Sintering of Alumina and the Effect of Porosity on Properties

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For their help in making the past three years appear that bit shorter, I would like to thank all my friends for the fun times. I am also grateful to my mum who fed, watered and sheltered me during the long writing-up period.

And finally I would like to thank Sophie for always being there and understanding during those more stressful times.

Thanks

Rob.
ABSTRACT

The sintering of alumina has been studied with a view to produce high quality experimental data to validate theoretical predictions made by a computational model designed to address two key issues in the sintering of real powders: variations in particle size and the removal of large pores. Having produced porous materials the effect of large pores on the mechanical properties and thermal shock behaviour of a monolith was examined.

The initial stage of solid state sintering of alumina has been studied using a high temperature in situ monitoring technique incorporating a method for accounting for sample radiance at high temperature. Data were acquired from compacts composed of nominally coarse and fine powders, and powder blends containing different proportions of these powders. Broad agreement was found between experimental observations and predictions with the model accurately describing some of the sintering characteristics associated with the variation of particle size found in real powders i.e. relative rates of shrinkage. Discrepancies between the model requirements and the characteristics of real powders preclude full agreement.

Changes in the size of large pores during the sintering of compacts were determined from measurements of sample density following sintering. The results showed that volume of the large pores decreased by a factor of 0.85 during the sintering process. These observations of pore shrinkage corroborate model predictions of sintering behaviour.

The effect of large pores on the mechanical properties and thermal shock resistance was subsequently examined. It was demonstrated that strength and Young's modulus decreased with increased levels of porosity, with strength exhibiting a higher porosity dependence. Experimental data was fitted using an exponential equation in the form of $X = X_0 \exp(-b V_{fp})$ where $b$ was found to be equal to 3.60 and 5.22 for Young's modulus and strength respectively. The porosity dependence observed was greater than that reported in the literature, and attributed to the local variation in pore concentration due to pore clustering. Measurements of work of fracture indicate that the effective surface energy increases by a factor of 1.4 over the range of porosity studied. Material property behaviour was then used to predict the effect of porosity on the thermal shock resistance parameters. It was shown that the critical temperature for the onset of crack growth should decrease and the resistance to crack propagation and the stability of existing cracks should increase with increases in the level of clustered porosity. Measurements of residual strength following thermal shock showed the presence of clustered porosity to result in increases in the relative retained strength comparable to those predicted.
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### SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>constant in equation 2.36</td>
</tr>
<tr>
<td>a_c</td>
<td>diameter of particles</td>
</tr>
<tr>
<td>a_p</td>
<td>diameter of pore perpendicular to direction of stress</td>
</tr>
<tr>
<td>a_\beta</td>
<td>characteristic dimension (i.e. half thickness of specimen)</td>
</tr>
<tr>
<td>A</td>
<td>area</td>
</tr>
<tr>
<td>A_c</td>
<td>mean area of cracks</td>
</tr>
<tr>
<td>A_{\text{diff}}</td>
<td>cross-sectional area of the diffusion path</td>
</tr>
<tr>
<td>A_H</td>
<td>constant in equations 2.37, 2.38</td>
</tr>
<tr>
<td>A_F</td>
<td>constant in equations 4.1, 4.2</td>
</tr>
<tr>
<td>A_x</td>
<td>area of solid phase</td>
</tr>
<tr>
<td>A_\beta</td>
<td>non-dimensional stress term</td>
</tr>
<tr>
<td>A_{f_{r}}</td>
<td>area fraction of solid material on fracture surface</td>
</tr>
<tr>
<td>A_{f_{\text{min}}}</td>
<td>minimum solid area fraction</td>
</tr>
<tr>
<td>b</td>
<td>specimen width</td>
</tr>
<tr>
<td>b_E</td>
<td>empirical constant in Spriggs' equation for Young's modulus</td>
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<td>b_G</td>
<td>empirical constant in Spriggs' equation for shear modulus</td>
</tr>
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<td>b_\sigma</td>
<td>empirical constant in Spriggs' equation for strength</td>
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<td>crack radius</td>
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<td>initial crack length</td>
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<tr>
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<td>constant in equation 2.51</td>
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<tr>
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<td>diameter of pore parallel with stress direction</td>
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<tr>
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<td>test line length</td>
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<td>C_{\text{eff}}</td>
<td>effective test line length</td>
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<td>vacancy concentration under flat surface</td>
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<td>\Delta C</td>
<td>change in vacancy concentration</td>
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<tr>
<td>d</td>
<td>specimen thickness</td>
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<tr>
<td>d_s</td>
<td>distance of sample cell from detector in particle size analyser</td>
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<td>d_x</td>
<td>thickness of element</td>
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<tr>
<td>D</td>
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<td>D_{gb}</td>
<td>grain boundary diffusion coefficient</td>
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<td>D_l</td>
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</tr>
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<td>E_0</td>
<td>Young's modulus of pore free material/matrix phase</td>
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<tr>
<td>E_r</td>
<td>Young's modulus of reinforcement phase</td>
</tr>
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<td>Symbol</td>
<td>Definition</td>
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<td>------------</td>
</tr>
<tr>
<td>$G$</td>
<td>shear modulus</td>
</tr>
<tr>
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</tr>
<tr>
<td>$G_s$</td>
<td>surface free energy</td>
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<tr>
<td>$G_t$</td>
<td>total free energy</td>
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<tr>
<td>$G_v$</td>
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</tr>
<tr>
<td>$G_S$</td>
<td>mean grain size</td>
</tr>
<tr>
<td>$H$</td>
<td></td>
</tr>
<tr>
<td>$h$</td>
<td>extension of particle/pore outside of unit cell</td>
</tr>
<tr>
<td>$h_T$</td>
<td>heat transfer coefficient</td>
</tr>
<tr>
<td>$J$</td>
<td>flux per unit area</td>
</tr>
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<td>$K$</td>
<td></td>
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<tr>
<td>$k$</td>
<td>Boltzmann’s constant</td>
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<tr>
<td>$K_{IC}$</td>
<td>mode I fracture toughness</td>
</tr>
<tr>
<td>$K_{IC lokal}$</td>
<td>local mode I fracture toughness</td>
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<tr>
<td>$K_{max}$</td>
<td>maximum stress concentration around a pore</td>
</tr>
<tr>
<td>$L$</td>
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</tr>
<tr>
<td>$l_s$</td>
<td>equilibrium lattice spacing</td>
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<tr>
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<td>length</td>
</tr>
<tr>
<td>$L_0$</td>
<td>original length</td>
</tr>
<tr>
<td>$L_B$</td>
<td>span (separation of bottom two rollers on 3-point bend rig)</td>
</tr>
<tr>
<td>$\Delta L$</td>
<td>change in length</td>
</tr>
<tr>
<td>$M$</td>
<td></td>
</tr>
<tr>
<td>$m$</td>
<td>constant in equations 2.16</td>
</tr>
<tr>
<td>$m'$</td>
<td>constant in equations 2.17</td>
</tr>
<tr>
<td>$m_a$</td>
<td>mass of ceramic in air</td>
</tr>
<tr>
<td>$m_b$</td>
<td>mass of binder</td>
</tr>
<tr>
<td>$m_c$</td>
<td>mass of ceramic</td>
</tr>
<tr>
<td>$m_n$</td>
<td>mass of ceramic suspended in fluid</td>
</tr>
<tr>
<td>$m_s$</td>
<td>mass of starch</td>
</tr>
<tr>
<td>$m_v$</td>
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<tr>
<td>$\Delta m$</td>
<td>change in mass</td>
</tr>
<tr>
<td>$M$</td>
<td>magnification</td>
</tr>
<tr>
<td>$M_{f_b}$</td>
<td>mass fraction of binder</td>
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<tr>
<td>$M_p$</td>
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<td>$N$</td>
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<tr>
<td>$n$</td>
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<td>$n_E$</td>
<td>constant in empirical equations 2.35, 2.36</td>
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<td>$n_p$</td>
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<td>$n_C$</td>
<td>constant in equation 2.60</td>
</tr>
<tr>
<td>$N$</td>
<td>grain boundary intercepts</td>
</tr>
<tr>
<td>$N_c$</td>
<td>number of cracks</td>
</tr>
<tr>
<td>$N_{aa}$</td>
<td>number of grain-grain boundary intercepts</td>
</tr>
</tbody>
</table>
Symbols

\( N_{ab} \) number of grain-pore boundary intercepts
\( N_{\text{eff}} \) effective number of intercepts
\( N_p \) number of pores

\( P \)
- \( P \) load
- \( P_{\text{max}} \) load at failure

\( R \)
- \( r \) radius of curvature of the particle join
- \( r^* \) radius of curvature of neck between two sintering particles
- \( r_0 \) radial position of particle prior to centrifuging
- \( r_a \) range of atomic force for bonding
- \( r_p \) radius of contact between sphere and unit cell
- \( r_t \) radial position of particle after centrifuging for time \( t \).
- \( R \) resistance to crack initiation (fast quench)
- \( R' \) resistance to crack initiation (slow quench)
- \( R^{''''} \) resistance to crack propagation
- \( R^{'''''} \) resistance to crack propagation
- \( R_p \) radius of particle/pore
- \( R_L \) radius of large particle
- \( R_s \) ratio of small to large particle size
- \( R_S \) radius of small particle
- \( R_{\text{st}} \) resistance to propagation of pre-existing cracks (fast quench)
- \( R_{\text{st}}' \) resistance to propagation of pre-existing cracks (slow quench)

\( T \)
- \( t \) time
- \( T \) absolute temperature
- \( \Delta t \) change in time
- \( \Delta T \) change in temperature

\( V \)
- \( V \) volume
- \( V_b \) volume of binder
- \( V_c \) volume of ceramic
- \( V_p \) volume of one pore
- \( V_p^* \) volume of one pore following sintering
- \( V_s \) volume of starch
- \( V_{f_1} \) volume fraction of phase 1
- \( V_{f_2} \) volume fraction of phase 2
- \( V_{f_p} \) volume fraction of porosity
- \( V_{f_R} \) volume fraction of reinforcement phase
- \( V_{f_Rs} \) volume fraction of small particle
- \( V_{f_s} \) volume fraction of starch

\( W \)
- \( W \) shrinkage
- \( W' \) shrinkage rate
- \( W_E \) stored elastic energy
- \( W_T \) total stored elastic energy
Symbols

\( X \)  
- radius of neck between two sintering particles
- \( x \) extension on failure
- \( X_f \) material property
- \( X_0 \) material property of pore free material
- \( X_c \) material property of composite
- \( X_1 \) material property of phase 1
- \( X_2 \) material property of phase 2

\( Y \)  
- \( y \) degree of overlap between sintering particles
- \( Y \) geometric shape factor

\( \alpha \)  
- thermal expansion coefficient
- \( \alpha^* \) constant in equation 2.21
- \( \alpha_c \) thermal expansion coefficient of composite
- \( \alpha_1 \) thermal expansion coefficient of phase 1
- \( \alpha_2 \) thermal expansion coefficient of phase 2

\( \beta \)  
- \( \beta \) Biot modulus
- \( \beta^* \) constant in equation 2.21

\( \delta \)  
- deflection
- \( \delta_{gb} \) thickness of grain boundary diffusion layer
- \( \delta_d \) thickness of diffusion layer
- \( \delta_x \) extension of element

\( \varepsilon \)  
- \( \varepsilon \) strain
- \( \varepsilon' \) strain rate
- \( \varepsilon_{gb}' \) reference strain rate

\( \Phi \)  
- dihedral angle

\( \gamma \)  
- \( \gamma_{eff} \) effective fracture energy
- \( \gamma_s \) surface energy
- \( \gamma_{gb} \) grain boundary energy

\( \eta \)  
- \( \eta_s \) viscosity of solvent

\( \kappa \)  
- \( \kappa \) principal surface curvature

\( \lambda \)  
- thermal conductivity
- \( \lambda_0 \) thermal conductivity of pore free material
- \( \lambda_c \) thermal conductivity of composite
- \( \lambda_m \) thermal conductivity of matrix
- \( \lambda_r \) thermal conductivity of reinforcement phase
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_h$</td>
<td>Herrings scaling parameter</td>
</tr>
<tr>
<td>$\lambda_{hA}$</td>
<td>scaling parameter for area effects</td>
</tr>
<tr>
<td>$\lambda_{hf}$</td>
<td>scaling parameter for flux effects</td>
</tr>
<tr>
<td>$\lambda_{hV}$</td>
<td>scaling parameter for volume effects</td>
</tr>
<tr>
<td>$\lambda_p$</td>
<td>constant in equation 2.23</td>
</tr>
<tr>
<td>$\mu$</td>
<td>grain boundary chemical potential</td>
</tr>
<tr>
<td>$\mu_{gb}$</td>
<td>surface chemical potential</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density</td>
</tr>
<tr>
<td>$\rho'$</td>
<td>densification rate</td>
</tr>
<tr>
<td>$\rho^*$</td>
<td>density of ceramic following sintering</td>
</tr>
<tr>
<td>$\rho_0$</td>
<td>density of pore free ceramic</td>
</tr>
<tr>
<td>$\rho_1$</td>
<td>density of phase 1</td>
</tr>
<tr>
<td>$\rho_2$</td>
<td>density of phase 2</td>
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<tr>
<td>$\rho_b$</td>
<td>density of binder</td>
</tr>
<tr>
<td>$\rho_c$</td>
<td>density of ceramic</td>
</tr>
<tr>
<td>$\rho_f$</td>
<td>density of fluid</td>
</tr>
<tr>
<td>$\rho_{Gc}$</td>
<td>green body density of ceramic</td>
</tr>
<tr>
<td>$\rho_{Gs}$</td>
<td>green body density of starch</td>
</tr>
<tr>
<td>$\rho_i$</td>
<td>initial density</td>
</tr>
<tr>
<td>$\rho_m$</td>
<td>density of matrix</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>density of starch</td>
</tr>
<tr>
<td>$\rho_{sol}$</td>
<td>density of solvent</td>
</tr>
<tr>
<td>$\rho_{th}$</td>
<td>theoretical density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stress</td>
</tr>
<tr>
<td>$\sigma_f$</td>
<td>Strength</td>
</tr>
<tr>
<td>$\sigma_{f0}$</td>
<td>Strength of pore free material</td>
</tr>
<tr>
<td>$\sigma_{gb}$</td>
<td>gradient of stress acting normal to the grain boundary</td>
</tr>
<tr>
<td>$\sigma_i$</td>
<td>stress required to initiate fracture</td>
</tr>
<tr>
<td>$\sigma_{\infty}$</td>
<td>applied stress during sintering</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Poisson’s ratio</td>
</tr>
<tr>
<td>$\nu_0$</td>
<td>Poisson’s ratio of pore free material</td>
</tr>
<tr>
<td>$\omega$</td>
<td>angular velocity</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>vacancy volume</td>
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1.1 Project background

Alumina is the most widely used engineering ceramic with £1.7 billion (42%) market share in 1997. This represented a tonnage production in excess of 50% of the advanced ceramics market. Despite such large quantities being manufactured routinely, the fundamental understanding of the sintering behaviour has not advanced significantly since the pioneering work by Coble in the 1960's. To determine the sinterability of a new powder it is still conventional to conduct experimental trials. Many of the models that have been developed to describe the sintering behaviour of ceramic powders have considered only ideal systems consisting of equisized interacting particles where matter transport is accomplished through one mechanism only. These models can provide only an indication of the factors that affect the sintering process. Hence, there is much interest in refining these simple sintering models facilitating better predictions of the densification of powders. With more representative sintering models it will become possible to sinter components to higher tolerances without extensive experimental trials, so minimising expensive post sintering machining. To describe the sintering behaviour of real powders better, sintering models must consider the effects of variations in particle size, particle shape, particle packing, the effect of large pores and the effect of multiple matter transport mechanisms. Such models are currently being developed. The current work aims to contribute to the development of such sintering models by producing high quality data to validate theoretical predictions made by a model designed to address the issues of variation in particle size and the sintering of large pores. Specifically,
the work will examine the initial stage of sintering of a powder with a bimodal powder size distribution. This is the first stage of addressing the issue of real powders which have a range of powder particle sizes. Model predictions of the sintering behaviour of large pores have previously stated that large pores will not shrink during sintering without grain growth. Development of new models that address the issue of variations in the size of grains surrounding the pores indicate that pore shrinkage is possible (Pan et al., 1999). Further experimental work will therefore examine the sintering behaviour of large pores to determine the accuracy of predictions of large pore instability.

With the production of ceramic bodies containing large isolated pores it is also of interest to examine the effect of porosity on the mechanical and thermal shock properties of alumina. A study of the effect of iron particulates in an alumina matrix (Aldridge, 1996) showed that an improvement in both the resistance to crack initiation and propagation as a result of thermal shock could be achieved through the addition of weakly bonded iron particles into an alumina matrix. Due to the weak interfacial bonding between the iron and alumina it was postulated that the improvements in thermal shock resistance were not caused by the plastic deformation of the iron particles in the crack wake. Instead it was considered that the role of iron was negligible and that the iron particles acted as pseudo-pores with crack paths following the weak iron-alumina interface. There is, however, considerable disagreement in the literature regarding the effect of porosity on the thermal shock resistance, with both increases and decreases in thermal shock resistance being reported. As a further aim this work will examine the effect of porosity on material properties and thermal shock resistance.
Chapter 1 - Introduction

1.2 Thesis outline

This thesis has been divided into eight chapters of which this is the first. The second chapter is the literature review which addresses separately the background information relevant to sintering and pore removal, porosity dependence of material properties and the thermal shock resistance of ceramics and the effect of porosity. Chapter 3 describes the materials and sample preparation techniques employed. Chapters 4, 5, 6 and 7 relate to the main experimental studies conducted as part of this work and each describe the experimental techniques employed, results and discussion. Chapter 4 reports the in situ sintering study and examines the applicability of a state-of-the-art densification model. Chapter 5 presents the work detailing the behaviour of large pores during sintering, and describes the microstructure of the porous samples used to study the effect of porosity. The effect of porosity on strength and Young’s modulus, and the effect of porosity on thermal shock behaviour are then described in chapters 6 and 7 respectively. Finally chapter 8 presents the conclusions from the study and directions for future work.
CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

The principal aims of this work are to examine the initial stage of the solid state sintering process and the shrinkage of large pores to aid in the development of new sintering models designed to better address the nature of real powders. A further aim of this work is to examine the effect of large isolated pores on material properties and thermal shock resistance. The review of literature has been divided into three sections to address separately the relevant issues of sintering and pore shrinkage, variation of mechanical properties with porosity and effect of porosity on the resistance to thermal shock.

