. It can be concluded that these types of profile could be used in an application where changes to the pore size distribution are important.
Chapter 6: Influence of microstructure on gas permeance

6 Influence of microstructure on gas permeance

6.1 Introduction

The gas tightness or gas leakage of ceramic layers plays a critical role in the design and performance of SOFCs. Fuel and air supplied to the anode and cathode of the fuel cell must be separated by the electrolyte to restrict combustion. Combustion can lead to degradation in performance and failure of the fuel cell structure. Therefore the electrolyte should be fully dense to prevent gases such as hydrogen and oxygen from mixing. Ideally the amount of gas leaking across the electrolyte would be measured using normal operating conditions of hydrogen and air at elevated temperatures. However, typically gas testing is conducted at room temperature using inert gases such as argon or helium thus saving time and reducing health and safety implications. Gas testing of the sintered ceramic layers is discussed in this chapter and includes the assessment of gas flow rate with respect to the microstructure. The gas flow rate is compared with published data for permeability and gas permeance testing of solid oxide electrolytes. These techniques are used to designate a gas flow level below which the SOFC can operate electrochemically without combustion limitations. The chapter concludes by determining the most suitable sintering profile for 3-mol% YSZ screen-printed thick-films by relating gas testing data to the microstructure.

6.2 Gas flow through a sintered film

6.2.1 Permeability

Permeability testing is a well established technique for determining the diffusion of a gas or liquid through a barrier or membrane, such as a ceramic thick-film. This technique requires the diffusing medium to be the same as the environment around the thick-film. In the case of a fuel cell this would require hydrogen to be diffusing into a hydrogen atmosphere. There is a considerable amount of published data on porous solids but only a small number of publications describe permeability testing of ceramic thick or thin-films. Therefore it is important to establish if permeability can be related to microstructural parameters such as sintered layer thickness, relative density, grain size and pore size.

The assumption made for fuel cell operation is that hydrogen at temperatures above 700°C cannot pass through a fully dense YSZ thick-film. This has been demonstrated by permeability testing of YSZ single crystals, where hydrogen and helium were used as the test gases and were shown not to permeate through the specimen (Nigara et al., 2004). As neither hydrogen nor helium diffuses across a single crystal of YSZ, this provides confidence that a gas tight YSZ electrolyte thick-film is feasible.
Glass and Green (1999) suggested that permeability should provide a measure of how the flow path changes as a function of density. The flow path or tortuosity is a function of the distance a molecule must travel to get through a film, divided by the thickness of the body. Using the Carmen-Kozeny prediction for permeability they found that there was good agreement for samples with relative densities below 0.75. Above this density the difference between the predicted and measured permeability values increased steadily, up to a relative density of 0.88, at which point a dramatic deviation was attributed to the occurrence of closed porosity. They suggested that the Carmen-Kozeny approach would still be useful if the tortuosity could be predicted at these higher densities. However, pore microstructure information such as porosity, pore size and connectivity would be required to achieve more accurate predictions of tortuosity. This work was carried out using samples nominally 16 mm in diameter and 10 mm thick, whereas a thick-film, such as those used in SOFCs, would be much thinner, typically less than 0.1 mm (Glass and Green, 1999).

Young and Todd (2005) have modelled the process of gas flow in porous bodies with sample thicknesses of 3.8 to 4.5 mm. The work was based on the principle that the pore network is the gas flow path through the structure. The factors considered were the pore diameter, amount of pores and how tortuous the gas path is through the body. The cylindrical pore interpolation model (CPIM) proposed by Young and Todd (2005) predicts that gas diffusing across the body is dominated by pore diameter while porosity and tortuosity can be ignored.

It is also has been suggested by Larbot et al., (1989) that membrane permeability is a function of the pore diameter and the interaction between the gas or fluid and the membrane. Levanen and Mântylä (2002) showed that in 100 μm thick free sintered alumina films the pore size remained relatively constant at 80 nm with increasing sintering temperature. For constrained films the pore size increased to 190 nm as the sintering temperature was increased. Permeability values for the alumina films were quoted as nominally zero for the free sintered film and $10^{-18}$ m$^2$ for constrained films sintered at 1400°C. The value for the constrained film was greater than permeability values of $10^{-18}$ m$^2$ and $10^{-19}$ m$^2$ quoted by Glass and Green (1999) and Dolien and Barnett (2005), respectively.
6.2.2 Gas permeance

Gas permeance testing is different to permeability testing in that the test gas is different to the test environment. Again the number of publications referring to this type of testing for fuel cell applications is low. Levanen and Mântylâ (2002) showed that sintering of sub-micrometre alumina powders to form a laminate structure resulted in larger grain sizes, larger pore sizes and higher gas leakage rates. This increase in the gas leakage was attributed to constraint in the sintering of additional layers.

Park et al., (2004) have investigated the application of YSZ thin-films onto nano-porous substrates. Their constrained arrangement was similar to that of the IP-SOFC design, only on a nano-scale where film thickness was between 35 and 410 nm. A hydrogen permeance of $7 \times 10^{11}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ was achieved for the 35 nm thin-film. The hydrogen permeance increased for the 410 nm sample sintered using the same sintering profile. Park et al., (2005) estimated that the hydrogen permeance for a SOFC electrolyte used in an industrial application should be $\leq 5 \times 10^9$ mol m$^{-2}$ s$^{-1}$ Pa. Gaudon et al., (2005) gas tested micrometre-sized YSZ powder applied as 5, 15 and 20 µm thick-films to porous substrates. In helium permeance testing the lowest value was $10^{-5}$ mbar l s$^{-1}$ cm$^{-2}$. This value was achieved with the 5 µm film, which was the thinnest film studied. Gaudon et al., (2005) suggest that the value of $10^{-5}$ mbar l s$^{-1}$ cm$^{-2}$ is below the level suitable for use in an industrial application.

The IP-SOFC design has a gas flow specification based on the Roll-Royce sub-systems requirement document (SSRD) (Rolls-Royce Fuel Cell Systems, 2004). The gas flow target for losses across the YSZ electrolyte must be $\leq 3\%$ for a commercial product although there are some system stability gains to be made down to a value of 1% (Collins, 2006). The value quoted by Park et al., (2005) for a hydrogen permeance ($10^9$ mol m$^{-2}$ s$^{-1}$ Pa) equates to an SSRD gas flow target of 3%. Helium permeance quoted by Gaudon et al., (2005) ($10^5$ mbar l s$^{-1}$ cm$^{-2}$) is equivalent to the lower SSRD target of 1% for gas losses in the IP-SOFC.

* The units taken from Park et al., (2004, 2005) are quoted as shown in the literature and assumed to be (mol m$^{-2}$ s$^{-1}$ Pa) for all conversions from hydrogen permeance to helium permeance and helium gas flow rate.
6.3 Experimental procedure

6.3.1 Gas testing procedure

Typically hydrogen and air are used as the fuel and oxidant gases, respectively during the operation of the IP-SOFC. The hydrogen gas stream has a slightly higher inlet pressure so that any gas flow across the electrolyte is from the fuel to the air side. This results in combustion on the air side of the cell and potentially reduces the cell performance. Simulating this process on individual parts of a fuel cell requires complex and potentially hazardous experimental equipment. A simpler approach is to use a room temperature gas testing method in which helium is the test gas. This allows a gas similar in molecular size to hydrogen to be used without the risk of combustion and it also removes the need to heat each sample to temperature. The molecular diameters for helium and hydrogen are $0.27 \times 10^{-10}$ and $0.23 \times 10^{-10}$ Å, respectively (Lide, 1994).

The room temperature method essentially compares the inlet flow with the outlet flow resulting in a measured gas flow rate of the helium that is lost through the thick-film. The fired sample is sealed onto a stainless steel sample holder, as shown in Figure 6.1, using an adhesive sealant. The sealant is then dried for 30 minutes to allow it to set. Between three and five samples were measured for each sample batch and the flow rate reported was the mean value of each batch.