2.2 SOLID STATE SINTERING

2.2.1 Introduction

At present, simple models exist for various stages of sintering but there is no coherent simple model able to deal with the complexities of real powders. An ideal model would predict microstructural evolution, densification rates, residual stresses and final component dimensions.

This section of the literature review describes the development of models from simple thermodynamic considerations, to computer simulations that begin to address the issues associated with real powders such as a range of particle sizes.
As the system geometry varies with sintering the sintering process is conventionally divided into three geometrically separate stages – initial, intermediate and final stages. During these three stages up to six separate diffusion mechanism operate simultaneously leading to densification and grain growth. Only the initial and final stages of densification are considered here as models for the intermediate stage do not accurately describe the geometry of the system (Ashby, 1974).

2.2.2 Driving force for sintering

The thermodynamic driving force for densification of a ceramic powder compact is the minimisation of the energy associated with the system which is given by the sum of the energies associated with the bulk, grain boundaries and surfaces of the material as shown by:

\[ G_t = G_v + G_{gb} + G_s \]  
Eqn. 2.1

where \( G \) is the free energy with subscripts \( t \), \( v \), \( gb \) and \( s \) indicating total, volume, grain boundary and surface respectively. A reduction in the total free energy of the system can be accomplished through the replacement of the free surfaces with grain boundaries (i.e. densification). These energy considerations show that it is thermodynamically feasible to densify a ceramic green body but give no indication of the rate at which densification will occur. Along with thermodynamic considerations, it is necessary also to examine the kinetics of densification to ascertain if densification will occur at a significant rate.

To produce densification rate equations for the sintering process, the geometric changes that occur must be considered. Conventionally, the solid state sintering of powders is divided into three stages each characterised by a different geometry. Initial stage sintering is considered to operate following the formation of spontaneous...
bonds between particles. These bonds are a result of the interaction of interparticle forces and give rise to a small curvature between particles (Prochazka & Coble, 1970, Swinkels & Ashby, 1981) and possible particle rearrangement (Petzow & Exner, 1976). During the initial stage of sintering the individual particles are clearly discernible and the size of the neck between particles increases until neighbouring necks begin to interact when their size is approximately 20 percent of the cross-sectional area of the particles. After this time the initial stage is considered to have terminated and the intermediate stage commenced (Coble, 1961). The interaction of particle necks results in a change in microstructure to one that can be characterised by a series of interconnecting pore channels. With continued neck growth the diameter of the pore channels become smaller until the pores become isolated and equiaxed at approximately 92% theoretical density. These isolated pores are characteristic of the final stage of sintering.

2.2.3 Initial stage sintering

The initial stage of sintering is generally simplified to a geometric model consisting of two interacting spheres which are isolated from the surrounding particles. To produce the densification rate equations, it is necessary to consider the flow of matter within the system which is controlled by differences in chemical potential between points. The chemical potential below a convex surface, such as the surface of a sphere, is higher than that for a flat surface. Conversely the chemical potential below a concave surface, such as the neck between particles, is lower than that for a flat surface. Within a system these differences in chemical potential will result in atom migration from areas of high potential to areas of low potential. For the simplified geometric model used to describe initial stage sintering, the differences in chemical potential will cause atom migration towards the neck region from the surface, bulk and/or grain boundary. With no externally applied pressure there will be six known
material transport mechanisms simultaneously contributing to the sintering process as shown in Fig. 2.1 (Ashby, 1974).

Figure 2.1 - Schematic of two sintering equisized particles with the six transport mechanisms shown (after Ashby, 1974)

Not all of the material transportation mechanisms can result in densification. For densification to occur it is necessary for the centres of the two particles to approach, hence material must be removed from the region between the particles. Only grain boundary and lattice diffusion, with matter diffusing away from the grain boundaries or dislocations within the grain, are able to effect densification. Surface diffusion, evaporation/condensation, and lattice diffusion of matter from the surface, will produce no densification and instead lead to coarsening of the particles. The effects of the various diffusion mechanisms are summarised in table 2.1.
Table 2.1 – Mechanisms for sintering (after Ashby, 1974)

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Diffusion path</th>
<th>Vacancy sink</th>
<th>Vacancy source</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Surface diffusion</td>
<td>Surface</td>
<td>Neck</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Lattice diffusion</td>
<td>Surface</td>
<td>Neck</td>
<td>Neck growth only</td>
</tr>
<tr>
<td>3</td>
<td>Vapour Transport</td>
<td>Surface</td>
<td>Neck</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Boundary diffusion</td>
<td>Boundary</td>
<td>Neck</td>
<td>Neck growth and densification</td>
</tr>
<tr>
<td>5</td>
<td>Lattice diffusion</td>
<td>Boundary</td>
<td>Neck</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Lattice diffusion</td>
<td>Dislocations</td>
<td>Neck</td>
<td></td>
</tr>
</tbody>
</table>

2.2.4 Initial stage sintering models

2.2.4.1 Geometry independent model

An early model used to describe the effect of the material transport mechanisms did not consider one specific geometry, but instead examined the effect of scale on the time taken to achieve a geometrically identical change (Herring, 1950). By relating the two geometries through a scaling parameter, $\lambda_h$, such that $R_1\lambda_h = R_2$, it was shown that the time taken to achieve geometrically identical changes was proportional to the volume of material moved and inversely proportional to the flux and size of the diffusion path as shown by:
Chapter 2 - Literature Review

\[ \Delta t \propto \frac{V}{J A_{\text{diff}}} \]  
Eqn. 2.2

hence

\[ \frac{\Delta t_1}{\Delta t_2} = \frac{V_1}{V_2} \frac{J_2 A_{\text{diff},2}}{J_1 A_{\text{diff},1}} = \frac{\lambda_{hv}}{\lambda_{hj} \lambda_{hA}} \]  
Eqn. 2.3

where \( \Delta t \) is time taken, \( V \) is the volume, \( J \) is the flux and \( A_{\text{diff}} \) is the cross-sectional area of the diffusion path. Table 2.2 describes how each of these contributions is affected to a different extent by the size of the system and hence results in a different scaling parameter. Using equation 2.2 to relate the scaling parameters to the time taken to achieve geometrically identical changes it can be seen that the net scaling parameter for surface and grain boundary diffusion is \( \lambda_h^4 \), while that for bulk diffusion is \( \lambda_h^3 \).

<table>
<thead>
<tr>
<th>Effect of system size</th>
<th>Scaling parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>( R^3 )</td>
</tr>
<tr>
<td>Flux</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>Diffusion path size</td>
<td>( R^2 ) (bulk diffusion)</td>
</tr>
<tr>
<td></td>
<td>( R ) (grain boundary/surface diffusion)</td>
</tr>
</tbody>
</table>

2.2.4.2 Equisized particle models

The scaling law can only be used to describe the effect on densification rate of varying the particle size in a known system. To predict the densification rate of an unknown system it is necessary to use analytical models to describing the sintering processes. The analytical models developed used the simplified initial stage sintering
geometry consisting of two interacting spheres. To simplify the modelling further, the two spheres were initially considered to be identical in size.

The various matter transport mechanisms that occur during sintering can be modelled by mathematically describing the geometric changes that occur as the two spheres interact. Figure 2.2 shows a simplified geometric arrangement used to model the bulk diffusion of matter from the grain boundary to the neck (mechanism 5).

Figure 2.2 – Geometric model used to describe the bulk diffusion of matter from the grain boundary to the neck where R is the particle radius, x is the radius of the neck, r is the curvature of the neck and y is the degree of overlap between particles

As the two particle centres approach, the matter from the overlap region is redistributed to the neck region. By convention this flow of matter is described by the reverse flow of vacancies through the material. There is no net change in the amount of matter present and therefore the flow of matter/vacancies must equate to the change in volume of the neck region. By equating the rate of change of volume of the neck region (equation 2.4) with the vacancy flux (equation 2.5) it is possible to determine the densification rate equation for mechanism 5 (Coble, 1958, Johnson & Cutler, 1963).
\[
\frac{dV}{dt} = \pi x^2 \frac{dy}{dt}
\]
Eqn. 2.4

\[
J \Omega r^* = 4\pi D_v \Delta C \Omega r^*
\]
Eqn. 2.5

where \(\frac{dV}{dt}\) is the rate of change of volume of the neck region, \(J\) is the vacancy flux per unit length, \(\Omega\) is the volume of a vacancy, \(D_v\) is the vacancy diffusion coefficient, \(\Delta C\) is the change in vacancy concentration between the source and sink, and \(r^*\) is the radius of curvature of the neck. The radius of curvature of the neck is given by equation 2.6 and is a function of two curvatures - the radius of the contact between the two particles and the radius of curvature of the particle join as shown in figure 2.3. As \(r \ll x\) the radius of the neck can be approximated by \(r\).

\[
\frac{1}{r^*} = \frac{1}{r} + \frac{1}{x} \approx \frac{1}{r} \quad \text{as} \quad \frac{1}{r} > \frac{1}{x}
\]
Eqn. 2.6

Figure 2.3 – Schematic representation of the neck region showing the radius of curvature of the contact between the two particles, \(x\), and the radius of curvature of the particle join, \(r\)
The change in vacancy concentration between the source and the sink, \( \Delta C \), is given by:

\[
\Delta C = \frac{C_0 \gamma_s \Omega}{kT r^*}
\]

Eqn. 2.7

where the vacancy diffusion coefficient can be related to the lattice diffusion of atoms such that:

\[
D_v C_0 = D_l / \Omega
\]

Eqn. 2.8

where \( C_0 \) is the vacancy concentration under a flat surface, \( \gamma_s \) is the surface energy, \( k \) is Boltzmann’s constant, \( T \) is the absolute temperature and \( D_l \) is the lattice diffusion coefficient. Substitution of equations 2.6, 2.7 and 2.8 into equation 2.5 gives equation 2.9 which shows that the rate of matter diffusion is proportional to the lattice diffusivity, surface energy, and volume of the vacancy and inversely proportional to temperature.

\[
J \Omega r = \frac{4 \pi D_l \gamma_s \Omega}{kT}
\]

Eqn. 2.9

Equating equation 2.9 with equation 2.4 results in:

\[
x^2 \frac{dy}{dt} = \frac{4 D_l \gamma_s \Omega}{kT}
\]

Eqn. 2.10

which can then be solved with the use of the continuity equation (equation 2.11) derived solely from considerations of the system geometry where:

\[
y = x^2 / 4R_p
\]

Eqn. 2.11
and hence:

\[
\frac{dy}{dx} = \frac{x}{2R_p}
\]

Eqn. 2.12

where \( y \) is the degree of overlap between the two particles, \( x \) is the radius of the area of contact between the two particles and \( R_p \) is the radius of the particles. Substitution of equation 2.12 into equation 2.10 results in:

\[
\int x^3 dx = \int \frac{8D_i \gamma_s \Omega R_p}{kT} dt
\]

Eqn. 2.13

which can be evaluated to give:

\[
\left( \frac{x}{R_p} \right)^4 = 32 \frac{D_i \gamma_s \Omega}{R_p^3 kT} t
\]

Eqn. 2.14

Substituting the continuity equation (equation 2.11) into equation 2.14 produces an equation to describe the shrinkage of the compact given by:

\[
\left( \frac{y}{R_p} \right)^2 = \left( \frac{\Delta L}{L_0} \right)^2 = 2 \frac{D_i \gamma_s \Omega}{R_p^3 kT} t
\]

Eqn. 2.15

Using different geometric models, and corresponding equations for flux, it is possible to produce equations to describe the sintering behaviour of powders as controlled by the other material transport mechanisms. The general form of these equations is given by equation 2.16 while table 2.3 gives details of the constants \( B \), \( n \) and \( m \) determined for some of the other systems.

\[
\frac{\Delta L}{L_0} = \left( B \frac{D_i \gamma_s \Omega}{R_p^m kT} t \right)^n
\]

Eqn. 2.16
Table 2.3 – Values for constants for equation \( \text{equation}2.16 \) for various diffusion models

<table>
<thead>
<tr>
<th>Vacancy source</th>
<th>Vacancy sink</th>
<th>Path</th>
<th>( B_s )</th>
<th>( n )</th>
<th>( m )</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>neck</td>
<td>boundary</td>
<td>Bulk</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>Coble (1958)</td>
</tr>
<tr>
<td>neck</td>
<td>boundary</td>
<td>Boundary</td>
<td>15( \delta_d )</td>
<td>3</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>dislocations</td>
<td>boundary</td>
<td>Bulk</td>
<td>-</td>
<td>2/3</td>
<td>3</td>
<td>Johnson &amp; Cutler (1963)</td>
</tr>
<tr>
<td>neck</td>
<td>boundary</td>
<td>Bulk</td>
<td>31/( \pi^2 )</td>
<td>2.17</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>neck</td>
<td>boundary</td>
<td>Boundary</td>
<td>50( \delta_d/7\pi )</td>
<td>3.23</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

where \( \delta_d \) is the thickness of the diffusion path (i.e. grain boundary thickness).

The models obtained for each system show a dependence on particle size, given by \( m \), which is related to the diffusion mechanism being modelled. There is excellent correlation with Herring’s scaling law which predicted the same grain size dependence for the respective diffusion mechanisms.

### 2.2.4.3 Initial stage sintering of alumina

A number of studies have been conducted to determine the sintering mechanisms that operate in alumina. Due to multiple material transport mechanisms giving rise to similar densification behaviour it is not possible to determine the sintering mechanism from density changes. Instead studies of neck growth behaviour of single crystal alumina on sapphire surfaces were used to identify the dominant material transport mechanism as lattice diffusion (Coble, 1958). To measure the size of the neck region accurately it was necessary to use relatively large particles (40 – 3000 \( \mu \)m) and associated high sintering temperatures (1600 °C). The large particle sizes and high temperatures employed in this study are not representative of a real system and hence lattice diffusion may not always be the dominant diffusion
mechanism. A combination of the lattice and grain boundary diffusion model (Johnson & Cutler, 1963) showed that the dominant diffusion mechanism was a function of particle size and temperature. Large particles, and the associated high temperatures required for sintering of these particles, favour the lattice diffusion mechanism. It is, therefore, reasonable to assume that boundary diffusion may dominate during the sintering of smaller particles at a lower temperature; however, direct experimental verification has not been possible.

The rate equations derived in the previous section assume that only one diffusion mechanism is operational. With the simultaneous action of multiple diffusion mechanisms it is impossible to use direct experimental observations to determine the dominant sintering mechanism as the rate equation exponents will be controlled by the relative contributions of each mechanism (Ashby, 1974). By equating the rate equations for the different diffusion mechanisms and solving for neck size as a function of temperature it is possible to construct a sintering diagram that shows which mechanism is dominant as a function of temperature and neck size or density (Ashby, 1974, Swinkles & Ashby, 1981). Examination of the sintering diagrams shows that powders composed of small particle sizes and sintered at medium temperatures are likely to be dominated by the grain boundary diffusion mechanism. This is in agreement with the findings of Johnson and Cutler.

The nature of the grain boundary diffusion mechanism (mechanism 4) has been re-examined in light of the simultaneous action of multiple mechanism. The densification rate equations developed previously assumed that matter arriving at the neck is instantly redistributed over the surface of the particles so allowing the curvature of the neck to be more readily defined. This rapid redistribution of matter has been questioned and a new coupled surface-boundary diffusion mechanism proposed where the matter arriving is not instantly redistributed. The coupled surface-boundary diffusion model considers the case of atoms arriving at the neck at
a faster rate than they are redistributed, resulting in a decrease in neck curvature and hence driving force. This decrease in driving force will alter the flux of atoms and again cause a change in the curvature of the neck. The final neck geometry is one where an equilibrium condition exists between the flux of arriving and departing atoms. The sintering diagrams, developed previously, were modified to account for this altered mechanism (Swinkles & Ashby, 1981) and it was shown that for low densities and low to moderate temperatures the dominant mechanism is that of coupled surface-boundary diffusion (Swinkles & Ashby, 1981, Pan et al., 1998). As the sintering of alumina is generally conducted at relatively low temperatures (1400 –1500 °C) the initial stages of sintering (low density) can be considered to be dominated by the coupled surface-boundary diffusion mechanism.

2.2.4.4 Effect of bimodal particle size distribution on sintering

Sintering equations have been developed that allow the densification and neck growth of powder compacts to be predicted approximately. Further work is required to predict better the densification behaviour of powders. The models used are unrepresentative of real powders which are not composed of particles of a single size. The effect of a range of particle sizes is too complex to solve as it would require the use of particle by particle computer simulations to model the sintering of a real powder. Currently the variations in particle size are incorporated into model predictions by examining the case of particles of two different sizes.

An early attempt to deal with the variation in particle sizes of real powders examined the case of a linear array of particles of two sizes (Coble, 1973). Using an identical analytical method as discussed previously it was possible to produce equations to describe the lattice and grain boundary diffusion controlled sintering mechanism. The two equations are of the form:
where $B_3$ is a constant. The constant $n$ was found to be the same as that predicted for monosized spheres, while the constant $m'$ was found to be 1 and 2 for volume diffusion and boundary diffusion respectively. It can be seen that by equating $R_L$ to $R_S$ the previously derived equations, for monosized powders, are obtained with the grain size dependence, $m$, of 3 and 4 as previously shown.

Due to the constantly varying conditions that occur with the coupled surface-boundary diffusion mechanisms it is not possible to obtain rate equations using the analytical techniques described (Johnson & Cutler, 1963, Pan et al., 1998). The coupled surface-boundary mechanism can be examined using computer simulation techniques from which rate equations can then be obtained. This technique has been used to study the sintering of two different sized spheres controlled by the coupled surface-boundary diffusion mechanism (Pan et al., 1998). As with previous work, the model considered the geometric system of two different sized spheres in contact with each other where there is no interaction between the particle pair and the neighbouring particles.

The flux of matter at any one point of the system can be defined by Fick's law (equation 2.18) enabling the flow of matter through the system to be modelled using a finite difference technique.

$$J = -\frac{D \delta_s}{kT} \Delta\mu$$

Eqn. 2.18

where $J$ is the volume of matter flowing across unit area perpendicular to the flux direction, $\delta_s$ is the thickness of the layer through which the material diffuses, $D$ is
diffusivity (surface or grain boundary), and $\mu$ is the chemical potential for grain boundary or surface diffusion given by equations 2.19 and 2.20 respectively:

$$\mu_{gb} = -\Omega \sigma_{gb} \quad \text{Eqn. 2.19}$$

$$\mu_s = -\Omega \gamma_s \kappa \quad \text{Eqn. 2.20}$$

where $\kappa$ is the principal curvature of the surface and $\sigma_{gb}$ is the gradient of stress acting normal to the grain boundary.

Computer simulations allow the changes in system geometry to be calculated for variations in the relative particle sizes, ratio of surface and boundary diffusivities, the ratio of boundary and surface energies and the level of applied stress. From these simulations it was shown that: (i) if the small particle is close in size to the large particle then it has a greater influence on the shape evolution of the system. This is reasonable as a small particle would be removed rapidly without the large particle undergoing large changes in shape and subsequent system evolution would be dictated by the large particles, (ii) variations in the ratios of the diffusivities were shown to control which diffusion process dominated with the rate of sintering controlled by the slower mechanism. However, the shape evolution of the system was found to be largely independent of the ratio of the two diffusivities, (iii) differences in the ratio of grain boundary and surface energies were found to have a large effect on the shape evolution of the system, where large grain boundary energies caused the small particle to maintain a rounder shape during sintering in order to minimise the size of the grain boundary. \cite{Pan et al., 1998}

The effect of variations in the ratio of the two particle sizes were examined further by keeping the ratio of surface energies and the ratio of diffusivities constant and plotting the approach velocity of the two particles against the radius of contact for different values of particle size ratio ($R_S/R_L$). The simulations showed that for
particle size ratios in excess of 0.5 the results could be described by a straight line where the position was a function of the particle size ratio as shown in figure 2.4.

Figure 2.4 – Computer simulation results showing relationship between shrinkage rate and contact radius for various ratios of particle size (after Pan et al., 1998)

A modified version of the equation proposed by Bouvard and McMeeking (1996) was used to describe the results generated by the computer simulations (equation 2.21).

\[
\frac{W'}{R_L e^*_{gb}} = 0.5 \left(1 + \frac{R_S}{R_L}\right) \left(\frac{\alpha^*}{(x/R_L)^4} + \frac{\beta^*}{(x/R_L)^2} \left(\frac{\sigma_{\infty} R_L}{\gamma_s}\right)\right)
\]

Eqn. 2.21
where $W'/R_L$ is the normalised shrinkage rate, $\sigma_\infty$ is the applied stress, $\alpha^*$ is a constant dependent on $D_s/D_g$, and $\beta^*$ is a constant dependent on $D_s/D_g$ and $\sigma_\infty$, and the reference strain rate ($\varepsilon'^*$) is given by:

$$
\varepsilon'^*_{gb} = \frac{D_{gb} \delta_{gb} \Omega \gamma_s}{k T R_L^4}
$$

Eqn. 2.22

The term $0.5(1-R_S/R_L)$ was included, in the equation proposed by Bouvard and McMeeking, to account for the decrease in approach velocity as the size of the small particle decreases. The results from the numerical analysis show that the value of $R_S/R_L$ does not significantly affect the relationship between the approach velocity and neck size provided that $R_S/R_L$ is greater than 0.5. A plot of normalised shrinkage ($W/R_L$) against normalised time ($t_{gb'}$) produced good agreement between the results for various values $R_S/R_L$ above 0.5. The resultant curve can be described by:

$$
\frac{W}{R_L} = \left(\lambda_p \ t \ \varepsilon'^*_{gb}\right)^{1/\sigma_p}
$$

Eqn. 2.23

where $n$ is a constant between 3 and 4 and $\lambda_p$ is a constant dependent on diffusivity and dihedral angle.

Within a powder compact, composed of small and large particles, there will be three types of contact – small-small, large-large and small-large. Assuming the normalised shrinkage rate will be the same for all of these contact types (see figure 2.4) then the strain rate can be given by:

$$
\varepsilon' = -\frac{1}{2} \chi(R_t, Vf_{Rs}) \frac{W'}{R_L}
$$

Eqn. 2.24

where $\chi(R_t, Vf_{Rs})$ is given by:
\[ \chi(R_r, Vf_{Rs}) = \frac{R_r^3(1 - Vf_{Rs})^2 + Vf_{Rs}(1 - Vf_{Rs})(1 + R_r)R_r + Vf_{Rs}^2}{R_r^3(1 - Vf_{Rs})^2 + 0.5 Vf_{Rs}(1 - Vf_{Rs})(1 + R_r)^2 R_r + Vf_{Rs}} \] Eqn. 2.25

where \( Vf_{Rs} \) is the volume fraction of small particles in the compact and \( R_r = R_s/R_L \).

The relative densification rate is given by:

\[ \frac{\rho'}{\rho} = -3e' \left( \frac{\rho}{\rho_i} \right)^{\frac{1}{3}} \] Eqn. 2.26

where \( \rho \) is the density of the compact, \( \rho' \) is the densification rate and \( \rho_i \) is the initial density of the compact. An expression for the relative densification rate can be obtained by substituting equation 2.24 and equation 2.23 (after differentiating with respect time) into equation 2.26:

\[ \frac{\rho'}{\rho} = \frac{2}{2n} \chi(R_r, Vf_{Rs}) \left( \frac{\rho}{\rho_i} \right)^{\frac{1}{3}} \left( \lambda_p e_{gb}' \right) \chi_{n_p} \left( \frac{t - \tau_p}{n_p} \right)^{n_p} \] Eqn. 2.27

Integration with respect to time of equation 2.27 produces:

\[ 1 - \left( \frac{\rho_i}{\rho} \right)^{\frac{1}{3}} = \frac{1}{2} \chi(R_r, Vf_{Rs}) \left( \lambda_p e_{gb}' \right) \frac{1}{n_p} \frac{1}{t^n_p} \] Eqn. 2.28

For a given system (i.e. constant temperature, material) it can be seen that the strain rate and \( \lambda_p \) will be constant hence densification will be a function of \( \chi(R_r, Vf_{Rs}) \) and time. A straight line plot can be obtained by taking logs of both sides of equation 2.28 such that:

\[ \ln \left[ 1 - \left( \frac{\rho_i}{\rho} \right)^{\frac{1}{3}} \right] = \frac{1}{n_p} \ln \left[ \frac{1}{2} \chi(R_r, Vf_{Rs}) \left( \lambda_p e_{gb}' \right) \right] + \frac{1}{n_p} \ln[t] \] Eqn. 2.29
where a plot of $\ln \left[1 - (\rho_0/\rho)^{1/3}\right]$ against $\ln$ (time) should result in a straight line of slope $1/n$. Examination of equation 2.29 reveals that particle size variations should have no effect on the slope of the curve. The bimodal nature of the particles will only affect the relative position of the curve as variation in particle size distribution will effect the term $\chi(R_s, V_f R_s)$. No experimental verification of these findings has been published to date.

All of the models developed to describe the initial stages of sintering are based on two interacting spheres that are isolated from the surrounding grains. Once the necks begin to interact with the necks from neighbouring grains then the driving force for sintering will be reduced and the two sphere model will no longer be applicable (Johnson and Cutler, 1963). Conventionally, once particle necks begin to interact the intermediate stage of sintering is considered to have commenced. Models for this stage of sintering generally assume that the interacting necks form pore channels that can be described as cylindrical. This is only true for sintering of wires and is not strictly applicable to the sintering of spherical particles (Ashby, 1974). To obtain model predictions for the intermediate stage of sintering, data from the end of the initial stage and the beginning of the final stages of sintering can be extrapolated.

### 2.2.5 Final stage sintering – removal of pores

#### 2.2.5.1 Introduction

Sintering models have shown that the densification rate will increase with a decreasing particle size due to the higher driving forces and shorter diffusion distances. This is not always observed in practice and experimental observations have shown that compacts composed of very small powders often have difficulty in attaining full density (Kellett & Lange, 1989). The very small nature of the particles involved means that inter-particle forces becoming significant and hard agglomerates can be formed that are not easily broken up. These hard agglomerates of small
powders lead to the formation of large inter-agglomerate pores that can be difficult to remove during sintering.

Modelling of pore removal using models based on identically sized grains has shown that large pores are stable and cannot be removed. This was shown to be erroneous (Slamovich & Lange, 1992, Pan et al., 1998) as real systems are not composed of grains of one size. The variation in grain size allows matter to diffuse between particles resulting in pore shrinkage.

2.2.5.2 Thermodynamics and kinetics

The nature of the pore surface is controlled by the number of grains surrounding the pore and the equilibrium dihedral angle (Φ) which is a function of the surface (γ_s) and boundary (γ_{gb}) energies as shown by figure 2.5.

\[ \gamma_{gb} = 2 \gamma_s \cos(\Phi / 2) \]

Figure 2.5 – Effect of surface (γ_s) and grain boundary (γ_{gb}) energies on dihedral angle

If the equilibrium dihedral angle is maintained at each pore/grain boundary junction then the pore co-ordination number will determine whether the pore surface is convex or concave as shown in figure 2.6. If the pore co-ordination number is above the critical value the pore surface will be convex (C), while if it is smaller than the critical value the pore surface will be concave (A). Case B represents the situation where the pore co-ordination number is equal to the critical value.
Figure 2.6 - schematic illustration of effect of the ratio of pore size and grain size on pore geometry. (A) large grain size - concave and unstable; (B) grain size = critical grain size; (C) small grain - convex and stable (after Slamovich and Lange, 1992)

The relative stability of the various pore configurations can be examined by considering the flow of matter within the system. For pore shrinkage to occur, it can be seen that matter must diffuse from the grain boundary to the pore surface. This transport of matter is driven by the difference in chemical potential between the grain boundary and the surface. The sign of this chemical potential difference depends on the curvature of the surface (Lange, 1984). A concave surface will promote matter transport into the pore and hence pore closure (Kellett & Lange, 1989). The concave surface is thus considered unstable while the convex surface is stable (Slamovich and Lange, 1994, Kellet & Lange, 1989). Increasing the dihedral angle, through the use of sintering aids that decrease the boundary energy, will both increase the driving force for sintering and the critical co-ordination number so allowing more pores to shrink leading to higher end densities.

By considering thermodynamics arguments alone, grain growth can be seen to be favourable (Zhao & Harmer, 1988) as it would result in the curvature of the large pores changing from convex to concave in shape and so causing the pore to become unstable. Modelling of grain growth during sintering (Evans & Hsueh, 1986) has shown that there would be a rapid rise in the densification rate as the grain size approached that of the pores. With the presence of a very large grain next to a pore
thermodynamic considerations also predict a short term rise in the driving force for
densification (Xue & Brook, 1989). However, it is not possible to only consider the
driving forces for densification as they give no indication of the rate at which such
changes may take place. Kinetic arguments suggest that a reduction in grain size is
beneficial for densification. Herring’s scaling law indicates that the time to achieve a
geometrically identical change is inversely proportional to the grain size to a power
which depends on the diffusion mechanism in operation. If kinetics are also
considered it can be seen that increasing the grain size, to increase the
thermodynamic driving force, will result in a decrease in the rate of densification.
Grain growth is, therefore, detrimental to the sintering process despite the increases
in driving force (Xue & Brook, 1989).

Thermodynamic considerations of ideal equisized grain systems show that it is not
thermodynamically feasible to remove pores above a critical size without grain
growth. However, experimental observations have shown that large pores do shrink
during sintering (Slamovich & Lange, 1992). Two ZrC powders (one doped with 3
mol % Y2O3 and one with 8 mol % Y2O3) were used to study the densification
behaviour of large pores. ZrO2 doped with 3 mol % Y2O3 exhibits very slow grain
growth while ZrO2 doped with 8 mol % Y2O3 has much faster grain growth. Large
pores were introduced into both materials through the use of polystyrene spheres that
were burnt out during sintering resulting in isolated pores. The nature of the pores
was such that they were the same size in each material and differed only in the nature
of the surface curvature with concave pores present in the 8 mol % material and
convex pores in the 3 mol % material. It was found that the material containing
convex pores always densified at a greater rate, and to a higher level, than the
material containing concave pores which contradicts previous thermodynamic
arguments. The differences in the diffusivities of the two forms of ZrO2 were
considered to be minimal as creep experiments had showed identical behaviour when

25
normalised with respect to grain size. Additionally the higher oxygen vacancies of the 8 mol % doped material would be expected to result in higher diffusivities if there were a difference hence favouring the material exhibiting the slower densification rate. As the 8 mol % doped material exhibited a slower densification rate than the 3 mol % doped material it was thought that the improvement in densification was a result of the pore shape and not changes in diffusivities.

This apparent discrepancy between experimental observations and thermodynamic considerations was addressed by Pan et al. (1999) through the application of the computer simulation techniques employed to model the sintering behaviour of particles. The three systems that were examined are shown in figure 2.7.

![Pore types A, B, and C](image)

Figure 2.7 – Three pore morphologies modelled by Pan et al.

Pore types A and B both represent the ideal systems that have been modelled previously using analytical techniques. In both cases the pore is surrounded by equisized grains, with pore type A representing the unstable concave pore and pore type B representing the convex pore. The third pore type, C, was envisaged to better describe the real pore system where pores are surrounded by alternating large and small grains. Computer simulations showed that pores of type A were unstable and shrank, while pores of type B were stable and tended to increase in size which is in agreement with conventional thermodynamic considerations. The results of the
computer simulations for pore type C, however, showed a marked increase in the shrinkage rate as shown by figure 2.8. Shrinkage of the pores was found to be accomplished by either of two mechanism where: (i) the small grains are squeezed into the pore as the large grains change shape (neighbour switching), or (ii) the small grains are consumed by the large grains (grain growth). These computer simulations have resolved the conflict between thermodynamic arguments and experimental observations by showing that shrinkage of large pores can be accomplished if there is a variation in the size of the grains surrounding the large pores.

![Figure 2.8](image)

Figure 2.8 – Schematic of predicted densification rates of ideal pore systems (after Pan *et al.*, 1999)

### 2.2.6 Summary

The processes of densification has been examined to gain an insight into the microstructural changes that occur during the sintering process. The driving force for densification to occur was shown to arise from the minimisation of system energy. Corresponding microscopic driving forces generated due to differences in chemical potential give rise to matter transport allowing densification to occur. This transport of matter can be mathematically described to produce a series of models to describe the various mechanisms that operate during the initial stages of sintering. The models developed utilised ideal geometric systems and did not account for the variations in
particle size found in real systems. A computer simulation technique has been presented that attempts to describe the effect of a variation in the size of the particles.

The final stage sintering process involving the removal of large pores has been examined and the conflict between thermodynamic predictions and experimental observation addressed. Conventional thermodynamic arguments indicated that large pores would not shrink while experimental observations indicated otherwise. Analysis of a number of model pores systems using computer simulations have revealed that the presence of a variation in grain size surrounding the pore gives rise to pore shrinkage. Without this grain size variation the pore was shown to increase in size as predicted by idealised thermodynamic considerations.

2.3 EFFECT OF POROSITY ON MATERIAL PROPERTIES

2.3.1 Introduction

Material properties vary in three different ways with increases in the level of porosity. The material behaviour can be described as porosity independent, dependent on the amount of porosity, and dependent on the amount and type of porosity.

The type of material properties that exhibit no porosity dependence are reliant on the nature of the atomic bonding within material. Such properties include lattice spacing and unit cell volume. Properties such as density and heat capacity are included in the second group and are dependent on only the amount of porosity. The third form of porosity dependence can be subdivided into three further groups where flux (or load) is transmitted though the solid phase (mechanical, electrical and thermal properties), where flux is transmitted through the pore phase (surface area, tortuosity) and where
flux is transmitted through both the solid and pore phase (thermal conductivity at high temperatures).

This section of the literature review describes the porosity dependence of the material properties that affect the thermal shock resistance of a material. The majority of data available relate to Young’s modulus which will, therefore, be considered in more detail. If other material properties depend on porosity in a similar manner, then theoretical models developed to describe Young’s modulus dependence on porosity can readily be applied to predict the porosity dependence of other properties. The most widely used technique to describe the porosity dependence is through the use of an empirically derived exponential relationship between material property and amount of porosity known as the Spriggs model. Of the properties examined only thermal expansion is not described by Spriggs’ model and exhibits no dependence on porosity as the pore phase is unable to exert a significant force on the solid phase.