![Figure 6.1: Gas test sample and holder with 50 x 50 mm sample sealed into position.](image)

The gas test uses a 2 litre min$^{-1}$ (hydrogen) mass flow controller supplied by Bronkhurst (High-tech, EL-flow) on the sample inlet and mass flow meter on the exhaust. Each sample was analysed using 100% helium supplied by BOC (Derby, UK). Each sample was analysed using an inlet flow rate of 1 litre min$^{-1}$ and the total outlet flow rate was measured by the mass flow meter with the exhaust gas analysed using a mass spectrometer (Minilab LM80, Spectra Products, Massachusetts, US). The mass spectrometer was used to detect nitrogen levels in the inlet and exhaust gas. Nitrogen levels in the air and helium gas were measured before and after each test to provide a baseline for the system. Increasing gas pressure was achieved by adjusting a needle valve and pressure was measured on the inlet and outlet gas.
stream using a pressure meter supplied by Digitron PM-20, (Torquay, UK), as shown in Figure 6.2.

![Image of gas testing apparatus](image_url)

Figure 6.2: Gas testing apparatus for measurement of helium flow rate through a sintered sample a) gas testing arrangement and b) mass spectrometer.

By measuring the nitrogen level in the sample stream relative to that present in the air, the amount of helium lost out through the sample was established. Then the flow in the outlet or exhaust is relative to the flow controller reading at the inlet as a function of the flow meter reading at the outlet. Therefore the helium flow rate in ml min$^{-1}$ out of the sample, $\text{Flow}_{\text{He}_{\text{out}}}$, is defined as:

$$\text{Flow}_{\text{He}_{\text{out}}} = \text{Flow}_{\text{exhaust}} \cdot H_{\text{He}_{\text{out}}}$$  \hspace{2cm} (6.1)

where $\text{Flow}_{\text{exhaust}}$ is the flow in the exhaust as a ratio of the inlet and outlet flow meter readings, and $H_{\text{He}_{\text{out}}}$ is the fraction of helium present (i.e. total minus the air in the stream). This equation is derived in appendix B.

The gas flow rate was plotted against pressure. The pressure of the system was increased incrementally from the initial pressure, typically 20 mbar, to a maximum pressure of 35 mbar, using the back pressure needle valve. It has been established that variation in gas testing values can be dependent on the fabrication process of both the printed layer and the substrate (Lapena-Rey et al., 2001). Gas testing was conducted on each sample to ensure that the inherent variability of the layer fabrication and substrate was reduced or at least reflected in the errors for each batch. Initial testing was conducted on samples with a single print-dry application applied to the substrate. It was evident that this single print-dry application was insufficient to get reliable gas flow data. The observed degree of inconsistency in the data was attributed to defects arising from airborne contamination within the fabrication area. This was subsequently reduced by the installation of a clean room facility during the period of this study.
Helium flow rates were measured for samples sintered using conventional, coarsening, two-step and three-step sintering profiles and were compared with control samples. A control sample batch was fabricated and measured with each experimental sample batch and compared with previous control samples. An example of the variability between individual control samples is shown in Figure 6.3.

![Figure 6.3](image)

Figure 6.3: Helium flow rate as a function of pressure showing the variation between individual control samples within a batch of three sintered YSZ thick-films. The pressure indicated at 30 mbar is equal to the differential pressure across the IP-SOFC during operation.

These data show a variation in helium flow rate of nominally ± 5 ml min⁻¹ between control samples A, B and C. A steep gradient and high intercept are indicative of a microstructure with large pores, holes or cracks. A small gradient, as shown in Figure 6.3, is typically associated with an open porous structure (Lapena-Rey et al., 2001). It is important to note that even in a microstructure with small defects or pores, helium flow may still occur through macro pores as well as along grain boundaries. However, the rate of diffusion through pores is expected to be much slower than that of bulk flow expected through pinholes or cracks (Lapena-Rey et al., 2001).
6.3.2 Microstructural characterisation

It has been shown that as grain size increases relative to film thickness, pore size also increases. Gorman and Anderson (2002) fabricated membranes with a thickness of 2 to 3 \( \mu \)m and a grain size ranging from 0.05 to 0.2 \( \mu \)m. The pore size increased from 3 to 80 nm with sintering temperature. This investigation did not include any gas testing but did indicate that pore size can be influenced by the ratio between grain size and layer thickness.

Grain size measurement and sintered layer thickness measurement were outlined previously (see sections 4.2.11.1 and 4.2.11.2). A potential relationship between gas flow rate and microstructure was assessed by using the variables of grain size and sintered layer thickness. The grain size was measured using the linear intercept method and the sintered layer thickness was measured from SEM micrographs. Initially, the surface micrographs were used to measure the grain size across the sintered layer thickness. Subsequently, polished cross-sections were used to assess the relationship between the surface and cross-sectional grain size. The samples were chemically etched in 40 vol.% hydrofluoric acid for 15 minutes to reveal the grain structure. This analysis showed that samples fired using short dwell times had fine grain structures. Increasing the time of the isothermal hold from 1 to 10 hours increased the grain size by more than ten times. In some cases the grain size was observed to approach the layer thickness value and in some samples the sintered layer was only one grain thick. The etched cross-section shown in Figure 6.4 shows the grain structure for the coarsened sample, 10-1100-2-1400-10-1, where the grain size is equal to or greater than the sintered thickness. Typical measurement errors between the mean surface and etched cross-sectional grain sizes were small (< 5%). As the grain size approached the layer thickness the errors increased to nominally 10% with the cross-sectional grain size being the smaller of the two values.
Chapter 6: Influence of microstructure on gas permeance

Figure 6.4: Cross-sectional reflected light micrograph of a sintered layer chemically etched for 15 minutes in 40 vol.% hydrofluoric acid. The image shows that the surface grain size is greater than the sintered layer thickness and potential gas flow paths can be observed.

This grain structure shows that the grain size has exceeded the sintered layer thickness and potential gas flow paths have been revealed. These paths, through pores and along grain boundaries, can be seen along each side of the top central grain in Figure 6.4. The flow path would be extended if the layer was more than one grain thick. This could in turn reduce the rate of gas flow rate across the sintered layer. Gas flow rate could also be reduced if the pore or grain boundaries were not aligned but offset, like bricks in a wall. The ratio, $z$, between the mean grain size and the sintered layer thickness can be expressed as:

$$
z = \frac{\text{mean grain size}}{\text{sintered layer thickness}} \quad (6.2)
$$

The relationship between mean grain size and the sintered layer thickness can be represented schematically as shown in Figure 6.5.
Chapter 6: Influence of microstructure on gas permeance

When the mean grain size is only one tenth of the sintered layer then the factor $z$ will be equal to 0.1. However, during densification the mean grain size increases and the layer thickness reduces until $z$ becomes equal to 1. As further thermal processing occurs the surface grain size continues to increase. When the surface grain size becomes greater than the thickness of the sintered layer, $z$ becomes greater than 1.

6.4 Results and discussion

6.4.1 Conventional sintering

6.4.1.1 Effect of deposited thickness on gas flow rate

The screen-printing process can be used to produce films of increasing sintered thickness through the use of different mesh sizes, as previously described in Chapter 4. The effect of pressure on helium flow rate was measured for each of these samples. Samples fabricated using the 325 mesh (black squares) had the largest pressure dependence. This sample also had the lowest sintered thickness. Pressure had the least effect on the samples printed using the 165 mesh size (red circles), as shown in Figure 6.6.
Chapter 6: Influence of microstructure on gas permeance

(a) 

(b)
Chapter 6: Influence of microstructure on gas permeance

c

Figure 6.6: Gas flow rate as a function of pressure a) sintered thickness of 2, 5, 6.6, 8.6 and 10.7 µm were achieved using two print-dry applications through the 325, 200, 165, 105 and 80 mesh sizes, respectively, b) sintered thickness of 3.1, 6.2, 9.3, 12.2 and 17.3 µm were achieved using three print-dry applications through the 325, 200, 165, 105 and 80 mesh sizes, respectively and c) sintered thickness of 4.1, 7.1, 11.7, 17.4 and 23.1 µm were achieved using four print-dry applications through the 325, 200, 165, 105 and 80 mesh sizes, respectively. Error bars represent one standard deviation from the mean.

For two print-dry applications, a sintered layer thickness of 5 µm (blue diamond), achieved with a 200 mesh size shows the lowest average gas flow rate, as shown in Figure 6.4a. The sintered thickness of 6.6 µm (red circle), achieved with the 165 mesh size, indicates that at a pressure of 30 mbar a gas flow rate similar to the sintered thickness of 5 µm is achievable, however the error bars suggest that the 165 mesh size produces a greater spread of results.

For three print-dry applications, the 200 and 165 mesh size also give the lowest gas flow rate corresponding to sintered thicknesses of 6.2 µm (blue diamond) and 9.3 µm (red circle), respectively as shown in Figure 6.6b. The samples with three print-dry applications result in a reduction in gas flow rate for the 325, 200, 165 and 105 mesh sizes compared with samples
with two print-dry applications. The 80 mesh size with a sintered thickness of 17.3 μm remains relatively unchanged with only a small increase in gas flow rate with increasing pressure.

In Figure 6.6c the 325 mesh size with a sintered thickness of 4.1 μm shows a reduction in gas flow rate, while the for the 80 mesh size (23.1 μm sintered thickness) increases compared with the 17.3 μm thick sintered layer achieved with three-print-dry applications. The lowest gas flow rates were measured for a sintered thickness of 7.1 μm and 11.7 μm for the 200 and 165 mesh sizes, respectively. It is difficult to separate the gas flow rate of mesh sizes 200 and 165 as well as the 105 and 80 mesh sizes as the error bars are separated by less than one standard deviation.

The dependence of gas flow rate on layer thickness is shown more clearly in Figure 6.7. The values shown in Figure 6.7 are plotted for a fixed pressure of 30 mbar.

![Figure 6.7: Sintered layer thickness and helium flow rate as a function of deposition thickness. As deposition thickness increases the resulting sintered thickness also increases. The increasing sintered thickness results in a reduction in helium flow rate. Gas flow rate values are quoted at a pressure of 30 mbar. Error bars represent one standard deviation from the mean.](image-url)
A 325 mesh size with three print-dry deposits results in a helium flow rate of 311 ± 8 ml min⁻¹ and this was reduced to 151 ± 7 ml min⁻¹ with a 200 mesh size with four print-dry deposits. The helium flow rate levels out for a deposition thickness between 130 and 194 µm for a 200 and 165 mesh size, respectively. This range represents samples with three (green cross and black square) and four (green triangle and black diamond) print-dry applications. The 105 and 80 mesh sizes with two print-dry applications result in an increased helium flow rate of 196 ± 8 and 192 ± 14 ml min⁻¹, respectively. In Chapter 4 it was indicated that with a similar total deposited thickness, a laminate of several thin layers resulted in a thinner sintered thickness compared a laminate of fewer thick layers. Comparing this with the effect on helium flow rate suggests that the intermediate mesh sizes, 200 and 165, provide lower helium flow rates when compared with 325, 105 or 80 mesh sizes. In combination these results indicate that a greater number of thin layers deposited through a 200 mesh size results in a thinner sintered layer and lower helium flow rate compared with fewer thick deposits through a 105 mesh size.

6.4.1.2 Relationship between microstructural parameters and gas flow rate for conventionally sintered samples

The characteristic microstructural features such as grain boundaries and pores will influence the path gas molecules take when flowing through a ceramic microstructure. The study conducted using different mesh sizes and number of print-dry applications provided the opportunity to study the microstructure relative to changes in thickness while the sintering profile remained constant. Any changes in the grain size to sintered layer thickness factor, z, were therefore only due to the application of additional thickness and were independent of sintering temperature and time. The effects on z of deposition thickness achieved with different mesh sizes and number of print-dry applications are shown in Figure 6.8.
Chapter 6: Influence of microstructure on gas permeance

Figure 6.8: Deposited thickness (wet ink) as a function of grain size to sintered layer thickness factor, $z$. Increasing the number of print-dry applications increases the thickness of ink deposited and the grain size to sintered layer thickness factor reduces.

The grain size to sintered thickness factor, $z$, reduces as the deposited thickness is increased. As the number of print-dry applications is increased $z$ reduces accordingly. This shows that the reduction is greatest between the 325, 200 and 165 mesh sizes as grain size to sintered thickness reduces most when the deposited thickness increases from 46 to 194 µm of deposited thickness. Above 194 µm the deposited thickness does not affect $z$. Deposited thickness is similar for two (97 µm) and four print-dry applications (92 µm). The variation in $z$ indicates that a laminate of two print-dry applications sinter differently when compared with a laminate of four print-dry applications. This change in the structure from two to four layers may be a function of how the particles are arranged within the printed layer and the subsequent release of organics during drying. The effect of gas flow rate was then plotted as a function of $z$ for two, three and four print-dry applications and the results are shown in Figure 6.9.
Figure 6.9: Gas flow rate as a function of grain size to sintered layer thickness.

At a $z$ factor value between approximately 0.1 and 0.3 the gas flow rate is at a minimum. On either side of this value there is an increase in gas flow rate, providing evidence that too many or too few grains relative to the layer thickness results in an increase in gas flow rate. This indicates that the details of the microstructure may be more influential than the degree of densification. To investigate this possibility, $z$ was determined as a function of relative density as shown in Figure 6.10.
Chapter 6: Influence of microstructure on gas permeance

Figure 6.10: Grain size to sintered thickness, $z$, as a function of relative density. The grain size to sintered thickness ratio increases as the relative density increases. A boundary condition has been defined based on the lowest gas flow rates.

The $z$ factor increases with increasing relative density. The highest value for $z$ (black square), 1.7, is related to the highest relative density of 0.94 which was obtained from a sample formed from two print-dry applications. This value can be compared with a sample formed from three print-dry applications which has the same density but for which $z$ is 0.7. These $z$ factors of 1.7 and 0.7 correspond to gas leakage rates of $364 \pm 6 \text{ ml min}^{-1}$ and $311 \pm 8 \text{ ml min}^{-1}$ for two and three print-dry applications using a 325 mesh size, respectively.

Samples sintered to a relative density below 0.94 have a lower $z$ factor and gas flow rate. The lowest gas flow rates were achieved with densities between 0.86 and 0.91. This range of relative density represented a gas flow rate range at 30 mbar of between $151 \pm 7 \text{ ml min}^{-1}$ and $155 \pm 7 \text{ ml min}^{-1}$. The gas flow rate data have been used to define boundary conditions from which the optimum relative density and $z$ values can be defined.
6.4.2 Non-conventional sintered samples

6.4.2.1 Effect of coarsening on gas flow rate

Establishing a gas flow rate measurement that distinguishes between the microstructures of different sintered layers provides a baseline measurement from which to assess modified sintering profiles. Non-conventional sintering profiles, as described here, are any profiles that deviate from the traditional constant heating to a temperature with an isothermal hold and then cooling to room temperature. Each sample was fabricated using a 165 mesh size with 3 print-dry applications prior to the sintering stage. The effects of coarsening, two-step and three-step sintering were compared with control samples prepared as part of each sample batch.

Coarsened samples were gas tested under the same conditions as the samples in the deposition study. The effect of a coarsening stage in the sintering profile on gas flow rate is shown in Figure 6.11.

![Helium flow rate as a function of pressure for conventionally sintered and coarsened thick-films.](image)

Figure 6.11: Helium flow rate as a function of pressure for conventionally sintered and coarsened thick-films. The addition of a coarsening step to the sintering profile results in an increase in the gas flow rate across the film. Error bars represent one standard deviation from the mean.
Chapter 6: Influence of microstructure on gas permeance

The coarsened sample has a gas flow rate, at 30 mbar pressure, of $142 \pm 11 \text{ ml min}^{-1}$ compared with $132 \pm 9 \text{ ml min}^{-1}$ for the conventional sample. The variations in data across the sample batches make it difficult to draw firm conclusions on the effect of a coarsening step in the sintering profile on gas flow rate, since the mean values are within one standard deviation of each other. However, it is possible that the addition of an isothermal hold for two hours results in a small increase in gas flow rate.