This section of the literature review has been organised such that the elastic, fracture and thermal properties are grouped together. Where possible, experimental data from the literature is included for completion.

2.3.2 Young’s modulus

2.3.2.1 Introduction

The development of an understanding of the way in which porosity affects the material properties began with the use of empirical equations based solely on experimental observations with no understanding of the mechanism involved. Modelling of simplified porous systems yielded semi-empirical models that were later improved upon with more detailed modelling of the pore structure. It was found that the material behaviour predicted by these theoretical models could be accurately
described using the empirical models originally developed. The simple form, and ease of use, of the empirical models facilitates comparisons between the observed variations in material properties with those predicted by the theoretical models.

2.3.2.2 Empirical models

One of the first studies on how mechanical properties altered with porosity concerned the variation of strength with porosity (Ryshkewitch, 1953). Analysis of the data revealed an exponential dependence of strength on porosity (Duckworth, 1953). This exponential equation was later used to describe the variation of Young's modulus with increase in porosity as shown by equation 2.30 (Spriggs, 1961)

\[ E = E_0 \exp(-b_E V_{fp}) \]  

Eqn. 2.30

where \( E \) and \( E_0 \) are the Young's modulus of the porous and pore free materials respectively, \( b_E \) is an empirical constant and \( V_{fp} \) is the volume fraction of porosity. Equation 2.30 is referred to as Spriggs' equation in literature.

There is no theoretical basis for the property-porosity dependence given by equation 2.30. A semi-empirical model was developed, to include an understanding of the physical processes involved, by considering the macro material behaviour of a porous body (Phani, 1987). A porous body can be defined as a block of material (figure 2.9) with an effective modulus \( E \) and a cross-sectional area, A. If the porous body is subjected to a load, \( P \), then the extension of the body will be given by:

\[ \delta = \frac{P/A}{E/l} \]  

Eqn. 2.31

where \( l \) is the length of the block. The porous body can also be considered to be composed of thin sections of thickness \( dx \) where the area and Young's modulus of
the solid material are given by $A_\times$ and $E_0$ respectively. When the element is subjected to a load $P$ the extension ($\delta_\times$) will be given by:

$$\Delta L = \frac{P/A_\times}{E_0/dx}$$

Eqn 2.32

![Figure 2.9 - Geometry of porous body and element of body](image)

Equations 2.31 and 2.32 can be related as the total extension of the body must be equal to the sum of the extensions of all of the individual elements. Hence it is possible to relate the effective Young’s modulus and the pore free Young’s modulus as shown by:

$$\Delta L = \frac{P/A}{E/L} = \int_0^L \frac{P/A_\times}{E_0} \, dx$$

Eqn. 2.33

Equation 2.33 can then be rearranged to relate the two Young’s moduli with the volume fraction of porosity as shown by:

$$E = E_0 \int_0^L \left(1 - Vf_p \right) \, dx$$

Eqn. 2.34

Due to the complex nature of porosity in a real system it is not feasible to evaluate equation 2.34. It is possible to predict that the resultant porosity dependence will be a
function of \((1-Vf_p)\). The simplest mathematical function that includes \((1-Vf_p)\) and satisfies the boundary conditions of \(E = E_0\) when \(Vf_p = 0\) and \(E = 0\) when \(Vf_p = 1\) is given by:

\[
E = E_0 \left(1 - Vf_p\right)^{n_e}
\]

Eqn. 2.35

where \(n_e\) is a constant. Observation of the dependence of Young’s modulus on porosity of materials showed that at a critical level of porosity (percolation limit) the material properties dropped abruptly to zero when material continuity was lost. A second term was subsequently added to equation 2.35 to account for this loss of material continuity as shown by:

\[
E = E_0 \left(1 - aVf_p\right)^{n_e}
\]

Eqn. 2.36

where \(a = 1/\)percolation limit. Equations 2.35 and 2.36 are still empirical in nature and offer no advantage over Spriggs’ model. Figure 2.10 shows a comparison of Spriggs’ equation and equations 2.35 and 2.36 which demonstrates that over a limited porosity range all three curves can describe the same behaviour through varying the empirical constants. Due to the abundance of literature data relating to Spriggs’ equation and the simplicity of its form, Spriggs’ equation is often used as a means of comparing the different predictions of material behaviour and experimental results as shown by table 2.4, in which empirical constants for Spriggs’ equation area given for a number of studies on the effect of porosity on Young’s modulus.
Figure 2.10 – Comparison of Spriggs’ equation and equations 2.35 and 2.36 demonstrating that good agreement can be obtained between the models by varying the value of the empirical constants

(Spriggs $b_\text{E} = 2.8$; eqn. 2.35 $n_\text{E} = 2.8$; eqn. 2.36 $n_\text{E} = 1.7$, $a = 1.5$)
Table 2.4 – Reported values of $b_E$ for variation of Young’s modulus with porosity

<table>
<thead>
<tr>
<th>Data</th>
<th>Material</th>
<th>Type of porosity and porosity range (%)</th>
<th>$b_E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coble &amp; Kingery (1956)</td>
<td>Alumina</td>
<td>Isolated pores 10.0-37.0 %</td>
<td>2.73$^\dagger$&lt;br&gt;$2.8^\ddagger$</td>
</tr>
<tr>
<td>Crandall et al (1960)</td>
<td>Alumina</td>
<td>Hot press partial sintered 0.3-4.32 %</td>
<td>4.08$^\dagger$</td>
</tr>
<tr>
<td>Spriggs &amp; Vasilos (1961)</td>
<td>Alumina</td>
<td>Hot press partial sintered 0.93-32.28 %</td>
<td>4.35$^\dagger$&lt;br&gt;$3.95^\ddagger$</td>
</tr>
<tr>
<td>Lang (1960)$^\dagger\ddagger$</td>
<td>Alumina</td>
<td>Cold press partial sintered 2.13-16.42 %</td>
<td>3.44$^\dagger$&lt;br&gt;$3.95^\ddagger$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cold press partial sintered 4.09-16.42 %</td>
<td>3.55$^\dagger$&lt;br&gt;$3.95^\ddagger$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hot press partial sintered 0.11-2.78 %</td>
<td>1.61-2.06$^\dagger$&lt;br&gt;$3.95^\ddagger$</td>
</tr>
<tr>
<td>Spriggs et al (1962)</td>
<td>Magnesia</td>
<td>Partial sintered 0-25 %</td>
<td>4.74</td>
</tr>
<tr>
<td>Hasselman et al. (1964)</td>
<td>Glass</td>
<td>Isolated pores</td>
<td>2.1$^\ddagger$</td>
</tr>
<tr>
<td>Biswas (1976)</td>
<td>PZT</td>
<td>Isolated pores</td>
<td>2.6$^\ddagger$</td>
</tr>
<tr>
<td>Wang (1984b)</td>
<td>Alumina</td>
<td>Partial sintered 0-30 %</td>
<td>5.16</td>
</tr>
<tr>
<td>Chen (1999)</td>
<td>Alumina</td>
<td>Isolated pores 0-50 %</td>
<td>~2.7</td>
</tr>
</tbody>
</table>

Where two values of $b_E$ are given they relate to analysis of the data by different investigators. $^\dagger$ reported by Spriggs (1961), $^\ddagger$ reported by Knudsen (1962), $^\ddagger$ reported by Rice (1998) (Bold indicates studies conducted on isolated pores produced using a fugitive phase.)

Comparison of the empirical constants obtained for studies using porosity introduced using a fugitive phase and porosity introduced through partial sintering show a larger porosity dependence (higher $b_E$) for cases of partial sintering. This indicates that the nature of the porosity plays an important role in determining the level of porosity dependence of Young’s modulus. Pores introduced through partial sintering are expected to show a higher degree of interconnection than the isolated pores produced using a fugitive phase, hence it was proposed that the porosity dependence was related to the proportions of continuous pore phase and continuous solid phase structure (Knudsen, 1959, Spriggs, 1961).
### 2.3.2.3 Composite sphere models

One technique employed to model the dependence of Young’s modulus on porosity was to consider the porous body as a composite composed of a solid phase and a gaseous phase with a Young’s modulus of zero. By examining the case of a pore-solid composite, with the second phase properties taken to be zero, it can be seen that the upper bound would be given by a simple rule of mixtures \( E = E_0(1-V_{fp}) \) while the lower bound would be given by \( E = 0 \) irrespective of the degree of porosity. This is of limited use as the actual structure would be better described as a particulate composite with material behaviour within the bounds described above. Particulate composite behaviour has been modelled (Hashin, 1962) by considering a microstructure composed of an assembly of spheres of matrix material with reinforcement material placed concentrically within them as shown in figure 2.11.

![Figure 2.11 - Spheres, with reinforcement placed concentrically within the spheres, used to describe a particulate reinforced composite](image)

The volume fraction of the reinforcement phase was varied by altering the relative sizes of the matrix and reinforcement spheres. It was shown that the composite modulus could be given by:

\[
E = E_0 \left[ 1 + \frac{A_H(1 - E_r/E_0)V_{rf}}{1 - B_H(E_r/E_0 + (1 - E_r/E_0)V_{rf})} \right]
\]

Eqn. 2.37
where \( E \) is the Young’s modulus, with subscripts \( 0 \) and \( r \) indicating the matrix and reinforcement phases respectively, and \( A \) and \( B \) are empirical constants where \( B = A + 1 \). By equating the properties of the reinforcement to those of a pore (i.e. \( E_r = 0 \)) equation 2.38, describing the Young’s modulus of a porous body, was obtained (Hasselman, 1962).

\[
E = E_0 \left[ 1 + \frac{A H Vf_p}{1 - (A H + 1)Vf_p} \right] \quad \text{Eqn. 2.38}
\]

Although equation 2.38 was derived from considerations of the pore structure it cannot be used to predict the effect of porosity as the empirical constant, \( A \), has not been rigorously defined.

The derivation, by Hashin, of the equation to describe the behaviour of a particulate reinforced composite (equation 2.37) assumed that there would be no interaction between the neighbouring spheres as the radial stresses at the surface of the spheres were taken to be zero. Analysis of the system assuming that the radial stresses are not equal to zero results in a dependence of Young’s modulus on porosity given by equation 2.39 (Ramakrishnan & Arunachalam, 1990).

\[
E = E_0 \frac{(1 - Vf_p)^2}{(1 + (2 - 3\nu_o)Vf_p)} \quad \text{Eqn. 2.39}
\]

where \( \nu_o \) is the Poisson’s ratio of the pore free material. Equation 2.39, unlike equation 2.38, can be used to predict the porosity dependence of Young’s modulus as all of the terms have been defined during the derivation process. The model system used to model the porosity dependence is based on spherical inclusions within a matrix, hence equation 2.39 cannot be used to describe the behaviour of porosity resulting from partial sintering.
2.3.2.4 Pore stress concentration models

Hashin (1962) also developed an equation to describe the effect of low levels of reinforcement phase. This model was modified to account for porosity as the reinforcement phase (Rossi, 1968) where it was shown that the predictions of material behaviour could be described by:

\[ E = E_0 \left( 1 - M_p V_{fp} \right) \]  
Eqn. 2.40

where \( M \) is a coefficient dependent on the Poisson's ratio of the fully dense material. It was found that if the coefficient, \( M \), was equal to 2 then the error between predictions made by equation 2.40 and the Hashin equation were less than 1 %. It was reasoned that the porosity modelled by the Hashin equation was spherical in nature and that 2 is the value of the stress concentration around a spherical pore. It was postulated that the effect of non-spherical pores could be described by substituting for the maximum stress concentration factor around ellipsoidal pores, \( K_{\text{max}} \) (equation 2.41) for \( M \) in equation 2.40.

\[ K_{\text{max}} = \frac{5a_p}{4c_p} + \frac{3}{4} \quad \text{for } \nu = 0.2 \]  
Eqn. 2.41

where \( K_{\text{max}} \) is the maximum stress concentration factor generated around an ellipsoid, \( a \) is the diameter of the pore perpendicular to the stress and \( c \) is the diameter of the pore parallel to the stress. Model predictions show that pores orientated parallel with the loading direction will show a small decrease in the porosity dependence while pores orientated perpendicularly to the stress direction will show a large increase in the porosity dependence.

The prediction of the degree of porosity dependence of Young's modulus using the composite sphere model is limited to situations where the porosity can be described as isolated and spherical. If porosity is introduced through partial sintering of the...
matrix phase it is likely to be interconnected and non-spherical in nature which has been shown experimentally to afford a greater porosity dependence than isolated pores. For a given pore volume the shapes of the pores introduced through the use of partial sintering and fugitive phases can be approximated as ‘star’ shaped and spherical as shown in figure 2.12.

![Partial sintering induced pore](image) ![Fugitive phase induced pore](image)

Figure 2.12 – Schematic of the difference in pore shape of pores introduced through (a) partial sintering and (b) a fugitive phase

If the two pores are considered to have the same volume it is reasonable to assume that the stress concentration generated around the partial sintering induced pore would be larger than that generated around the spherical pore. By approximating the pores produced through partial sintering as ellipsoids orientated perpendicularly to the direction of stress it can be seen that pores introduced through partial sintering would give rise to a greater porosity dependence in comparison to spherical pores.

The validity of the stress concentration model is disputed (Rice, 1993b) because increases in the degree of porosity result in the inter-pore separation approaching that of the pore size. This decrease in the effective pore separation causes the stress concentrations, generated around each pore, to begin to interact so resulting in a decrease in the porosity dependence of material properties. This stress concentration interaction begins to occur when the separation between the pores approaches that of the pore size which occurs between 0.05 and 0.1 volume fraction porosity depending
on the pore packing. Experimental observations show no decrease in the porosity dependence of Young’s modulus as would be predicted. Extrapolation of this interaction behaviour, as shown in figure 2.13, shows that as the pores become closer together the load is transferred to the central section of material between the pores. This condition, where the load is carried by the central section of the body, is the basis of the minimum solid area model (Rice, 1993b, 1997).

![Figure 2.13 - Effect of interpore spacing on stress concentration](image)

The equation derived by Hashin, and subsequently described by equation 2.40, was developed for describing the behaviour of composites reinforced with low concentrations of second phase. Therefore, the pore stress concentration model is only applicable for relatively low levels of porosity. This limited applicability and questions about the validity of the stress concentration model have favoured the use of other theoretical models used to describe porosity dependence of Young’s modulus.
2.3.2.5 Minimum solid area model

The extrapolation of the pore stress concentration model to high porosities and consideration of the nature of porous material indicates that it is reasonable to assume that the mechanical properties may be controlled by the cross-sectional area of the solid material (Knudsen, 1959, Rice, 1993a). The transmission of load (or flux) will be limited by the minimum cross-sectional area, hence it is reasonable to assume that the minimum solid area controls the material properties.

Due to the complex nature of real systems it is necessary to consider an idealised structure. The most simple structure to visualise, and one that approximates random packing of spheres (Rice, 1993a), is that of a cubic array of equisized spheres as shown in figure 2.14. It is possible to use this cubic array of spheres to model both the case of isolated spherical porosity and porosity arising due to partial sintering by either considering the spheres as pores or solid material (Knudsen, 1959, Rice, 1993a).

![Cubic array of equisized spheres](image)

Figure 2.14 – Cubic array of equisized spheres

For the purposes of modelling it is assumed that each sphere is located in the centre of a unit cell such that the ratio of the volume of the sphere to that of the unit cell is equal to the volume fraction of the sphere phase. During the evolution of the model
microstructure it is assumed that the spheres shrink or grow such that their relative positions do not change. Further, when the spheres interact with each other it is assumed that they flatten where in contact with their neighbours.

Considering, first, the case of spherical porosity. It can be seen that when the spheres in the cubic array are just touching the cube faces (and each other) the volume fraction of porosity will be equal to 0.52. Decreases in the volume fraction of porosity can be described by reducing the size of the sphere (pore). During this stage the volume fraction of porosity is given by:

\[ V_{f_p} = \frac{4}{3} \pi R_p^3 \]

Eqn. 2.42

where \( R_p \) is the radius of the pore and \( L \) is the unit cell edge length. The corresponding minimum area fraction will be given by:

\[ A_{f_s(min)} = 1 - \frac{\pi R_p^2}{L^2} \]

Eqn. 2.43

where \( A_{f_s(min)} \) is the minimum solid area fraction. Using equations 2.42 and 2.43 it is possible to establish a relationship between volume fraction of porosity and Young’s modulus (\( E \) proportional to \( A_{f_s(min)} \)) for porosity volume fractions between 0 and 0.52. Predictions of Young’s modulus for porosity volume fractions greater than 0.52 requires the modification of equations 2.42 and 2.43 to account for the proportion of the pore outside of the unit cell as shown by the grey field in figure 2.15.
The modified equations for volume fraction porosity and minimum solid area fraction are given by equations 2.44 and 2.45. These equations are valid from porosity volume fractions of 0.52 to 0.97. At the porosity volume fraction of 0.97 the material continuity is lost and all material properties fall to zero.

\[
V_{f_p} = \frac{4/3 \pi R_p^3 - \pi h (h^2 - r_p^2)}{L^3}
\]

Eqn. 2.44

\[
A_{f_s(min)} = 1 - \frac{\pi R_p^2 - 4R_p^2 \cos^{-1}(L/2R_p) + 2 L (R_p^2 - L/4)^{1/2}}{L^2}
\]

Eqn. 2.45

To describe the porosity dependence of Young’s modulus for the case of porosity introduced through partial sintering it is necessary to consider the spheres as the solid phase. The starting condition of equisized spheres just touching now represents a volume fraction of porosity of 0.48. Higher volume fractions of porosity cannot be achieved as it would result in the material continuity being lost (i.e. \(V_{f_p} = 0.48\) is the percolation limit). The volume fraction of porosity present is now equal to the volume fraction of solid phase calculated for the previous case of isolated porosity so the equations are similar. The minimum solid area fraction equations are, however, different as a different area is now being considered. For the case of porosity
introduced using partial sintering the area fraction of interest is the linkage between the two particles given by $\pi r_p^2$ as shown in figure 2.15. The volume fraction and minimum area fraction equations are thus given by equations 2.46 and 2.47.

\[
V_{f_p} = 1 - \frac{4}{3} \pi R_p^3 - \pi h \left( h^2 - r_p^2 \right)
\]

Eqn. 2.46

\[
A_{f,(min)} = \frac{\pi r_p^2}{L^2}
\]

Eqn. 2.47

These two equations are valid up to a solid phase volume fraction of 0.97. At higher densities it is necessary to account further for the interactions of the protruding domes. Due to the complex mathematical relations and narrow porosity range it is convenient to approximate the change in Young’s modulus to a straight line between the results predicted at zero porosity ($E = E_0$) and the predicted value for a porosity volume fraction of 0.04. The results from the predictions of porosity dependence of Young’s modulus on porosity, introduced through partial sintering, and isolated spherical pores are presented in figure 2.16.