6.4.2.2 Effect of two-step sintering on Gas flow rate

Gas flow rates for the two-step sintered samples were measured and compared with gas flow rates for conventionally sintered control samples as shown in Figure 6.12.

Figure 6.12: Helium flow rate as a function of pressure through thick-film layers sintered using a range of two-step sintering profiles. The lowest mean gas flow rate was obtained for samples sintered with peak and dwell temperatures of 1500 and 1300°C, respectively. Error bars represent one standard deviation from the mean.

The conventionally sintered sample has a higher gas flow rate than three non-conventionally sintered samples, 10-1500-1300-10-2, 10-1367-1300-10-2 and 10-1600-1150-10-2 but the variations within a batch makes it difficult to make clear comparisons between samples. The
maximum gas flow rate of \(311 \pm 39 \text{ ml min}^{-1}\) at 30 mbar was shown by sample 10-1400-1200-10-2. Any isothermal hold below 1300°C gave a gas flow rate greater than that of the conventional sample sintered to 1450°C for 1 hour. The lowest gas flow rate of \(115 \pm 8 \text{ ml min}^{-1}\) at 30 mbar was shown by sample 10-1500-1300-10-2.

### 6.4.2.3 Effect of three-step sintering on gas flow rate

The coarsening and two-step sintering profiles were combined and designated as 'three-step' sintering. This was designed to combine the low temperature homogenisation of the particle network provided by coarsening with the grain growth suppression from two-step sintering. Each sample batch was gas tested under the same conditions and compared with the control samples. The gas flow rate results are shown in Figure 6.13.

![Figure 6.13: Helium flow rate as a function of pressure through thick-film layers sintered using three-step sintering profiles. Error bars represent one standard deviation from the mean.](image)

The conventionally sintered sample has a higher gas flow rate than three samples: 10-1100-2-1600-1150-10-3, 10-1100-2-1500-1300-10-3 and 10-1100-2-1367-1300-10-3. The gas flow rate for sample 10-1100-2-1400-1200-10-3 was \(410 \pm 22 \text{ ml min}^{-1}\) at 30 mbar which represents an increase of \(~100 \text{ ml min}^{-1}\) when compared with the two-step equivalent.
sample. The minimum gas flow rate for three-step sintering is $111 \pm 5 \text{ ml min}^{-1}$ at 30 mbar for sample 10-1100-2-1367-1300-10-3. This represents a lower mean gas flow rate relative to the two-step equivalent sample at $129 \pm 32 \text{ ml min}^{-1}$. Although the mean gas flow rate values are lower in three-step samples the error bars overlap with the two-step equivalent samples.

6.4.3 Relationship between gas flow rate and microstructural parameters for non-conventionally sintered samples

A relationship between the ratio of grain size to sintered layer thickness, $z$, and gas flow rate has been proposed for conventional sintering (see section 6.3.2). For conventionally sintered samples, an optimum value for $z$ of 0.1 - 0.3 resulted in the lowest values for gas flow rate. The same ratio has been determined from the microstructures of non-conventionally sintered samples. Values of gas flow rate as a function of $z$ are given in Figure 6.14.

![Figure 6.14](image)

Figure 6.14: Helium flow rate at a pressure of 30 mbar as a function of the ratio of grain size to sintered layer thickness, $z$.

The lowest gas flow rates for two-step and three-step samples correspond to $z$ factors of 0.4 and 0.1, respectively. This is similar to the range calculated for the conventionally sintered samples from the deposition study, (red circles), where $z$ ranged from 0.1 to 0.3.
Chapter 6: Influence of microstructure on gas permeance

However, many of the non-conventionally sintered samples with z values in this range have much higher gas flow rates. This indicates that to achieve lower gas flow rates in non-conventionally sintered samples the z range shifts to higher values i.e. from 0.3 to 0.7.

In general terms, the sintering profiles for conventional and non-conventional sintering result in samples with similar values for z. Where gas flow rate through the non-conventional samples differ, this could imply a higher dependency on relative density, compared with the conventionally sintered films. The relationship between relative density and z for two-step and three-step samples is shown in Figure 6.15.

Figure 6.15: Grain size to sintered thickness ratio as a function of relative density. An increase in the grain size to sintered thickness ratio, z, is associated with an increase in relative density.

The z factor increases with increasing relative density. This trend is in good agreement with conventionally sintered samples. Three-step sintering shows that a slightly higher relative density can be reached with a constant z factor, than for two-step. For example, sample 10-1367-1300-10-2 has a relative density of 0.87 with z = 0.1 and this increases to 0.89 (z = 0.1) for the equivalent three-step sample (10-1100-2-1367-1300-10-3).
Chapter 6: Influence of microstructure on gas permeance

Taking the data obtained from samples 10-1500-1300-10-2, 10-1100-2-1367-1300-10-3 and 10-1100-2-1500-1300-10-3 enables boundary conditions associated with the lowest gas flow rates to be determined. The boundaries are at relative densities of 0.89 and 0.94 and z factors of 0.1 and 0.7. These boundary conditions represent a shift to higher values of relative density and z factor when compared with the boundary region defined for conventional sintering.

A number of samples located within the boundary conditions have higher gas flow rates than the values of the samples used to define it. These are the conventional sample A-165-3-3-1450-1, the two-step samples 10-1400-1200-10-2 and 10-1450-1400-10-2, and the three-step sample 10-1100-2-1450-1400-10-3. This suggests that there is at least one other factor which needs to be considered. Porosity was investigated in terms of gas flow rate.

The relationship between gas flow rate and pore size range for two-step and three-step samples are shown in Figure 6.16 with respect to the gas flow rate at a pressure of 30 mbar.

![Figure 6.16: Helium flow rate as a function of pore size range.](image)

The pore size range is the difference between the largest and smallest pore size as measured from the surface micrographs of the samples. The conventionally sintered samples have a pore size range between 2.6 \( \mu \text{m} \) and 4.6 \( \mu \text{m} \). Two-step samples have a pore size range
between 1.2 µm and 3.4 µm and the range lies between 1.5 µm and 3.2 µm for the three-step samples. Thus, a narrowing of the pore size range is seen as additional steps are added to the sintering profile. However, the sample with the lowest gas flow rate does not have the smallest pore size range. Pore size range does not determine gas flow rate in isolation. If the pore size range changes due to variation of the sintering profile then this may also affect the number of surface pores. The number of surface pores relative to the grain size to thickness factor, z, is shown in Figure 6.17.

![Figure 6.17](image)

Figure 6.17: Surface pore population per unit area as a function of grain size to sintered thickness factor, z. The number of pores counted has been normalised for an area of 0.0025 m² based on screen-printed samples of dimension 50 x 50 mm.

The conventional sample (red circle) has the highest number of pores per unit area of all the samples within the boundary shown in Figure 6.15. Samples 10-1400-1200-10-2, 10-1450-1400-10-2, and 10-1100-2-1450-1400-10-3 have higher surface pore populations when compared with samples 10-1500-1300-10-2, 10-1100-2-1367-1300-10-3 and 10-1100-2-1500-1300-10-3. These three samples have a similar number of pores within the surface and the values are up to an order of magnitude lower than for conventional sintering. This would indicate that the z factor, pore size range, relative density and number of surface pores are interrelated. Therefore the gas flow path through the microstructure may be a
function of all of these parameters. These parameters are shown in Table 6.1 with each value assessed by boundary conditions for low gas flow rates and classified as either a pass (green numbers) or fail (red numbers). Subsequently the only samples which have a pass for every parameter are samples: 10-1100-2-1367-1300-10-3, 10-1500-1300-10-2, and 10-1100-2-1500-1300-10-3.