Figure 2.16 – Comparison of predicted porosity dependence of Young’s modulus for porosity introduced through partial sintering and a fugitive phase
2.3.2.6 Total solid area model

The total solid area model differs from the minimum solid area model in that the extension of the unit cell is not assumed to be uniform (i.e. equal to a body of uniform solid cross-sectional area equal to $A_{s(min)}$). The total solid area model assumes that the degree of extension of the solid phase varies as the solid area cross-section changes (Wang, 1984a). Using the same cubic stacking of spherical particles, as used by the minimum solid area model, it was shown that the total elongation of the unit cell, subjected to a load $P$, would be given by the sum of the individual elements of solid material such that equation 2.48 can be used to describe the elongation

$$\Delta L = \int_{-\frac{L}{2}}^{\frac{L}{2}} \frac{P/A}{E_0} \, dz$$  \hspace{1cm} \text{Eqn. 2.48}$$

This elongation can be substituted into an equation for the effective Young's modulus of a unit cell:

$$E = \frac{P/L^2}{\Delta L/L}$$  \hspace{1cm} \text{Eqn 2.49}$$

The resultant equation provides a relationship between the apparent and pore free Young's modulus as shown by:

$$E = \frac{E_0}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} A \, dz$$  \hspace{1cm} \text{Eqn. 2.50}$$

where $A$ is a function of $z$ defined by the model system. The volume fraction of porosity can simply be given by the same equation used to describe volume fraction in the minimum solid area model (equation 2.42). In essence the total solid area
model is the same as the empirical model developed by Phani (1987) except that the geometry of the system has been defined, thus enabling a relationship to be derived.

If the model system is loaded such that the cubic array of spheres is aligned with the stress direction then a relatively low degree of porosity dependence is obtained as shown by the ‘aligned array’ curve in figure 2.17. A higher porosity dependence can be obtained if the cubic array of spheres is considered not to be aligned with the direction for stress as shown by the ‘non-aligned’ array curve. In this instance bending moments and shear stresses are generated between the particles leading to an increased porosity dependence being observed.

Figure 2.17 – Total solid area model predictions for Young’s modulus dependence on spherical porosity, showing effect of aligned and non-aligned array

An approximate solution, given by equation 2.51, was proposed to describe the results predicted by the total solid area model (Wang, 1984a).

\[ E = E_0 \exp\left(-\left(b_\epsilon Vf_p + c_\epsilon Vf_p^2\right)\right) \]  \hspace{1cm} \text{Eqn 2.51}

where \(b\) and \(c\) are empirical constants determined to be 0.946 and 2.54 for the case of the spherical particle array aligned with the direction of stress and 2.15 and 4.01 for
the case of a non-aligned spherical particle array. It can be seen that at relatively low volume fractions of porosity the $V_{fp}^2$ term will tend to be negligible in comparison to the other terms. Hence at low porosities equation 2.51 will reduce to Spriggs' equation.

2.3.2.7 Comparison of models

A number of empirical and semi-empirical equations have been proposed to describe the porosity dependence of Young's modulus. It can be seen in figure 2.10 that over the limited porosity range of interest to this study ($V_{fp} < 0.2$) all of the empirical models can exhibit a similar behaviour (by varying the empirical constants) such that no one model is significantly superior to the others. The simplicity of, and the availability of data relating to, Spriggs' equation merit its use in describing the porosity dependence of Young's modulus and use in comparing theoretical model predictions.

When comparing the predictions afforded by the different theoretical models it is important to consider the type of porosity that is being modelled as this has a large influence on the porosity dependence of the material. Examining, first, the effect of isolated spherical pores introduced using a fugitive phase, it is possible to use all of the theoretical models to describe the effect of this type of porosity on Young's modulus. Figure 2.18 shows the predictions of porosity dependence given by the composite sphere (CSM), pore stress concentration (PSC), and minimum (MSA) and total (TSA) solid area models. When examining the relative merits of each model it is important to consider how the theoretical predictions compare to experimental data and the accuracy of the prediction of the percolation limit, where material continuity is lost. It can be seen from figure 2.18 that the pore stress concentration model fails to predict a reasonable percolation limit. As was discussed previously, the underlying theory of the pore stress concentration model has also been questioned, limiting its
potential applicability to low porosity volume fractions ($V_{fp} < 0.05$). Only the minimum and total solid area model predicts a percolation limit close to, but not equal to, $V_{fp} = 1$. A further indication that the composite sphere model does not accurately predict material behaviour is that the application of Spriggs’ equation to predictions made using the composite sphere model ($0 < V_{fp} < 0.2$) leads to a larger $b_E$ value of 3.34 which is greater than observed in practice. From the theoretical models examined here the minimum solid area model appears to offer the most accurate prediction of the Young’s modulus behaviour of porous bodies with a $b_E$ value of 2.55 and a predicted percolation limit of $V_{fp} = 0.97$.

![Comparison of theoretical model predictions for the case isolated spherical pores](image)

**Figure 2.18** – Comparison of theoretical model predictions for the case isolated spherical pores (inset graph shows the behaviour at low porosity levels)

Consider, now, the effect of porosity introduced through partial sintering which can only be modelled by the minimum solid area (MSA) and total solid area (TSA) models. The results of the predictions of porosity dependence are presented in figure 2.19. If the criteria of good agreement with experimental data and accurate prediction
of the percolation limit are again considered, it is evident that both models fulfil the
requirements and offer suitable predictions for material behaviour with $b_E$ values of
5.11 and 4.52 for the minimum solid area and total solid area models respectively.

![Graph showing comparison between MSA (partial sinter) and TSA models]

Figure 2.19 – Comparison of theoretical model predictions for porosity introduced
through partial sintering (inset graph shows the behaviour at low porosity levels)

Through comparison with experimental data, and examination of the model
applicability to multiple pore systems, the minimum solid area model is considered
to be the most applicable for describing the porosity dependence of Young’s
modulus. Material properties that are also dependent on the amount and nature of the
porosity should exhibit porosity dependence that can be described using the
minimum solid area and Spriggs’ equation.

### 2.3.3 Poisson’s ratio

Poisson’s ratio cannot be described using the models developed to model the
porosity dependence of Young’s modulus. However, Poisson’s ratio can be related to
Young's, shear and bulk moduli (as shown by equation 2.52) which can all be described using the Spriggs equation.

\[ v = \frac{E}{2G} - 1 = \frac{1}{2} \left( \frac{E}{3K} - 1 \right) \quad \text{Eqn. 2.52} \]

where \( v \) is Poisson’s ratio, \( G \) is shear modulus and \( K \) is bulk modulus. By substituting Spriggs’ equation for Young’s modulus and shear modulus, in equation 2.52, it is possible to determine the porosity dependence of Poisson’s ratio as shown by equation 2.53 (Spriggs & Brissette, 1962)

\[ v + 1 = (v_0 + 1) \exp \left( - (b_E - b_G) V_{fp} \right) \quad \text{Eqn. 2.53} \]

where \( b_E \) and \( b_G \) are the empirical constants relating to Young’s modulus and shear modulus respectively. It can be seen that Poisson’s ratio is dependent on the difference between the porosity dependence of the two modulii. The minimum solid area model predicts that both Young’s modulus and shear modulus exhibit the same porosity dependence. This indicates that Poisson’s ratio should be independent of porosity. Equation 2.53 can be approximated by a straight line as given by equation 2.54 (Spriggs & Brissette, 1962).

\[ v = v_0 + m V_{fp} \quad \text{Eqn. 2.54} \]

where \( v_0 \) is the Poisson’s ratio of a pore free material and \( m \) is an empirical constant. If the dependence of Young’s and shear modulus on porosity are identical then Poisson’s ratio should remain constant with increases in porosity (i.e. \( m = 0 \)). Table 2.5 shows values of \( v_0 \) and \( m \) determined for a number of systems where it can be seen that there is significant variation (\( m \) varies between +0.23 and −0.35) in the behaviour of Poisson’s ratio with increases in the level of porosity.
Table 2.5 - Dependence of Poisson’s ratio on porosity (calculated from observations of Young’s and shear moduli)

<table>
<thead>
<tr>
<th>Data</th>
<th>Material</th>
<th>Type of porosity</th>
<th>(v_0)</th>
<th>(m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spriggs &amp; Brissette (1962)</td>
<td>Al(_2)O(_3)</td>
<td>Partial sintered</td>
<td>0.257</td>
<td>-0.35</td>
</tr>
<tr>
<td>Coble &amp; Kingery (1956)</td>
<td>Al(_2)O(_3)</td>
<td>Isolated pores</td>
<td>0.23</td>
<td>+0.23</td>
</tr>
<tr>
<td>Lang (1960)</td>
<td>Al(_2)O(_3)</td>
<td>Partial sintered</td>
<td>0.24*</td>
<td>-0.21*</td>
</tr>
<tr>
<td>Spriggs et al. (1962)</td>
<td>MgO</td>
<td>Partial sintered</td>
<td>0.14</td>
<td>+0.19</td>
</tr>
</tbody>
</table>

* calculated using porosity dependence of E and G presented by Hasselman (1962) and Spriggs & Brissette (1962)

These variations in the porosity dependence of Poisson’s ratio may be a result of the difficulty in obtaining accurate data. Small variations in Young’s modulus and shear modulus will give rise to significant errors in Poisson’s ratio making it difficult to obtain experimental verification of the effect of porosity on Poisson’s ratio.

Due to the difficulty in obtaining accurate experimental data for examining the effect of porosity on Poisson’s ratio, a number of theoretical examinations have been conducted to gain a better understanding of the effect of porosity. One approach employed was to use the hollow spheres employed in the composite sphere model. This lead to an expression for Poisson’s ratio shown in equation 2.55 (Ramakrishnan et al., 1990).

\[
\nu = \frac{(4v_0 + 3Vf_p - 7v_0 Vf_p)}{4(1 + 2Vf_p - 3v_0 Vf_p)} \tag{Eqn. 2.55}
\]

The analysis predicted that the porosity dependence of Poisson’s ratio would depend on the value of Poisson’s ratio for a pore free material. Equation 2.55 predicts that
Poisson’s ratio will increase if $v_0$ is below 0.25 and decrease if it is above 0.25. This behaviour was also predicted by finite element analysis using a two dimensional mesh composed of sets of concentric circles where the volume fraction of porosity within the system was varied by changing the number of elements assigned with a modulus of zero (Ramakrishnan & Arunachalam, 1993). The applicability of 2-D analysis to model the effect of spherical porosity was questioned (Rice, 1998) as it was considered to describe the effect of aligned cylinders and not the case of spherical pores.

3-D finite element analysis, where the pores are described as spheres, has also been conducted (Agerwal, 1971) which shows that Poisson’s ratio decreases with increasing levels of porosity. Figure 2.20 shows a comparison of experimental data, and 2-D and 3-D finite element analysis relating to the effect of isolated spherical porosity on Poisson’s ratio. Due to the scatter in the experimental data it is not possible to determine the manner in which Poisson’s ratio depends on porosity. Comparison of all of the 3 sets of data indicate that with low level of porosity ($V_{fp} < 0.2$) the change in Poisson’s ratio can be considered to be minimal.
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Figure 2.20 – Comparison of experimental data (Coble & Kingery, 1956) and predictions using 2-D (Ramakrishnan & Arunachah, 1993) and 3-D (Agarwal et al., 1971) finite element analysis

2.3.4 Effective surface energy

The energy required to create a fracture surface in a fully dense homogenous material is given by equation 2.56 (Rice, 1998)

\[ \gamma_s \sim \frac{E}{l_s} \left( \frac{r}{\pi} \right)^2 \]  

Eqn. 2.56

where \( l_s \) is the equilibrium lattice spacing and \( r \) is the range of atomic force for bonding which are both independent of porosity. It was suggested that the Young’s modulus term could be modelled using the minimum solid area model (Rice, 1996b, 1998). However, this is not strictly applicable as the Young’s modulus term used in equation 2.56 is not the macro Young’s modulus, but instead describes the local value of Young’s modulus and is related to the strength of the atomic bonds. As the strength of these atomic bonds is constant the local Young’s modulus can also be considered to be independent of porosity. These considerations would indicate that the surface energy of a material is independent of porosity.
When considering the energy to fracture a porous body it can be seen that it is not necessary to create a fracture surface in the porous phase. Hence, the effective surface energy, given by the energy required to create a fracture surface in a porous body, will be proportional to the surface energy of alumina and the proportions of solid and pore phase present (equation 2.57)

$$\gamma_{\text{eff}} = A_f \gamma_s$$  \hspace{1cm} \text{Eqn. 2.57}

where $\gamma_{\text{eff}}$ is the effective surface energy and $A_f$ is the area fraction of solid material at the fracture surface. If the pores are homogeneously distributed throughout the body and the fracture surface cuts through the body on a plane normal to the direction of applied stress then the area fraction of the solid phase will be equal to the volume fraction of solid present. The effective surface energy will then be dependent on only the amount of porosity present as shown in equation 2.58.

$$\gamma_{\text{eff}} = (1 - V_{fp})\gamma_s$$  \hspace{1cm} \text{Eqn. 2.58}

A more realistic approach is to consider that fracture is likely to occur along the path of least resistance which can be approximated by the minimum solid area. It is thus reasonable to model the effective surface energy dependence on porosity in terms of the minimum solid area model.

A second fracture parameter to consider is the fracture toughness which can be related to the effective surface energy and the Young's modulus as shown in equation 2.59.

$$K_{IC} \sim (2E\gamma_{\text{eff}})^{1/2}$$  \hspace{1cm} \text{Eqn. 2.59}

where $K_{IC}$ is the mode 1 fracture toughness. In this instance $E$ is the macro Young's modulus and therefore can be described using the minimum solid area model. As both Young's modulus and effective surface energy can be described by the same model it
can be seen that fracture toughness too should exhibit a similar dependence on porosity.

Few experimental data are available to describe the porosity dependence of the effective surface energy or the fracture toughness of porous materials. Available data show that three trends are observed where fracture energy either shows the same, higher or lower dependence to that predicted by the minimum solid area model (Rice, 1996b, 1998). In a study of PZT containing spherical pores, introduced using a fugitive phase, fracture toughness and Young's modulus were shown to have a porosity dependence such that $b_K$ and $b_E$ were equal to 2.4 and 2.6 respectively (Biswaith & Fulrath, 1980 – reported by Rice, 1998). This degree of porosity dependence is in good agreement with that predicted by the minimum solid area model.

Other studies have shown that the effective surface energy and fracture toughness exhibit greater porosity dependence than is shown by Young’s modulus (Rice, 1998). This greater porosity dependence of fracture properties in comparison with Young’s modulus has only been observed in samples where porosity has been controlled through partial sintering. To achieve lower densities it is necessary to sinter the sample for longer periods of time so leading to grain growth which will give rise to increases in the energy required to fracture the sample. At low porosity levels the fracture energy will be high due to the low degree of porosity and the effects of large grain size. With increasing levels of porosity the effective surface energy will decrease due to increases in porosity and decreases in the grain size, hence exhibiting a higher porosity dependence in comparison to Young’s modulus which is only affected by the reduction in porosity. This effect highlights the need to consider all of the microstructural changes that occur. Where porosity is introduced using a fugitive phase the volume fraction of porosity is altered by varying the amount or size of the
fugitive phase. The matrix microstructure is, therefore, unaffected provided that the same sintering regime is used.

Decreases in the porosity dependence of fracture properties have also been observed where the effective surface energy decreases at a lower rate in comparison to Young's modulus and occasionally increases with increased levels of porosity. A lower porosity dependence of effective surface energy will be observed if crack advance is hindered by the presence of the pores (Roysten & Barrell, 1958). Examination of a model crack advancing through a porous body shows that the crack advancement could be hindered by bridging effects arising from crack blunting at pores or alternative fracture paths. Crack blunting may occur when a crack interacts with a pore and the stress concentration at the crack tip is reduced by the large curvature of the pore (Passmore et al., 1965). This pore-crack interaction will pin the advancing crack much as inclusions can pin cracks in composite materials. Alternative fracture paths can develop if a crack is temporarily halted by a local increase in the fracture energy ahead of the crack tip caused by variations in the concentration of pores. When the cracks become temporarily halted by either of these two mechanisms increases in energy are required to further propagate the macro crack. Chen (1999) reported an increase in fracture energy for samples containing low levels of porosity (0 - 0.2 Vfp) which was attributed to crack branching and deflection. Further increases in the level of porosity were shown to result in a decrease in fracture energy.