Table 6.1: Boundary conditions applied to z factor, pore size range, relative density and number of surface pores per unit area classified as pass (green) or fail (red). The errors represent one standard deviation from the mean.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>z, grain size to sintered thickness (µm/µm)</th>
<th>Pore size range (µm)</th>
<th>Relative density</th>
<th>Number of surface pores per unit area (x 10^6)</th>
<th>Helium flow rate (ml min^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-1100-2-1367-1300-10-3</td>
<td>0.1</td>
<td>1.5</td>
<td>0.89</td>
<td>0.9</td>
<td>111 ± 5</td>
</tr>
<tr>
<td>10-1500-1300-10-2</td>
<td>0.4</td>
<td>2.7</td>
<td>0.92</td>
<td>1.9</td>
<td>115 ± 8</td>
</tr>
<tr>
<td>10-1100-2-1500-1300-10-3</td>
<td>0.7</td>
<td>2.0</td>
<td>0.94</td>
<td>2.3</td>
<td>117 ± 13</td>
</tr>
<tr>
<td>10-1367-1300-10-2</td>
<td>0.1</td>
<td>1.5</td>
<td>0.87</td>
<td>5.8</td>
<td>129 ± 32</td>
</tr>
<tr>
<td>10-1100-2-1600-1150-10-3</td>
<td>1.0</td>
<td>2.0</td>
<td>0.98</td>
<td>0.1</td>
<td>140 ± 2</td>
</tr>
<tr>
<td>10-1600-1150-10-2</td>
<td>1.3</td>
<td>3.4</td>
<td>0.97</td>
<td>0.4</td>
<td>145 ± 10</td>
</tr>
<tr>
<td>A-165-3-3-1450-1</td>
<td>0.1</td>
<td>2.6</td>
<td>0.89</td>
<td>13.8</td>
<td>155 ± 24</td>
</tr>
<tr>
<td>A-200-3-3-1450-1</td>
<td>0.3</td>
<td>3.8</td>
<td>0.90</td>
<td>10.3</td>
<td>155 ± 6</td>
</tr>
<tr>
<td>A-105-3-3-1450-1</td>
<td>0.1</td>
<td>4.1</td>
<td>0.84</td>
<td>14.1</td>
<td>169 ± 3</td>
</tr>
<tr>
<td>A-80-3-3-1450-1</td>
<td>&lt;0.1</td>
<td>4.1</td>
<td>0.83</td>
<td>12.0</td>
<td>199 ± 10</td>
</tr>
<tr>
<td>10-1450-1400-10-2</td>
<td>0.2</td>
<td>2.2</td>
<td>0.91</td>
<td>8.7</td>
<td>242 ± 4</td>
</tr>
<tr>
<td>10-1450-1400-10-2</td>
<td>0.2</td>
<td>2.2</td>
<td>0.91</td>
<td>8.7</td>
<td>242 ± 4</td>
</tr>
<tr>
<td>10-1100-2-1450-1400-10-3</td>
<td>0.2</td>
<td>2.0</td>
<td>0.93</td>
<td>6.3</td>
<td>244 ± 17</td>
</tr>
<tr>
<td>10-1330-1100-10-2</td>
<td>&lt;0.1</td>
<td>1.4</td>
<td>0.80</td>
<td>68.8</td>
<td>252 ± 9</td>
</tr>
<tr>
<td>10-1100-2-1330-1150-10-3</td>
<td>&lt;0.1</td>
<td>1.6</td>
<td>0.79</td>
<td>72.0</td>
<td>297 ± 33</td>
</tr>
<tr>
<td>10-1100-2-1330-1100-10-3</td>
<td>&lt;0.1</td>
<td>1.8</td>
<td>0.80</td>
<td>78.6</td>
<td>298 ± 26</td>
</tr>
<tr>
<td>A-325-3-3-1450-1</td>
<td>0.7</td>
<td>2.1</td>
<td>0.93</td>
<td>6.0</td>
<td>311 ± 8</td>
</tr>
<tr>
<td>10-1400-1200-10-2</td>
<td>0.2</td>
<td>2.4</td>
<td>0.90</td>
<td>10.2</td>
<td>311 ± 39</td>
</tr>
<tr>
<td>10-1330-1150-10-2</td>
<td>&lt;0.1</td>
<td>1.2</td>
<td>0.79</td>
<td>57.8</td>
<td>315 ± 22</td>
</tr>
<tr>
<td>10-1100-2-1400-1200-10-3</td>
<td>0.1</td>
<td>3.2</td>
<td>0.82</td>
<td>29.9</td>
<td>410 ± 22</td>
</tr>
</tbody>
</table>

Boundary conditions: z (0.1-0.7), pore size range (0-3), relative density (0.89-0.94), number of surface pores per unit area (0.0025 m²) area (0-3 x 10^6).
Chapter 6: Influence of microstructure on gas permeance

Two of the three samples with a pass for every parameter use three-step sintering profiles. Looking at these two samples i.e. 10-1100-2-1367-1300-10-3 and 10-1100-2-1500-1300-10-3 with gas flow rates of 111 ± 5 ml min⁻¹ and 117 ± 13 ml min⁻¹, respectively, shows that the microstructures are quite different as shown in Figure 6.18.

Figure 6.18: Scanning electron surface micrographs of the three-step sintering samples
a) 10-1100-2-1367-1300-10-3 which has a relative density of 0.89 and
b) 10-1100-2-1500-1300-10-3 which has a relative density of 0.94.

The sample 10-1100-2-1367-1300-10-3 has a lower relative density (0.89) when compared with sample 10-1100-2-1500-1300-10-3 (0.94). When the relative density increases to near full density (0.98) for sample 10-1100-2-1600-1150-10-3, surprisingly this results in an increased gas flow rate (140 ± 2 ml min⁻¹). This increase in gas flow rate may be explained by microstructural parameters other than relative density. When the z factor is considered with a relative density of 0.98, z is 1, indicating that sample 10-1100-2-1600-1150-10-3 has less than one grain across the thickness of the sintered layer and thus lies outside the boundary condition. Sample 10-1100-2-1600-1150-10-3 has a narrow pore size range (2 μm) and low number of surface pores (0.1 x 10⁵). These values are within the boundary conditions of 0-3 for both parameters. This would indicate that the z factor and relative density have a significant influence on the gas flow rate despite the other parameters being acceptable.
However, a reduction in $z$ below 0.1 is also associated with an increase in the gas flow rate. Sample 10-1100-1400-1200-10-3 has a $z$ of 0.1 (within the boundary condition) but has the highest gas flow rate measured during this study ($410 \pm 22$ ml min$^{-1}$). This gas flow rate is attributed to a pore size range (3.2 μm), relative density (0.82) and number of surface pores ($30 \times 10^6$) all being outside the boundary conditions. Interestingly the conventionally sintered sample (A-325-3-3-1450-1) and three-step sintered sample (10-1100-2-1450-1400-10-3) have similar microstructural parameters however, the gas flow rates are different; $311 \pm 8$ ml min$^{-1}$ and $244 \pm 17$ ml min$^{-1}$, respectively. In this case only the $z$ factor is significantly different, 0.7 for sample A-325-3-3-1450-1 and 0.2 for sample 10-1100-2-1450-1400-10-3. This indicates that each microstructural parameter is important and any change can influence the gas flow rate.

Samples 10-1100-2-1367-1300-10-3, 10-1500-1300-10-2 and 10-1100-2-1500-1300-10-3 all show values for $z$ factor, pore size range, relative density and number of surface pores within the boundary conditions of 0.1-0.7, 0-3, 0.89-0.94 and $0-3 \times 10^6$, respectively. Having each parameter within the boundary conditions results in a 25% reduction in the gas flow rate for the two-step sintered sample (10-1500-1300-10-2) compared with the conventionally sintered sample (A-165-3-3-1450-1). This reduction in gas flow rate is 30% for the three-step sintered sample (10-1100-2-1367-1300-10-3). Further optimisation of the microstructure for $z$, pore size range, relative density and number of surface pores per unit area would be required to reduce the gas flow rate beyond the values obtained in this study.
6.4.4 Gas permeance suitable for an industrial application

The ultimate test of a thick-film is whether or not it is possible to achieve a level of gas flow rate that is suitable for use in an industrial application. Gaudon et al., (2005) and Park et al., (2005) have published gas permeance values that would allow a fuel cell to operate successfully in the field. In order to compare data from this study with these published values, helium permeance has been calculated for the samples sintered using two-step and three-step sintering techniques. The gas flow rate values quoted previously in this chapter have been converted from a flow rate per unit time to include differential pressure and sample area. A detailed explanation of the conversion from gas flow rate to gas permeance is given in appendix B. Data for samples sintered using two-step and three-step techniques which give the lowest gas permeance values are shown in Figure 6.19.