With samples containing porosity introduced through a fugitive phase the effective fracture energy is expected to exhibit a porosity dependence as characterised by the minimum solid area method unless pore-crack interactions occur that could give rise to lesser dependence on porosity.
2.3.5 Strength

2.3.5.1 Empirical models

The first attempts to study the effect of porosity on mechanical properties examined the variation of strength with increase in the level of porosity. In common with modelling of Young’s modulus these first models were empirical in nature and were developed by fitting equations to experimental data. One of the first empirical models (equation 2.60) was proposed by Bal’shin (1949 – reported by Knudsen, 1959) following work on partially sintered porous metal and cermet materials.

\[
\sigma_f = \sigma_{f0} \left( 1 - V_{fp} \right)^{n_a} \quad \text{Eqn 2.60}
\]

where \( \sigma_f \) and \( \sigma_{f0} \) are the strength of the porous and pore free materials and \( n_a \) is an empirical constant ranging between 3 and 6 for cermets. This model is of the same form as equation 2.35 developed to describe the porosity dependence of Young’s modulus. A good agreement between equation 2.35 (or 2.60) and the minimum solid area model for partial sintering is obtained if \( m \) is equated to 4.9 which agrees well with the findings of Bal’shin for partially sintered cermets.

Following observations that strength varied exponentially with volume fraction of porosity (Ryshkewitch, 1953) an alternative empirical model, given by equation 2.61, was proposed (Duckworth, 1953).

\[
\sigma_f = \sigma_{f0} \exp \left( - b_{\sigma} V_{fp} \right) \quad \text{Eqn. 2.61}
\]

where \( b_{\sigma} \) is an empirical constant. Equation 2.61 was later modified for use in describing the changes in Young’s modulus, and other properties, with porosity and is referred to as the Spriggs equation in the literature. A number of experimental studies have been analysed using equation 2.61 to describe the effect of porosity on strength, the results of which are given in table 2.6. As shown by the experimental
results obtained from Young's modulus measurements (table 2.4) the results of the analysis of stress show a lower porosity dependence for cases of isolated pores than for case of pores introduced through partial sintering. Greater variations in b are also obtained such that an overlap between the results for isolated pores and pores introduced through partial sintering is observed.

Table 2.6 - Reported values of b, for variation of strength with porosity

<table>
<thead>
<tr>
<th>Data</th>
<th>Material</th>
<th>Type of porosity and porosity range (%)</th>
<th>b (σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ryshewitch (1953)</td>
<td>Alumina</td>
<td>Pores preferentially aligned ⊥ to load</td>
<td>9*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pores preferentially aligned // to load</td>
<td>8*</td>
</tr>
<tr>
<td></td>
<td>Zirconia</td>
<td>Isolated pores</td>
<td>7*</td>
</tr>
<tr>
<td>Coble &amp; Kingery (1956)</td>
<td>Alumina</td>
<td>Isolated pores 10.0-37.0 %</td>
<td>4*</td>
</tr>
<tr>
<td>Knudsen (1959)</td>
<td>Thoria</td>
<td>Partial sintering 6.7-31.3 %</td>
<td>4.2</td>
</tr>
<tr>
<td>Passmore et al (1965)</td>
<td>Alumina</td>
<td>Partial sintering 0.2-3.0 %</td>
<td>9.35</td>
</tr>
<tr>
<td>Biswas (1976)</td>
<td>PZT</td>
<td>Isolated pores</td>
<td>3.4§</td>
</tr>
<tr>
<td>Ali et al. (1967)</td>
<td>glass</td>
<td>Isolated pores 0.01 - 0.35 %</td>
<td>2.8§</td>
</tr>
<tr>
<td>Wallace (1976)</td>
<td>Alumina</td>
<td>Isolated pores 0.02-0.12 %</td>
<td>2.5 - 2.9§</td>
</tr>
<tr>
<td>Kawai &amp; Yamakawa (1997)</td>
<td>Si₃N₄</td>
<td>Partial sinter of spherical grains 12.1-49.0 %</td>
<td>6.19</td>
</tr>
<tr>
<td>Chen (1999)</td>
<td>Alumina</td>
<td>Isolated pores 0-50 %</td>
<td>~2.7</td>
</tr>
</tbody>
</table>

* reported by Knudsen (1959), § reported by Rice (1998)

(Bold indicates studies conducted on isolated pores produced using a fugitive phase.)

2.3.5.2 Theoretical considerations

For the purposes of modelling the behaviour of strength as a function of porosity it is necessary to consider carefully the applicability of relevant equations. The stress required to initiate crack growth, σ, from a strength limiting flaw is a function of the local fracture toughness, $K_{IC(local)}$ and is given by:
\[ \sigma_i = Y K_{IC lokal} \left( \frac{1}{c} \right)^{1/2} \]  
Eqn. 2.62

where \( Y \) is a geometric constant dependent on specimen and pore geometry and \( c \) is the half crack length. Once a stress, \( \sigma_i \), has been attained then the crack will advance catastrophically leading to sample failure. As \( K_{IC lokal} \) relates to the fracture toughness of the alumina just ahead of the defect it is independent of the level of porosity (to a first approximation). Hence the stress, at the defect, required to initiate fracture should be independent of the level of porosity (assuming the level of porosity does not affect \( c \)). However, the level of stress at the defect will be controlled by the level of porosity, hence the component strength will be a function of porosity. The level of stress will be greatest at the points of minimum solid area hence it is reasonable to assume that the strength of the porous body should be described using the minimum solid area model.

For the case of samples containing pores introduced using a constant sized fugitive phase it is reasonable to assume that the pore size would remain constant so that the effect of porosity can be described using the minimum solid area model. Examination of experimental data (table 2.6) shows that isolated pores exhibit a porosity dependence such that \( b_\sigma \) is between 2.5 and 4. The minimum solid area model predicts a value of \( b_\sigma \) of 2.55 for the porosity dependence which is in good agreement with the lower limit of observed results. The increased porosity dependence observed can be explained in terms of pore clustering or increases in the size of the pores due to pore combination. Pore clustering can be seen to result in an increase in the porosity dependence as fracture initiation would occur preferentially in the more porous phase. Once fracture had initiated the crack would propagate rapidly through the component. If pores coalesce to form larger pores then the defect size will increase leading to a decrease in the stress required to initiate fracture.
2.3.6 Thermal conductivity

When considering the thermal conductivity of a porous material it is necessary to consider: (i) the path of heat conduction through the solid phase, (ii) areas of low conductivity caused by inhomogeneities within the solid phase, (iii) convective heat transfer across the pores and (iv) conduction of heat across the pores through radiation. Only (i) is likely to affect significantly the thermal conductivity of a porous body. The porous bodies examined in this study are of high purity alumina, and hence unlikely to contain inhomogeneities. The uniformity of the matrix phase between samples also minimises the effect of possible inhomogeneities. Transfer of heat across the pores though convection has been shown not to occur with pore sizes below 1 mm and transfer of heat across pores though radiation is unlikely to occur at temperatures below 400 °C (maximum temperature of interest for thermal shocking of samples in the present study). It can be assumed that at low to moderate temperatures thermal conductivity of materials containing small pores (<1 mm) is only controlled by the conductive path where the rate controlling stage would be the heat transfer across the smallest solid section. This rate limiting step indicates that the minimum solid area model is applicable for the modelling of the porosity dependence of thermal conductivity. The limited experimental data available on the thermal conductivity of porous materials can be described using Spriggs’ equation where b values of 2.6 and 2.7 were obtained (Rice, 1998, Chen, 1999) which is in good agreement with that of 2.55 predicted by the minimum solid area model.

The Maxwell-Euchen model has been used to describe the thermal conductivity of a particulate reinforced composite (Kingery et al., 1976) and is given by:

$$\lambda_c = \lambda_m \frac{1 + 2 Vf_r (1 - \frac{\lambda_m}{\lambda_r})/(2 \frac{\lambda_m}{\lambda_r} + 1)}{1 + Vf_r (1 - \frac{\lambda_m}{\lambda_r})/(\frac{\lambda_m}{\lambda_r} + 1)}$$

Eqn. 2.63
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where $\lambda$ is the thermal conductivity with subscripts c, m and r indicating composite, matrix and reinforcement. When $\lambda_m > \lambda_r$ (i.e. porous body) the resultant conductivity can be given by:

$$\lambda = \lambda_0 \left( \frac{1 - Vf_p}{1 + Vf_p} \right)$$  
Eqn. 2.64

where $\lambda$ and $\lambda_0$ are the thermal conductivity of the porous and pore free materials. The application of Sprigg's equation to equation 2.64, over a limited porosity range, results in a $b_\lambda$ value of 2.03 which is below that observed in literature indicating that the minimum solid area model is more applicable for describing the effect of porosity on thermal conductivity.

2.3.7 Thermal expansion coefficient

The thermal expansion coefficient of a single phase material is related to the nature and strength of the atomic bonds. Changes in the thermal expansion coefficient of a composite body are a result of the different expansion coefficients of the individual components and the degree to which each phase restricts the other. In a composite body the porous phase is not capable of exerting a significant force on the matrix phase and will not affect the thermal expansion coefficient of the body. The thermal expansion coefficient of a composite body, $\alpha_c$, (Kingery et al., 1976) can be described by:

$$\alpha_c = \frac{\alpha_1 K_1 Vf_1/\rho_1 + \alpha_2 K_2 Vf_2/\rho_2}{K_1 Vf_1/\rho_1 + K_2 Vf_2/\rho_2}$$  
Eqn. 2.65

where $K$ is bulk modulus and subscripts 1 and 2 relate to the two phases. For a porous body the bulk modulus of a pore can be regarded as 0 such that $\alpha_c = \alpha_1$. Experimental studies on polycrystalline alumina containing isolated spherical pores...
(Coble & Kingery, 1956) have shown that the thermal expansion coefficient is unaffected by the addition of porosity.

2.3.8 Summary

The effect of porosity on the mechanical and thermal properties of ceramics has been examined. Analysis of the literature data relating to strength, Young’s modulus and thermal conductivity indicates that all three material properties exhibit similar behaviour. A number of empirical models have been proposed to describe the dependence of these material properties on porosity. Of the equations proposed, Spriggs’ equation was favoured due to the availability of data in the literature and the simplicity of its form. Theoretical models designed to predict the behaviour of bodies containing isolated pores and pores introduced through partial sintering have also been presented.

The theoretical models were then compared with experimental data using Spriggs’ equation. Both the total and minimum solid area models were shown to describe the variation in material properties over a wide range of porosities. Analysis using the Spriggs equation shows that over the porosity range of interest for this study ($V_{fp} < 0.2$) the dependence of Young’s modulus, strength and thermal conductivity on isolated, spherical pores can be described using an empirical constant of between 2.5 and 2.8.

Effective surface energy has been reported to exhibit similar behaviour to that described by the Spriggs equation. However, increases in the effective fracture energy have been reported for samples containing isolated spherical pores with the range of 0 to 0.2 volume fraction porosity.

The dependence of Poisson’s ratio on porosity is unclear with contradictory observations having been reported due to the difficulty in obtaining sufficiently
accurate measurements of the moduli used to calculate Poisson’s ratio. Theoretical analysis using 2 and 3D finite element analysis is also inconclusive. Over the range of porosity studied in this work the variation in Poisson’s ratio are small and to a first approximation can be regarded as negligible.

2.4 THERMAL SHOCK RESISTANCE

2.4.1 Introduction

Ceramic materials, due to their brittle nature, are very prone to failure during rapid changes in temperature. When the temperature of a ceramic component is decreased rapidly (down shock) the surface of the body cools at a faster rate than the bulk which results in the surface contracting relative to the bulk material. This relative contraction causes tensile stresses to be generated within the surface layer of the material. The magnitude of these stresses is related to the difference in contraction between the surface and bulk and hence increases with increased temperature difference until the stress generated in the surface layer is sufficient to cause failure. The same phenomenon occurs when a sample is heated rapidly (up shock) but now the tensile stresses are generated in the bulk of the material. As the flaws on the surface are generally more likely to control strength, component failure is more often observed on rapid cooling (Davidge & Tappin, 1967). The importance of temperature difference was observed as early as 1760 when Josiah Wedgewood noted that thin sections were less prone to failure (Roysten & Barrett, 1958). The temperature differences between bulk and surface are expected to be lower for thin material sections due to the more rapid transfer of heat from the centre of the component. This demonstrates that careful design of components can decrease the risk of thermal shock failure.
To further increase the resistance to failure under transient thermal conditions it is necessary to examine the properties of the material. Thermal shock resistance parameters have been developed to rank materials in order of their ability to resist crack initiation and crack propagation when subjected to thermal shock. Six thermal shock parameters, that describe the resistance to crack growth initiation (i.e. the propagation of a natural defect) and crack propagation, will be considered in this section. The effect of porosity on these thermal shock resistance parameters will then be examined in light of the porosity dependence of material properties discussed in section 2.3.

2.4.2 Thermal shock resistance parameters

2.4.2.1 Resistance to the initiation of crack growth

The most simple approach to quantifying thermal shock is to consider the stresses generated in a fully elastic body subjected to a temperature change, ΔT (Kingery, 1955). If the body is free to expand, an increase in temperature of ΔT will give rise to an extension ΔL, due to thermal expansion, as shown by:

\[ \Delta L = L_0 \alpha \Delta T \]  
Eqn. 2.66

where \( L_0 \) is the original length and \( \alpha \) is the thermal expansion coefficient. If the body is now constrained in two directions (as the surface of a body would be) a stress, \( \sigma \), will be generated if the body is cooled by ΔT (equation 2.67).

\[ \sigma = \frac{E \varepsilon}{(1-v)} = \frac{E \Delta L}{(1-v)L_0} = \frac{E \alpha \Delta T}{(1-v)} \]  
Eqn. 2.67

where \( E \) is the Young's modulus, \( \varepsilon \) is the strain and \( v \) is the Poisson’s ratio (introduced due to the biaxial nature of the stress). For a given material the stress will continue to increase with increases in ΔT. As the stress cannot be relieved through
plastic deformation, as in metals, the sample will fail when the temperature change causes the stress level to exceed the failure stress of the material. This maximum temperature change prior to failure is taken as the first thermal shock resistance parameter, R, and is given by:

\[ R = \Delta T = \frac{\sigma_f (1 - \nu)}{E \alpha} \]  

Eqn. 2.68

In order to increase the resistance to crack initiation, R, it is necessary to increase the strength of the material and decrease the Young's modulus, thermal expansion coefficient and Poisson's ratio.

The derivation of R assumes that the temperature of the bulk material does not change during quenching. This assumption is only valid for situations where the quenching rate is sufficiently high to prevent heat transfer from the bulk material prior to failure. When the rate of quenching is reduced it is necessary to introduce a further term into equation 2.67 to account for the reduction in stress caused by the bulk temperature approaching that of the quench medium. The application of this extra term, the stress-reduction factor, is shown by:

\[ \sigma = \frac{A_\beta E \alpha \Delta T}{(1 - \nu)} \]  

Eqn. 2.69

where \( A_\beta \) is the non-dimensional stress term which varies between 0 and 1 and can be related to material properties and quenching conditions through the Biot modulus, \( \beta \), given by:

\[ \beta = \frac{a_\beta h_T}{\lambda} \]  

Eqn. 2.70

where \( a_\beta \) is the characteristic dimension e.g. the half thickness of the specimen, \( h_T \) is the heat transfer coefficient between the body and quenching medium, and \( \lambda \) is the
thermal conductivity of the material. Figure 2.21 shows how the non-dimensional stress and Biot modulus are related (Davidge & Tappin, 1967).

![Figure 2.21 - Variation of non-dimensional stress with time for various values of Biot modulus (after Davidge, 1979)](image)

From figure 2.21 it can be seen that for conditions of fast quenching (high h) the Biot modulus will be large resulting in a stress-reduction factor close to 1.0. Hence, for conditions of fast quenching it can be seen that equation 2.69 will tend towards equation 2.67 resulting in the first thermal shock resistance parameter being produced. A lesser rate of cooling can be seen to reduce the value of the stress-reduction factor and hence reduce the stress experienced by the body. For a given sample size and quenching condition (constant h and a) the stress-reduction factor will only be affected by variations in thermal conductivity. Hence equation 2.69 can be modified to give the second thermal shock resistance parameter, $R'$ (equation 2.71).
The two thermal shock resistance parameters, \( R \) and \( R' \), respectively indicate the resistance of a material to crack initiation for conditions of infinitely fast quench and slower quenching. Both resistance parameters show that the resistance to crack initiation can be increased by selecting materials with high strength and low Young's modulus, thermal expansion and Poisson's ratio. Intuitively this can be seen as correct as a lower Young's modulus and degree of thermal expansion will result in a lower stress being generated, while a high strength will allow the material to withstand a higher stress prior to failure. Examination of \( R' \) also shows that for situations of slow quenching a high thermal conductivity is also beneficial which can be explained in terms of reducing the temperature difference across the sample and hence reducing the degree of mismatch caused by thermal expansion.