Figure 6.19: Helium permeance as a function of relative density. The gas flow rate of the sintered thick-film have been compared with the values published by Gaudon et al., (2005) and Park et al., (2005), which are stated to be suitable for use in an industrial application. Error bars represent one standard deviation from the mean.
The lowest gas permeance value achieved for the optimised fabrication process used a 165 mesh size with three print-dry applications and conventional sintering was $10^{-4}$ mbar l s$^{-1}$ cm$^{-2}$. This level is below $10^{-5}$ mbar l s$^{-1}$ cm$^{-2}$ which was stated by Gaudon et al., (2005) as a gas permeance where cracks were present within the sintered film. The conventionally sintered thick-films were not identified as having cracks and this comparison provides a good indication of how the gas permeance levels change with the presence of larger defects such as cracks or holes. Two-step sintering reduced the gas permeance to a level of $8 \times 10^{-5}$ mbar l s$^{-1}$ cm$^{-2}$ for sample 10-1500-1300-10-2. The three-step sintering profile reduced this value slightly further to $7 \times 10^{-5}$ mbar l s$^{-1}$ cm$^{-2}$ (black diamond, 10-1100-2-1500-1300-10-3).

The gas permeance value that is suitable for an industrial application indicated by Gaudon et al., (2005) is $10^{-5}$ mbar l s$^{-1}$ cm$^{-2}$ while Park et al., (2005) suggest that this value is slightly higher at $5 \times 10^{-5}$ mbar l s$^{-1}$ cm$^{-2}$. Gaudon et al., (2005) indicates that $10^{-5}$ mbar l s$^{-1}$ cm$^{-2}$ is below the level required for an industrial application. This represents a gas flow of 1% when compared with the values used to set for the IP-SOFC design (Rolls-Royce Fuel Cell Systems, 2004). A 3% loss of gas is the target for the IP-SOFC design. This value equates to $5 \times 10^{-5}$ mbar l s$^{-1}$ cm$^{-2}$ and this target is indicated in Figure 6.19.

The modified two-step sintering profiles originally proposed by Lee, (2004) and Leite et al., (2003) are 10-1100-2-1500-1300-10-3 and 10-1100-2-1367-1300-10-3, respectively. While these sintering profiles represent a reduction in gas permeance from $10^{-4}$ mbar l s$^{-1}$ cm$^{-2}$ (conventional sintering) to $7 \times 10^{-5}$ mbar l s$^{-1}$ cm$^{-2}$ a further reduction in gas flow rate would be required for implementation in an industrial application.
6.5 Concluding remarks

The method of sintering of the body is critical to the final microstructure, specifically the relative density and grain size. It has been shown that while these are important parameters for mechanical integrity they cannot be considered in isolation when considering gas flow rates through the microstructure. The gas flow rate through a sintered thick-film is a function of the grain size to sintered thickness ratio, factor z, pore size range, relative density and number of surface pores per unit area (0.0025 m$^3$). Boundary conditions have been proposed for each microstructural parameter: z factor (0.1-0.7), pore size range (0-3 μm), relative density (0.89-0.94) and number of surface pores per unit area (0-3 x 10$^5$). The influence of these parameters has shown that two-step and three-step sintered samples 10-1100-2-1367-1300-10-3, 10-1500-1300-10-2 and 10-1100-2-1500-1300-10-3 all show values for z factor, pore size range, relative density and number of surface pores within the boundary conditions. The gas flow rate was lowest for sample (10-1100-2-1367-1300-10-3) at 111 ± 5 ml min$^{-1}$ which can be compared with the equivalent conventionally sintered sample (A-165-3-3-1450-1) 155 ± 24 ml min$^{-1}$. This represents a reduction in gas flow rate of approximately 30% when compared with a conventional sintering profile. The sample (10-1100-2-1367-1300-10-3) has a lower peak temperature (1367°C) when compared with the baseline temperature (1450°C) for conventional sintering. This reduction in the peak sintering temperature is beneficial to the other fuel cell components. Although two-step and three-step sintering is not effective in every case a reduction in gas flow rate can be achieved. Further investigation would be required to ensure that these sintering schemes do not have a detrimental effect on the ionic conductivity. Essentially this study has shown that a combination of microstructural parameters determines the gas flow rate and the route to obtain a microstructure with the correct combination is unimportant.
Chapter 7: Concluding remarks

7 Concluding remarks

7.1 Conclusions from current work

7.1.1 Overview

Throughout the course of this study the primary focus has been the achievement of a yttria stabilised zirconia (YSZ) thick-film fabricated using screen-printing technology that is suitable for use as a solid oxide fuel cell (SOFC) electrolyte in an industrial application. The fabrication requirement was a minimum number of screen-printing applications and a single sintering cycle in order to reduce the unit cost. This programme of work has shown how the microstructure of the electrolyte changes due to modification of the fabrication and sintering processes and has demonstrated how the resulting microstructure influences the gas flow rate. The microstructural data provides a basis from which to assess the critical parameters for improvements to the fabrication process and further reductions in gas flow rate. Furthermore this work may provide design rules and data which allow the process to be modelled.

7.1.2 Deposition thickness and conventional sintering parameters

Based on the specification for the IP-SOFC design the electrolyte thickness is required to be between 10 and 20 μm. A sintered thickness of 9 ± 0.8 μm achieved using a 165 mesh size with three print-dry applications is at the lower end of this requirement. Additional print deposits or the use of thicker screens such as the 105 and 80 mesh screens resulted in thicker sintered layers up to a maximum of 23 ± 0.8 μm. Increasing screen thickness leads to a reduction in relative density and grain size, while additional print-dry applications only have a minor effect on microstructure. Therefore it was concluded that the screen thickness is major factor influencing relative density and grain size when other parameters are kept constant.

While several of the mesh sizes could have been chosen the 165 mesh size with three print-dry applications was selected for use as the baseline. The resultant layer thickness of 9 ± 0.8 μm, while falling slightly below the prescribed range, might hold the benefit of reduced electrical resistance when compared with thicker layers. This simple approach has shown that for a particular ink formulation a baseline construction has been established, allowing a conventional sintering profile to be used to optimise the microstructure.
Chapter 7: Concluding remarks

The individual elements of the sintering profile were investigated, and each was shown to influence the final microstructure. The data from the heating rate study were difficult to interpret as they included the effects of both sintering temperature and sintering time. However, increasing the heating rate beyond 5°C min⁻¹ resulted in a significant change in relative density, and grain size doubled for the increase from 10 to 20°C min⁻¹. While both of these microstructural parameters were influenced by heating rate minimal change was observed in the sintered layer thickness. A heating rate of 10°C min⁻¹, a sintering temperature of 1450°C and a sintering time of 10 hours provided the elements of a baseline sintering profile while accommodating the restrictions imposed by the IP-SOFC design.

7.1.3 Non-conventional sintering profiles

Non-conventional sintering profiles are described in this study as any deviation from a conventional ramp to the peak sintering temperature with an isothermal hold until full density is reached. The first modification was the addition of a coarsening step to the sintering profile. This resulted in a slight increase in the relative density while the grain size increased by a factor of three compared with a conventionally sintered equivalent sample. This indicated that a coarsening mechanism does occur in a constrained thick-film.

Secondly, two-step sintering has been described in the literature as a means of suppressing grain growth in nano and sub-micrometre powders. It has been shown in this study that two-step sintering can similarly reduce the amount of grain growth in micrometre-sized powders. However, the results obtained for micrometre-sized YSZ indicate that the suppression of grain growth is associated with exhaustion of the densification process and therefore full density is not achieved. Full density can be achieved with two-step sintering of YSZ but not without grain growth. Two-step sintering was also shown to change the pore structure by reducing the pore size range. This reduction or homogenising of the pore structure was evident in both 'normal' two-step and 'reverse' two-step sintering.

Finally, the coarsening step was combined with two-step sintering and designated 'three-step sintering'. The three-step sintering process was shown to provide a slight increase in relative density when compared with some two-step examples. This increase in relative density was also associated with a further reduction in the pore size range. This was illustrated by samples sintered using the modified two-step profiles 10-1367-1300-10-2 and 10-1500-1300-10-2 taken from literature. Three-step sintering results in a thick-film with a homogenised pore structure. Two-step and three-step sintering change the pore structure and result in full density being achieved but not without grain growth.
7.1.4 Gas testing

Gas testing showed that thin layers with high density and thicker layers with lower densities did not result in the lowest gas flow rates. Changes in the mesh size dominated the variation in gas flow rate and the results indicated that more than one print-dry application would be required for fabrication of a gas-tight layer, regardless of the mesh size. The 165 mesh size with a screen thickness of 110 μm with three print-dry applications provided the lowest gas flow rate when sintered according to the baseline profile. Samples fabricated with this mesh size had an intermediate sintered layer thickness, relative density and grain size compared with the 325, 200, 105 and 80 mesh sizes. Calculation of the ratio between the grain size and sintered layer thickness, z factor, showed that a minimum gas flow rate was achieved for a value between 0.1 and 0.3. This corresponds to a relative density range between 0.86 and 0.91.

Two-step and three-step sintering resulted in reduced gas flow rates compared with the conventional sintering profile used in the mesh study. The grain size to sintered layer thickness, z factor, ranged from 0.1 and 0.4 at a relative density of 0.89 to 0.94 compared with a z factor of 0.1 to 0.3 and relative density between 0.86 and 0.91 for conventional sintering. However, there were two-step and three-step samples which met the boundary conditions defined for z factor and relative density while showing higher gas flow rates. These samples were also shown to have a similar pore size range but had a larger number of surface pores which contributed to the increase in gas flow rate. It was concluded that gas flow rate is a function of z factor (grain size to sintered layer thickness), pore size range, relative density and number of surface pores per unit area. The samples sintered using three-step sintering profiles, 10-1100-2-1367-1300-10-3 and 10-1100-2-1500-1300-10-3, reduced the gas flow rate by 20% and 30%, respectively compared with conventional sintering. This reduction in gas flow rate for sample (10-1100-2-1367-1300-10-3) also corresponds with lowering of the peak temperature from 1450°C to 1367°C which will be beneficial to the other components within the fuel cell. Further study would be required to ensure that these sintering schemes do not have a detrimental effect on the ionic conductivity. The gas flow rate reduction achieved in this study was just above the value required for use in an industrial application.
Chapter 7: Concluding remarks

7.2 Suggestions for further work

This study has assessed the effect of changes to the screen-printing and sintering processes for constrained YSZ thick-films. The aim of reducing the gas flow rate across the sintered film has been achieved, although these levels remain slightly above those required for an electrolyte to operate in an industrial application. During the course of the study several areas for further work were identified, as follows:

1. The modified sintering schemes in this study have shown that a reduction in gas flow rate across the electrolyte has been achieved. A study of the effect of these sintering profiles on the ionic conductivity of the electrolyte is required.

2. This study has shown that fabrication parameters such as the number of print-dry applications and heating rate influence the microstructure of the constrained layers. The effect on the green body of many thin and fewer thick print applications when the deposited thickness is the same requires further study. At a heating rate of 5°C min\(^{-1}\) the microstructural parameters did not fit the trend with the faster or slower heating rates. The effect of heating rates between 1 and 10°C min\(^{-1}\) require further evaluation.

3. A baseline was established for fabrication of the screen-printed layers and sintering profile based on conventional sintering. Evaluation of an alternative baseline to investigate the trends that exist between microstructural evolution and gas flow rate is required.

4. A future expansion of this work would be to develop a master sintering curve for conventional sintering of 3-mol% YSZ. This would allow a comparison to be made with two-step and three-step sintering. On a longer term basis this would provide a usable tool within the production environment where process variables such as powder particle size and fabrication parameters can be managed by the prediction of sintering cycles to reduce the impact of the fabrication process. A 'kinetic window' has been established in the literature for two-step sintering of materials such as yttria, barium titanite and iron nickel ferrites. This approach should be applied to free sintered and constrained 3-mol% YSZ to establish whether full density can be achieved while suppressing grain growth.
References


References


Reference


References


References


References


References


DOI: 10.1111/j.1551-2916.2005.00625.x
Appendix A

Wilcoxon signed-rank test

The Wilcoxon signed-rank test is a nonparametric test for comparing two related samples of data. This test has been applied to assess grain sizes measured from a range of samples and has been used to determine if changes to the processing route of YSZ thick-films are significant. The nonparametric test for comparing two related samples will be explained by the following two examples;

Example A

The sample set consisted of the three types of mesh size (165, 105 and 80) and three different print-dry applications (2, 3 and 4) as shown in table A1. All of these samples were constructed using the same powder and ink and were sintered using the same scheme and furnace.

Table A1: Wilcoxon signed-rank test sample comparison of mean grain size for mesh size and number of print-dry applications

<table>
<thead>
<tr>
<th>Site</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesh size (1&lt;sup&gt;st&lt;/sup&gt; sample)</td>
<td>165</td>
<td>165</td>
<td>165</td>
<td>105</td>
<td>105</td>
<td>105</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Number of print deposits (1&lt;sup&gt;st&lt;/sup&gt; sample)</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Grain size (μm) (1&lt;sup&gt;st&lt;/sup&gt; sample)</td>
<td>1.2</td>
<td>1.3</td>
<td>1.3</td>
<td>1.1</td>
<td>1.2</td>
<td>1.2</td>
<td>1.0</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Mesh size (2&lt;sup&gt;nd&lt;/sup&gt; sample)</td>
<td>165</td>
<td>165</td>
<td>165</td>
<td>105</td>
<td>105</td>
<td>105</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Number of print deposits (2&lt;sup&gt;nd&lt;/sup&gt; sample)</td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Grain size (μm) (2&lt;sup&gt;nd&lt;/sup&gt; sample)</td>
<td>1.3</td>
<td>1.3</td>
<td>1.2</td>
<td>1.2</td>
<td>1.1</td>
<td>0.9</td>
<td>1.1</td>
<td>1.0</td>
<td>1.1</td>
</tr>
</tbody>
</table>

1. Firstly the difference between the first and second samples is calculated for each mesh type. Difference in grain size = grain size (1<sup>st</sup> sample) – grain size (2<sup>nd</sup> sample).

2. The magnitude of the differences is ranked from the highest to the lowest, while the sign is ignored.
Appendix A

3. A summation of the ranks of the positive differences, \( \sum R_+ \) = 23.3, and the negative differences, \( \sum R_- \) = 21.7, are made. The smaller of these values (21.7) is the calculated value of T, where T is the sum of the inconsistent ranks. The total of the sums of the ranks of the positive and negative differences can be checked using the following equation;

\[
\sum R_+ + \sum R_- = \frac{n(n+1)}{2} \tag{A1}
\]

where, \( n \) is the number of subsets of data (9).

4. A comparison is made of the calculated value of T and the critical value taken from the Wilcoxon’s signed rank test percentage points (Hinton, 2004). The number of subsets, \( n \), is used to find the correct value and the calculated value of T must be equal to or smaller than the value in the table to be statistically significant.

5. In this example, \( n = 9 \) and the Wilcoxon’s signed rank test percentage points table gives the critical value at the 95% confidence level of 5. The test value of 21.7 is greater than this and under the rules of the Wilcoxon test, the null hypothesis at the 95% confidence level is accepted. Therefore the mean grain size for the number of print-dry applications in the first sample is not significantly different than that for the number of print-dry applications in the second sample.