2.4.2.2 Resistance to crack propagation

The derivation of \( R \) and \( R' \) suggests that material has failed completely but in reality the cracks may not traverse the whole sample. Hence an alternative approach to considering the resistance to crack initiation is to consider the minimisation of damage once crack initiation has occurred (Hasselman, 1969). It is desirable to minimise the degree of crack propagation in order to maximise the retained properties. The Griffith criteria for crack advance states that the crack will continue to propagate until the released elastic strain energy has decreased to be at least equal to the energy required to create a new crack surface. The extent to which the crack propagates is, therefore, related to the amount of stored elastic energy. The exact relationship between stored elastic energy and propagation distance is complex; it can be assumed, however, that the two are proportional (Hasselman, 1969). By again considering a fully elastic body where the thermal stress is given by equation 2.67, it
Chapter 2 - Literature Review

is possible to determine the third thermal shock resistance parameter. From equation 2.67 it can be shown that the extension of the body at failure, \( x_f \), is given by:

\[
x_f = \Delta T \alpha = \frac{\sigma_f (1 - \nu)}{E} \quad \text{Eqn. 2.72}
\]

At the point of failure the stored elastic energy within a body subjected to a stress, \( \sigma_f \), is given by:

\[
W_E = \frac{P x_f}{2} = \frac{\sigma_f A x_f}{2} \quad \text{Eqn. 2.73}
\]

where \( W_E \) is the stored elastic energy and \( P \) is the force acting on the body. By combining equations 2.72 and 2.73 it is possible to relate the energy stored at failure to the material properties as shown by:

\[
W_E = \frac{A \sigma_f^2 (1 - \nu)}{2E} \quad \text{Eqn. 2.74}
\]

As the extent of crack propagation is proportional to the stored elastic energy it can be seen that by minimising the stored elastic energy at failure it is possible to minimise the extent of crack propagation and hence maximise the retained properties. The third thermal shock resistance parameter (\( R''' \)) is, therefore, given by equation 2.75 and is a function of the material properties affecting the amount of elastic energy stored at failure.

\[
R''' = \frac{E}{\sigma_f^2 (1 - \nu)} \quad \text{Eqn. 2.75}
\]

\( R''' \) was obtained by considering the stored elastic energy prior to failure. A fourth thermal shock resistance parameter (\( R'''' \)) can be obtained when the energy required to propagate cracks is considered. The energy required to propagate the cracks is a
function of the area of a crack, the number of cracks, and the effective surface energy of the cracks. Using the Griffith crack criterion it can be seen that the energy required to propagate the cracks is also equal to the stored elastic energy as shown by:

\[ W_E = \frac{A_c \sigma_f^2 (1 - \nu)}{2} = A_c N_c \gamma_{eff} \]  

Eqn. 2.76

where \( A_c \) is the mean crack surface area, \( N_c \) is the number of cracks and \( \gamma_{eff} \) is the effective surface energy of the cracks which is composed of the thermodynamic free energy of the surface and the energy dissipated by inhomogeneities within the material. The retained properties of the material will be maximised if the length of the crack (i.e. crack area) is minimised, hence the fourth thermal shock resistance parameter, \( R'''' \), can be obtained by considering the material properties required to minimise the mean crack surface area as shown by:

\[ R'''' = \frac{E \gamma_{eff}}{\sigma_f^2 (1 - \nu)} \]  

Eqn. 2.77

\( R'''' \) has been determined on the basis that the number of propagating cracks remains constant. Further increases in the resistance parameter would be obtained if the number of propagating cracks was increased. The third and fourth thermal shock resistance parameters show that high values of Young's modulus, Poisson's ratio and effective surface energy, and low values of strength, are beneficial for minimising the degree of crack propagation. These requirements are in direct contradiction with the requirement for a resistance to crack initiation. The primary concern, when considering thermal shock, is to ensure the component does not fail. Hence materials should be selected on a basis of their resistance to crack initiation. If it is not possible to prevent crack initiation, the primary concern becomes one of minimising the extent of crack propagation (Hasselman, 1970).
2.4.2.3. Unified theory of thermal shock resistance

It has been possible to produce a unified approach to thermal shock resistance by determining the thermal shock conditions for the instability of cracks of different lengths (Hasselman, 1969). As has been stated previously, the driving force for crack propagation is produced solely from stresses generated by the temperature differences within the material. This constant displacement situation is analogous to the case of 'fixed grips' employed in considerations of fracture mechanics. If cracks are introduced into this stressed body, under 'fixed grips' conditions, then the effective Young's modulus is reduced which results in a relaxation of the stress, which in turn reduces the driving force for crack propagation. A simplified geometry was considered consisting of a solid body cooled by \( \Delta T \) and constrained such that the exterior surfaces could not move. The stresses generated are given by:

\[
\sigma = \frac{\alpha E \Delta T}{(1 - 2v)}
\]

Eqn. 2.78

Equation 2.78 is identical to equation 2.67 except in its Poisson's ratio dependence which arises from the triaxial stress state. It was assumed that the body contained a uniform distribution of circular mechanical flaws (Griffith microcracks) of uniform size and that crack advancement would occur through the simultaneous growth of \( N \) cracks per unit volume such that there is no interaction between neighbouring stress fields. The total stored energy per unit volume can then be given as the sum of the stored elastic energy and the fracture energy of the cracks as shown by:

\[
W_T = \frac{3(\alpha \Delta T)^2 E_0}{2(1-2v)} \left[ 1 + \frac{16(1-v^2)N_c^3}{9(1-2v)} \right]^{-1} + 2\pi N_c c^2 \gamma_{\text{eff}}
\]

Eqn. 2.79

where \( W_T \) is the total stored energy and \( c \) is the crack radius. For a crack to advance the decrease in stored elastic energy must at least equal the energy required to create
a new crack surface (Griffith criterion), hence the cracks will be unstable between
the limits given by \( \frac{dW_f}{dc} = 0 \). Differentiation of equation 2.79 enables an equation
to be obtained that describes the change in critical temperature for various crack
lengths as shown by:

\[
\Delta T = \left[ \frac{\pi \gamma_{eff} (1 - 2v)^2}{2E_0 \alpha^2 (1 - v^2)} \right]^{1/2} \left[ 1 + \frac{16(1 - v^2)N_c c^3}{9(1 - 2v)} \right]^{1/2}
\]

Eqn. 2.80

Equation 2.80 is graphically represented by the solid lines in figure 2.22 which
shows the regions of crack stability and instability.

Figure 2.22 - Minimum temperature difference required to initiate crack propagation
as a function of crack length. (Solid lines represent equation 2.80 and dashed lines
represent results derived from equation 2.85)

The maximum temperature difference that a body can withstand without further
 crack growth can be determined from figure 2.22. For bodies containing short cracks
(crack size is to the left of the minima) examination of equation 2.80 shows that the
term \(16(1-\nu^2)N_c c^3/9(1-2\nu)\) is small in comparison to 1 and can be neglected resulting in:

\[
\Delta T = \left[ \frac{\pi \gamma_{\text{eff}} (1 - 2\nu)^2}{2 E_0 \alpha^2 (1 - \nu^2)c} \right]^{1/2} \tag{Eqn. 2.81}
\]

Conversely for bodies that contain large cracks (to the right of the minima) the term \(16(1-\nu^2)N_c c^3/9(1-2\nu)\) becomes large in comparison to 1 and equation 2.80 can be approximated by:

\[
\Delta T = \left[ \frac{128 \pi \gamma_{\text{eff}} (1 - \nu^2)N_c c^5}{81 E_0 \alpha^2} \right]^{1/2} \tag{Eqn. 2.82}
\]

The point of crack instability, given by equations 2.81 and 2.82, can be used to specify a further thermal shock resistance parameter. Examination of the two equations shows that to maximise the temperature difference that the body can withstand prior to continued crack growth it is necessary to increase the effective surface energy, and minimise the Young’s modulus and thermal expansion coefficient. The fifth thermal shock resistance parameter, \(R_{st}\), can thus be given as:

\[
R_{st} = \left( \frac{\gamma_{\text{eff}}}{\alpha^2 E} \right)^{1/2} \tag{Eqn. 2.83}
\]

The role of thermal conductivity can be introduced into \(R_{st}\) in an analogous way to that of \(R\) and \(R'\) (equations 2.68 and 2.71) to produce the sixth thermal shock resistance parameter \(R_{st}'\) (equation 2.84).

\[
R_{st}' = \left( \frac{k^2 \gamma_{\text{eff}}}{\alpha^2 E} \right)^{1/2} \tag{Eqn. 2.84}
\]
Equation 2.80 can be used to show the point at which a crack becomes unstable and continues to propagate. It is also possible to use similar arguments, as those used to determine equation 2.80, to predict the extent of crack propagation once crack instability has been achieved. When an initially short crack becomes unstable and propagates the energy released on fracture exceeds that required to create the new fracture surface. This excess energy is transformed into kinetic energy which continues to drive the advancing crack past the point of stability predicted by equations 2.80. The crack will continue to propagate until the energy released is equal to the total surface fracture energy as shown in equation 2.85. The derivation of equation 2.85 is represented by the dashed line in figure 2.22.

\[
\frac{3(\alpha \Delta T_c)^2 E_0}{2(1-2v)} \left[ 1 + \frac{16(1-v^2)N_c c_0^3}{9(1-2v)} \right]^{-1} = 2\pi N_c \gamma (c_r^2 - c_0^2) \quad \text{Eqn. 2.85}
\]

Hasselman showed that for short initial cracks \((c_0 \ll c_f)\) the final crack length would be given by:

\[
c_f = \left[ \frac{3(1-2v)}{8(1-v^2)} \right]^{1/2} c_0 N_c \quad \text{Eqn. 2.86}
\]

which can then be substituted into an equation for the critical fracture stress \((\sigma_f)\) for a penny shaped crack.

\[
\sigma_f = \left[ \frac{\gamma_{\text{eff}} E}{2 c_0 (1-v^2)} \right]^{1/2} \quad \text{Eqn. 2.87}
\]

to obtain an indication of the material properties that affect the final crack length:

\[
c_f = \left[ \frac{3(1-2v)}{4\pi (1-v^2)} \gamma_{\text{eff}} N E \right]^{1/2} \quad \text{Eqn. 2.88}
\]
By considering the material properties required to minimise the degree of crack propagation it is possible to obtain an equation identical to that for \( R''' \) (equation 2.77) apart from a Poisson’s ratio dependence of \((1-2v)\).

The equations derived in this section provide a uniform approach to describing the thermal shock resistance of a ceramic. In real systems it is unlikely that the component will be free from defects hence equations 2.83 and 2.84 can be used to provide an indication of resistance of a material to the initial growth of intrinsic defects. The work to describe the effect material properties on the final crack length indicate that the equation for \( R''' \) is appropriate for describing the resistance to crack propagation.

2.4.3 Effect of porosity on thermal shock resistance

A number of studies have focused on the effect of porosity on the resistance of ceramics to cracking during thermal shock. An early investigation examined the effect of isolated spherical pores on the resistance to crack initiation (Coble & Kingery, 1956). Using equation 2.68 the resistance to crack initiation was calculated from the measured properties. It was found that for conditions of rapid quenching the resistance to crack initiation decreased with increased levels of porosity. Subsequent evaluation of the resistance to crack initiation under less rapid quenching conditions indicated an even greater reduction due to the decrease in thermal conductivity with increased levels of porosity. Smith et al. (1976) examined the effect of porosity on both the resistance to crack initiation and crack propagation by rapidly quenching alumina samples containing 3.5 vol % isolated pores and measuring the retained strength and degree of cracking. It was found that the critical temperature to initiate cracking remained approximately constant indicating no change in the resistance to crack initiation. Examination of the degree of cracking following crack initiation revealed that the crack density increased and the crack depth decreased.
with increases in porosity. This beneficial role of porosity, resulting in increased residual strengths, was thought to be caused by the pores acting as sources for crack initiation in the first instance and also as crack arrestors. Increases in the resistance to crack propagation were also observed by Chen (1999) where the rise was attributed to an increase in the fracture energy of the ceramic at low porosity levels ($V_{fp} < 0.2$).

The effect of porosity on the thermal shock resistance has been addressed further by examining the effect of porosity on the mechanical properties that control the resistance to crack initiation (Arnold et al., 1996). The analysis indicated that the resistance to crack initiation would initially increase and peak at approximately 1 vol % porosity and then decrease with increased levels of porosity. Experimental data presented in the study exhibited a large degree of scatter and did not corroborate the temporary increase in the resistance to crack initiation. If Spriggs type equations are used to describe the behaviour of material properties with increases in porosity there is no temporary increase in the resistance to crack initiation evident. This indicates that the temporary increase reported is a result of the different forms of property-porosity dependence equations used to describe each material property.

The effect of partial sintering induced porosity on the resistance to thermal shock will not be addressed in this work due to the difficulty in isolating the effect of porosity from that of grain size. For samples where porosity is controlled through partial sintered there will be a simultaneous increase in grain size and density with continued sintering. Gupta (1972) observed that increases in grain size lead to changes in thermal shock behaviour which would be coupled with the changes in thermal shock behaviour caused by a reduction in porosity.

2.4.4 Summary

Six thermal shock resistance parameters have been developed to describe the resistance to crack initiation, crack propagation upon initiation and propagation of
existing cracks. The resistance parameters relating to crack initiation have been used, along with equations describing the porosity dependence of material properties, to describe the effect of porosity on the resistance to crack initiation. The results indicate that there should be a small reduction in the maximum thermal stress sustainable by the material. Experimental observation of cracks following thermal shock indicate that porosity plays a beneficial role in increasing the residual strength of the ceramic following thermal shock. The presence of the pores appears to increase the density of cracks and also decrease the extent of crack propagation. the effect of partial sintering induced porosity has not been addressed in this work.
CHAPTER 3

MATERIALS AND SAMPLE PREPARATION

3.1 INTRODUCTION

This chapter has been divided into two sections to examine separately the studies concerned with the initial stages of sintering and the studies concerned with large pores. Each section presents the starting powders, the powder processing and refinement techniques employed and the consolidation techniques used to produce green bodies and sintered bodies. Where pertinent a short description of the theory is given prior to the description of the experimental methodology and relevant results.

3.2 INITIAL STAGE SINTERING STUDIES

3.2.1 Powders

The in situ work is concerned with the study of initial stages of the solid state sintering phenomena. For this purpose it was necessary to use powders with high purity, comprising approximately equiaxed single crystal particles with a mean particle size greater than 1 \( \mu \text{m} \). These requirements enable the coupled boundary and surface diffusion sintering conditions encountered by single crystal spherical particles in the absence of sintering aids to be examined.

Powders A-43-M and A-42-2 (Showa Denko K.K., Japan) satisfied these requirements with purities of 99.7 % \( \text{Al}_2\text{O}_3 \) and quoted mean particle sizes of 1.8 and 4.0 \( \mu \text{m} \) respectively. Table 3.1 gives details for the powder properties as supplied by the manufacturer.
Table 3.1 – Manufacturer quoted properties of A-43-M and A-42-2

<table>
<thead>
<tr>
<th></th>
<th>A-43-M</th>
<th>A-42-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>molar % Al₂O₃</td>
<td>99.7</td>
<td>99.7</td>
</tr>
<tr>
<td>density (g/cm³)</td>
<td>3.94</td>
<td>3.95</td>
</tr>
<tr>
<td>mean particle size (µm)</td>
<td>1.8</td>
<td>4.0</td>
</tr>
<tr>
<td>ultimate crystal size (µm)</td>
<td>1.5</td>
<td>4.0</td>
</tr>
</tbody>
</table>

3.2.2 Particle size analysis

3.2.2.1 Theory

Particle size distributions of the powders were obtained using a laser particle size analyser (Malvern MasterSizer). The MasterSizer employs the optical configuration shown in figure 3.1 to measure the particle size distribution of a powder in the range of 0.1 µm to 80 µm. The sample cell is mounted between the lens and detector in the path of the converging analyser beam to allow the detection of high angle scattered light from small particles.

![Optical arrangement of Malvern MasterSizer](image)

Figure 3.1 – Optical arrangement of Malvern MasterSizer
Chapter 3 - Materials and Sample Preparation

A helium-neon laser is used to produce a collimated, monochromatic beam of light, approximately 18 mm in diameter. This analyser beam is focused to a point in the plane of the detector by a lens. The sample cell is positioned in the converging analyser beam at a distance, $d_s$, from the detector plane. During analysis the sample suspension is circulated through the cell. The degree to which particles present in the sample cell diffract the light depends on the particle diameter. Large and small particles diffract light by a small and large angles respectively.

The diffracted light strikes a detector containing 31 rings that measure the intensity of light incident upon them. The presence of a large number of particles within the analyser beam ensures that the scattered light measured by the detector is the sum of all the individual patterns overlaid on the central axis so increasing the intensity of the diffracted light. By time averaging the observations, as particles are continuously passed through the cell, it is possible to obtain a statistically significant and representative indication of the light scattering. Light scattering theories are then used to interpret the detector results and calculate a particle size distribution of the powder.

3.2.2.2 Experimental procedure

A small sample of each test powder was added to the suspension liquid (water containing a dispersant) until the required concentration had been achieved. For the purposes of this study it was necessary to add a dispersant (1.1 g/l sodium pyrophosphate - $\text{Na}_2\text{P}_2\text{O}_{7}$) to prevent particles smaller than 1 $\mu$m from agglomerating during measurement leading to erroneous results. The dilute suspension was mixed using a mechanical stirrer and ultrasound for 1 minute to ensure thorough break up of any agglomerates present. During measurement ultrasonic agitation was discontinued to prevent bubbles from entering the sample cell.
3.2.2.3 Particle size analysis results

The particle size distributions of as-received A-43-M and A-42-2 are shown in figures 3.2 and 3.3 respectively. It can be seen that both as-received A-43-M and A-42-2 contain a proportion of particles that deviate from the Gaussian log-normal distribution. These particles are undesirable for the present study due to the resultant widening of the particle size distribution and overlap with the particle size distribution of the other powder.

![Figure 3.2 - Particle size distributions of as-received A-43-M](image)

![Figure 3.3 - Particle size distributions of as-received A-42-2](image)
Chapter 3 - Materials and Sample Preparation

For the purposes of the in situ studies it is desirable to remove the unwanted components of the particle size distributions. Centrifuging was ultimately selected for the purposes of powder refinement following trials using filtering and milling that proved ineffective.