Example B

The grain size of samples fabricated using the thinner 325 mesh size were compared with the 165, 105 and 80 mesh sizes. The Wilcoxon test was applied with the second sample being the 165, 105 and 80 mesh sizes with two, three and four print-dry applications.

1. Firstly the difference between the first and second samples is calculated at each site. Difference in grain size = grain size (1st sample) – grain size (2nd sample).

2. The magnitude of the differences is ranked from the highest to the lowest, while the sign is ignored.
3. A summation of the ranks of the positive differences, \( \sum R_+ \) = 0, and the negative differences, \( \sum R_- \) = 45, are made. The smaller of the positive and negative sums (0) of the ranks is the calculated value of T.

4. Compare the calculated value of T with the critical value taken from the Wilcoxon's signed-rank test percentage points (Hinton, 2004). The number of subsets, n, is used to find the correct value and the calculated value of T must be equal to or smaller than the value in the table for significance.

5. This example also had n = 9 so the critical value at the 95% confidence level was 5. With nine subsets there are \( 2^9 = 512 \) different possibilities in total. There is only one way of achieving a positive rank total of zero and the probability of getting zero by chance is 1/512 or 0.002. A T value of zero suggests that the mean grain sizes measured for the 325 mesh size are different to that measured for the 165, 105 and 80 mesh sizes with a probability of as much as 99% (Maca and Simonikova, 2005). The mean grain size values used for each subset are shown in table A2.

Table A2: Mean grain sizes for the 325 mesh size compared with the 165, 105 and 80 mesh sizes used for the Wilcoxon signed-rank test

<table>
<thead>
<tr>
<th>Site</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>325</td>
<td>325</td>
<td>325</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>165</td>
<td>165</td>
<td>165</td>
<td>165</td>
<td>105</td>
<td>105</td>
<td>105</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>105</td>
<td>105</td>
<td>105</td>
<td>105</td>
<td>105</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>80</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>1.2</td>
<td>1.3</td>
<td>1.3</td>
<td>1.1</td>
<td>1.2</td>
<td>1.2</td>
<td>1.0</td>
<td>0.9</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Gas flow calculations

In comparison to testing gas flow rate under normal SOFC operating conditions, a simpler approach is to use a room temperature gas testing method in which helium is the test gas. This allows a gas similar in molecular size to hydrogen to be used without the risk of combustion and it also removes the need to heat each sample to temperature. The room temperature method essentially compares the inlet flow with the outlet flow resulting in a measured gas flow rate of the helium that is lost through the thick-film. A mass spectrometer was used to measure nitrogen in the air and helium. Helium is the test gas and air is used as a reference. By measuring the nitrogen levels in the reference air and the helium in the exhaust, the helium flow rate can be established using

\[
\text{Air}_{\text{in}} = \frac{N_{2_{\text{exhaust}}}}{N_{2_{\text{in}}}} \quad \text{(B1)}
\]

where \(\text{Air}_{\text{in}}\) is the fraction of air calculated as a ratio of the air in the atmosphere and that present in the gas stream, and

\[
\text{He}_{\text{out}} = 1 - \text{Air}_{\text{in}} \quad \text{(B2)}
\]

where \(\text{He}_{\text{out}}\) is the fraction of helium in the exhaust stream.

\[
\text{He}_{\text{out}} = \text{Flow}_{\text{exhaust}} \cdot \text{He}_{\text{out}} \quad \text{(B3)}
\]

where \(\text{Flow}_{\text{exhaust}}\) is the measured reading.

The total flow rates in \(\text{ml min}^{-1}\) for helium can then be defined as;

\[
\text{Flow}_{\text{He}} = \text{Flow}_{\text{exhaust}} \cdot \text{He}_{\text{out}} \quad \text{(B4)}
\]
Appendix B

The flow in the exhaust can then be expressed as follows:

\[ C_{\text{mix}} = \frac{1}{x_{\text{mix}}} \]  

(B5)

where \( C_{\text{mix}} \) is a conversion factor for the gas mixture and \( x_{\text{mix}} \) is derived from:

\[ x_{\text{mix}} = \frac{\text{Air}_\text{in}}{C_{\text{Air}}} + \frac{\text{He}_\text{out}}{C_{\text{He}}} = \frac{\text{Air}_\text{in}}{1} + \frac{\text{He}_\text{out}}{1.41} \]  

(B6)

where \( x_{\text{mix}} \) is the total concentration of air and helium with \( C_{\text{Air}} \) and \( C_{\text{He}} \) correction factors applied. Therefore the flows can be expressed with respect to the gas correction factors:

\[ \text{Flow}_{\text{exhaust}} = \left( \frac{\text{Flowmeter}_{\text{exhaust}}}{\text{Flowmeter}_{\text{inlet}}} \right) \cdot \text{inlet flow} \cdot \frac{C_{\text{mix}}}{C_{\text{He}}} \]  

(B7)

where the flow in the exhaust is a ratio of the two flow meter readings and \( \frac{C_{\text{mix}}}{C_{\text{He}}} \) is the conversion factor for composition correction.
Appendix B

Gas permeance calculation

The gas flow targets set by Rolls-Royce Fuel Cell Systems (RRFCS) are stated in the sub-system requirement document (SSRD, 2004) as 3%. Gas permeance quoted by Gaudon et al., (2005) can be converted to percentage gas flow to provide a comparison between the two systems as follows:

Table B1: Data and assumptions for gas flow rate measurement

<table>
<thead>
<tr>
<th>Gas permeance (mbar l s⁻¹ cm⁻²)</th>
<th>Sample area (cm²)</th>
<th>Differential pressure (ΔP) (mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 x 10⁻⁵</td>
<td>14</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The gas flow rate can be calculated from the gas permeance, differential pressure and sample area.

\[
Flow\ rate = \left(\frac{\text{gas permeance}}{\Delta P}\right) \times (1000 \cdot 60 \cdot \text{Area}) \ (\text{ml min}^{-1}) \quad (B8)
\]

\[
\therefore \ Flow\ rate = 28 \ \text{ml min}^{-1}
\]

The inlet flow is assumed to be the full scale of the flow meter, therefore the inlet flow is;

\[
100\% = 2000 \times \left(\frac{1.41}{1.01}\right) = 2792.07 \ \text{ml min}^{-1} \ \text{helium} \quad (B9)
\]

\[
\text{Percentage gas flow} = \frac{\text{Flow rate}}{\text{Inlet flow}} = 1\% \quad (B10)
\]

Therefore the gas permeance quoted by Gaudon et al., (2005) and shown in equation B10 as the percentage of gas lost to the system is below the 3% level required by RRFCS to operate the IP-SOFC system in an industrial application.
Appendix B

The following example calculates the gas permeance from the 3% gas flow value, at a 
\( \Delta P \) of 0.5 mbar, stated in the SSRD:

\[
\text{Flow rate} = \text{Inlet flow} \times \text{percentage gas flow (ml min}^{-1}) \tag{B11}
\]

\[\therefore \text{Flow rate} = 84 \text{ ml min}^{-1}\]

\[
\text{Gas permeance} = \frac{\text{Flow rate} \times \text{Area}}{\Delta P} = 5 \times 10^{-5} \text{ mbar l s}^{-1} \text{ cm}^{-2} \tag{B12}
\]

Equation B12 provides the equivalent gas permeance value that is required for use in an
industrial application for the IP-SOFC design.

Table B2: Equivalent gas permeance values for hydrogen and helium

<table>
<thead>
<tr>
<th>Hydrogen permeance mol m(^2) s Pa (Park et al., 2005)</th>
<th>Helium permeance mbar l s(^{-1}) cm(^{-2}) (Gaudon et al., 2005)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 \times 10^{-10}</td>
<td>1 \times 10^{-5}</td>
<td>Gaudon et al., 2005 value acceptable for an industrial application</td>
</tr>
<tr>
<td>1 \times 10^{-9}</td>
<td>4 \times 10^{-6}</td>
<td>Park et al., 2005 value acceptable for an industrial application</td>
</tr>
</tbody>
</table>