3.2.3 Centrifuging

3.2.3.1 Theory

Stokes' settling equation (equation 3.1) can be used to relate material properties and experimental parameters to the centrifuging time, $t_s$ (Atkins, 1990).

$$t_s = \frac{18 \eta_s \ln(r_i/r_0)}{a_c^2 (\rho_c - \rho_{sol}) \omega^2}$$

Eqn. 3.1

where $\rho_{sol}$ is the density of the solvent (water), $\rho_c$ is the density of the ceramic, $\eta_s$ is the viscosity of the solvent, $r_0$ and $r_i$ are the radial positions of the particles before and after centrifuging, $a_c$ is the diameter of the particle and $\omega$ is the angular velocity of the centrifuge. It can be seen from equation 3.1 that for a given experimental configuration and material $\eta_s$, $\rho_s$, $\rho_c$, $r_0$ and $r_i$ are constant. The time required for particles of different radii to settle out of suspension is, therefore, inversely proportional to both the square of the particle radius and the square of the speed at which the centrifuge is rotating. The removal rate of the particles can be controlled by varying either the time or the speed of centrifuge.

It is not possible to achieve distinct cut-offs in particle size distributions due to the random starting positions of the particles and the tendency for large particles to drag smaller particles with them as they settle out.
3.2.3.2 **Experimental procedure**

Alumina powder and water were mixed ultrasonically for 2 minutes to form a 16.7wt% alumina suspension. The suspension was placed in a number of 60 ml polypropylene bottles held in the centrifuge (MSE, Griffin George Ltd). The suspension was then centrifuged at 800 rpm for 2 minutes to remove particles greater than 10 μm in diameter. The upper suspension, containing the required particles, was then removed and transferred to a further set of polypropylene bottles and treated to further centrifuging at 2000 rpm for 5 minutes in order to remove a large proportion of the water to facilitate drying. This resultant paste was then dried at 75 °C for 24 hours prior to further treatment.

3.2.3.3 **Centrifuging results**

Figure 3.4 demonstrates the effect of a 2 minute 800 rpm centrifuge cycle on as-received A-43-M. It can be seen that the unwanted portion of the particle size distribution has been effectively removed. Extended centrifuging times result in much reduced yields with minimal reduction in the width of the particle size distribution.
As-received A-43-M was successfully refined to produce the required distribution. It was not possible to further refine as-received A-42-2 due to the limitations of centrifuging. Following the centrifuging process the suspension was relatively free of large particles. The sediment contained both large and small particles due to the tendency of the large particle to drag smaller particles with them as they move to the bottom of the vessel. This makes it impossible to effectively remove the small particles from a suspension containing larger particles. For the purposes of this study refined A-43-M and unrefined A-42-2 were utilised.

### 3.2.4 Powder blending

Blending of A-42-2 and A-43-M was conducted using a wet method. No binder was added to these powders as binder burn out would have affected the dimensional changes during the sintering study. The starting powders were combined in mass ratios of 3:1, 1:1 and 1:3. Water was added to the powder blend in a mass ratio of 2:1 and the suspension was then thoroughly mixed in a rotating ball mill for 1 hour. Following wet mixing the suspension was dried at 75 °C for 24 hours. The dry powder was then ball milled for a further 1 hour to break up agglomerates formed.
during the drying process. Table 3.2 gives details of the powders used in the *in situ* study.

Table 3.2 – Powders used in study of initial stage sintering

<table>
<thead>
<tr>
<th>Powder</th>
<th>Mean particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-received A-43-M</td>
<td>1.05</td>
</tr>
<tr>
<td>Refined A-43-M</td>
<td>0.82</td>
</tr>
<tr>
<td>A-42-2</td>
<td>4.97</td>
</tr>
<tr>
<td>3:1 blend of (refined) A-43-M and A-42-2</td>
<td>N/A</td>
</tr>
<tr>
<td>1:1 blend of (refined) A-43-M and A-42-2</td>
<td>N/A</td>
</tr>
<tr>
<td>1:3 blend of (refined) A-43-M and A-42-2</td>
<td>N/A</td>
</tr>
</tbody>
</table>

3.2.5 **Green body production**

Following powder refinement it is necessary to produce a green body for the study of densification during the sintering process. Green bodies were produced by cold uniaxial pressing in a hardened steel die mounted in an Instron 1175 testing machine operating in compression using a cross head speed of 1 mm/min. Cylindrical samples for *in situ* studies were produced from 6 g of powder pressed using a 25 mm diameter die and a load of 10 kN (20.4 MPa). On attaining the required pressing pressure the load was removed.

Following pressing the green bodies were extracted from the die by removing the lower ram, inverting the pressing rig and pushing the compact out using a cross head speed of 5 mm/min.
3.2.6 Summary

The two starting powders, A-43-M and A-42-2, were selected on the basis of high purity and appropriate grain and crystallite size. Particle size analysis of the powders indicated that it was necessary to further narrow the particle size distribution. Centrifuging techniques were employed to refine A-43-M. It was not possible to refine A-42-2 due to the difficulty in removing small particles from a distribution. Powder blends were then produced using wet mixing methods. Following drying and milling of the powders green bodies were produced for the *in situ* observation studies discussed in Chapter 4.

3.3 LARGE PORE STUDIES

3.3.1 Powders

The study of the effect of pores on the mechanical and thermal properties of alumina arose from previous work examining the effect of metal particulate reinforcements. It was envisaged that discrete large (pore size > grain size) pores could be introduced into the structure through the use of a fugitive phase that would be removed during thermal processing.

AKP30 (Sumitomo Chemical Co, Japan) was selected as the alumina matrix material due to its high sinterability and previous use in studies concerned with metal particle reinforcement.

The requirements for the fugitive phase were that it would be available in a uniform particle size in the region of 10 μm and burn off leaving little or no residue. Expancel® (thermoplastic hollow sphere) was initially tested but was found to be unsuitable due to excessive expansion on heating above 100 °C resulting in sample
breakage. Corn starch with an average particle size of 15 μm was ultimately selected for the study.

Details of powder properties are given in table 3.3.

<table>
<thead>
<tr>
<th></th>
<th>AKP30</th>
<th>Corn starch</th>
</tr>
</thead>
<tbody>
<tr>
<td>density (g/cm³)</td>
<td>3.97</td>
<td>1.49</td>
</tr>
<tr>
<td>mean particle size (μm)</td>
<td>0.3-0.5</td>
<td>15</td>
</tr>
<tr>
<td>molar % Al₂O₃</td>
<td>&gt; 99.99</td>
<td>—</td>
</tr>
</tbody>
</table>

3.3.2 Powder blending

3.3.2.1 Experimental procedure

Green bodies made from of AKP30 required the addition of a binder to facilitate handling. 2 g of polyethylglycol (PEG, molecular weight = 20,000) was dissolved in 15 ml warm water. 100 g of AKP30, 200 ml water and the PEG solution were then mixed in a rotating ball mill for 1 hour. Following blending the suspension was dried at 75 °C for 24 hours. The powder was then ball milled for a further 1 hour to break up loose agglomerates formed during the drying process. Further crushing of agglomerates was carried out using a pestle and mortar to produce a fine powder prior to passing through a sieve.

Starch was blended using a dry method to prevent the action of heat and moisture from damaging the starch particles. The required proportions of starch and AKP30 with binder were blended in a ball mill for 30 minutes to minimise damage to the starch particles. Alumina and starch were combined in mass ratios of 51.5:1, 24.4:1,
15.4:1 and 10.9:1 to produce powders containing volume fractions of starch of 0, 0.05, 0.10, 0.15 and 0.20.

3.3.2.2 Determination of powder blend starch and binder content

Following final milling, samples of each powder were analysed by measuring the powder mass before and after a burn out treatment at 600 °C. The two masses were used to calculate the degree of binder and starch present in each sample. In the case the powder containing only binder the change in mass will be equal to the mass of binder present and equation 3.2 can be used to calculate the mass fraction of binder present in the alumina binder mix.

\[
M_f^b = \frac{m_b}{m_c + m_b} = \frac{\Delta m}{m_c + \Delta m} \tag{Eqn. 3.2}
\]

where \(M_f^b\) is the mass fraction of binder added, \(m_b\) is the mass of binder, \(m_c\) is the mass of ceramic and \(\Delta m\) is the change in mass of the powder following burn out. The change in mass of the powder containing both binder and starch will be equal to the mass of binder and starch combined. As the mass ratio of binder to alumina is constant (for a given alumina/binder blend starting powder) the mass of binder present in any powder can be calculated from the mass of ceramic and volume fraction of binder using equation 3.3.

\[
m_b = \frac{M_f^b m_c}{1 - M_f^b} \tag{Eqn. 3.3}
\]

The mass of starch added can thus be determined from the change in mass following burnout and the mass of binder calculated. The volume fraction of starch present (\(V_{fs}\)) can then be calculated using equation 3.4.
Chapter 3 - Materials and Sample Preparation

\[
V_{f_s} = \frac{V_s}{V_c + V_s + V_b} = \frac{m_s/\rho_s}{m_c/\rho_c + m_s/\rho_s + m_b/\rho_b}
\]  
Eqn. 3.4

where \(V\) and \(\rho\) are volume and density with subscripts \(s, c\) and \(b\) indicating starch, ceramic and binder respectively. Table 3.4 gives the results of the burnout tests designed to determine the amounts of binder and starch present in the powders.

Table 3.4 – Composition of alumina/starch blend starting powder

<table>
<thead>
<tr>
<th>Desired volume fraction</th>
<th>Measured volume fraction following milling</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.05</td>
<td>0.044</td>
</tr>
<tr>
<td>0.10</td>
<td>0.098</td>
</tr>
<tr>
<td>0.15</td>
<td>0.130</td>
</tr>
<tr>
<td>0.20</td>
<td>0.181</td>
</tr>
</tbody>
</table>

3.3.3 Powder consolidation

3.3.3.1 Uniaxial pressing

Green bodies were produced by cold uniaxial pressing in a hardened steel die mounted in an Instron 1175 testing machine operating in compression using a cross head speed of 1 mm/min. Two green body geometries were produced for the purpose of this study. Cylindrical samples were produced by compacting 6 g of powder in a 25 mm diameter die at a load of 10 kN (20.4 MPa). Test bars for mechanical testing, measuring 63 x 6 x 6 mm, were produced by compacting 5 g of alumina at a load of 8 kN (21.2 MPa). In both cases the load was removed on attaining the required level.
Following pressing the green bodies were extracted from the die by removing the lower ram, inverting the pressing rig and pushing the compact out using a cross head speed of 5 mm/min.

3.3.3.2 Pressureless sintering

Pressureless sintering was conducted in air using a tube furnace (Lenton 1650 high temperature tube furnace) and chamber furnace (Lenton). Ramp rates were maintained at a constant 5 °C/min in both furnaces in order to produce comparable sintering histories. The optimum sintering conditions were determined by sintering alumina green bodies at 1500 °C and 1600 °C for various lengths of times. Following sintering the density and grain size were determined as described in sections 5.2.4 and 5.2.7. The sintering schedule was selected to maximise density while minimising grain size in order to achieve good mechanical properties. The optimum sintering conditions were determined to be 1500 °C with a dwell time of 45 minutes prior to furnace cooling. Using this schedule densities of approximately 3.82 g/cm³ (96.1 % theoretical) and a mean grain size of 2.17 µm were obtained.

3.3.4 Summary

Powder blends were made by wet mixing AKP30 with polyethylglycol. Following drying starch was dry mixed with the alumina/binder blend to produce various volume fractions of starch addition. The exact amount of starch present following blending was determined from burnout tests at 600 °C. Green bodies were produced from the powder blends using cold uniaxial pressing. Green bodies were sintered to approximately 96.1 % theoretical density at 1500 °C for 45 minutes.
CHAPTER 4

IN SITU OBSERVATIONS OF SINTERING

4.1 INTRODUCTION

It is often beneficial to have accurate data relating to the sintering behaviour of powder compacts in order to predict component shrinkage and so minimise post sintering machining. Such data are also of use in verifying predictions made by models that are being developed to describe sintering of real powders. With the full development of such models it should become possible to predict the sintering behaviour with a minimum of expensive, time consuming experiments.

Shrinkage data are often obtained from a series of samples sintered for different lengths of time at a constant temperature. This method is both time and material intensive and may introduce inaccuracies due to continued densification during heating and cooling. An alternative technique is to monitor the densification behaviour of a single sample continuously using dilatometry techniques. Contact dilatometry is limited in the number of directions of shrinkage that can easily be monitored simultaneously, and there is the possibility of introducing contact stresses that may affect the sintering process. A different approach is to use optical dilatometry which eliminates the need for physical contact with the sample and allows two dimensions to be measured simultaneously. With the selection of a suitable specimen geometry (i.e. cylindrical) it is possible to monitor changes in sample volume.

This chapter presents a method for accurately measuring the volume, and hence density, change of green bodies. The method incorporates a procedure for
eliminating the effect of sample radiance at high temperatures that would otherwise lead to an overestimation of the sample volume. The technique is used to obtain accurate sintering data for powders composed of small (A-43-M) and large (A-42-2) particles along with three powder blends of the two starting powders combined to give volume ratios of 3:1, 1:1 and 1:3. The results generated from this study are then used to provide experimental verification for a theoretical model for sintering of powders with a bimodal particle size distribution, proposed by Pan et al. (1998) and described in section 2.2.4.4.

4.2 EXPERIMENTAL PROCEDURE

Powders with different particle size distributions, centred around mean diameters of 0.8 and 5.5 µm, were produced by refining and blending A-43-M and A-42-2 powders as described in sections 3.2.3 and 3.2.4. The processed powders were then formed into compacts by uniaxial pressing in a 25 mm diameter hardened steel die using a pressure of 25 MPa (section 3.2.5). Prior to insertion into the furnace the compacts were placed on 'U-shaped' holders to facilitate handling and measurement of the dimensional changes whilst minimising the degree of contact and hence the action of external forces during sintering.

Green body densities were determined from dimension and mass measurements as the samples contained significant open porosity and were not stable in water. Due to the fragile nature of the samples, measurements were performed on a separate set of green bodies, produced in an identical manner, and an average value was taken.

The in situ study apparatus was arranged such that the green body and holder were positioned in the centre of a 1 m long tube furnace (Lenton 1850 High Temperature Tube Furnace). A thermocouple was mounted directly behind the sample to measure the near sample temperature. A 35 mm SLR camera was positioned outside of the
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furnace, on the opposite side to the thermocouple, to enable images of the sample to be recorded. The tube furnace remained open at both ends throughout the experiment to allow observation of the sample and access for the thermocouple. The high aspect ratio of the tube prevented any temperature fluctuations from occurring within the heating zone.

The sample was initially heated at a rate of 5 °C/min to 500 °C to prevent thermal shock failure of the furnace tube. The fastest ramp rate afforded by the furnace was then used to raise the sample temperature to 1560 °C in order to minimise the time spent heating the sample and so reduce the degree of sintering prior to attaining the isothermal sintering temperature. The sample was held at the isothermal sintering temperature for 160 minutes and then furnace cooled. The furnace temperature, as measured by the thermocouple, is shown along with the results from the in situ studies. Photographs were taken at regular intervals during the process in order to monitor the changes in sample dimensions occurring due to thermal expansion and sintering processes. Prior to removal from the furnace the sample was again photographed, at room temperature, for purposes of calibration with the final density measured on removal. A schematic representation and photomontage of a negative image of the sample and sample holder are shown in figure 4.1.
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Figure 4.1 - Schematic and photomontage of negative image of sample and holder.
(The central cut-out of the support is not visible in the negative image due to the presence of the thermocouple behind the sample)

The photographic negatives were clamped between two glass plates and converted to digital images using a digital camera (Pixera PVC 100C) attached to a light microscope (Zeiss Axiophot) operating in transmitted light mode. A graphics package (Paintshop Pro v4&5) was used to record the positions of the four corners of the sample and hence enable the calculation of the sample diameter and height. By assuming that the sample mass remained constant throughout the test, it was possible to calculate the relative density changes of the sample.

To confirm the validity of the results obtained from the in situ observations four green bodies of as-received A-43-M and A-42-2 were sintered using identical heating and cooling rates with dwell times at 1560 °C of 0, 40, 80 and 120 minutes. Following sintering, sample densities were determined from mass and dimension measurements and compared to results obtained from the in situ study.
4.3 RESULTS

4.3.1 Variations in initial and final density

Green and final densities of the six samples are given in Table 4.1 along with the powder compositions. Refined A-42-2 could not be studied due to the difficulty in removing the small particles from the particle size distribution using centrifuging techniques.

Table 4.1 - Green and fired densities of powder compacts showing both the actual and percent theoretical density

<table>
<thead>
<tr>
<th>Powder</th>
<th>Green density (g/cm³)</th>
<th>Sample end density (g/cm³)</th>
<th>In situ end density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) as-received A-42-2</td>
<td>2.10 (53.0%)</td>
<td>2.45 (61.8%)</td>
<td>2.54 (64.0%)</td>
</tr>
<tr>
<td>b) as-received A-43-M</td>
<td>1.94 (48.8%)</td>
<td>3.24 (81.6%)</td>
<td>3.42 (86.1%)</td>
</tr>
<tr>
<td>c) refined A-43-M</td>
<td>1.90 (47.9%)</td>
<td>3.47 (87.5%)</td>
<td>3.47 (87.5%)</td>
</tr>
<tr>
<td>d) 3:1</td>
<td>2.08 (52.5%)</td>
<td>3.25 (82.0%)</td>
<td>3.34 (84.1%)</td>
</tr>
<tr>
<td>e) 1:1</td>
<td>2.23 (56.3%)</td>
<td>3.10 (78.0%)</td>
<td>3.24 (81.6%)</td>
</tr>
<tr>
<td>f) 1:3</td>
<td>2.26 (57.0%)</td>
<td>2.93 (74.0%)</td>
<td>2.87 (72.3%)</td>
</tr>
</tbody>
</table>

Although not directly related to this work, it is of interest to note the variation in green density exhibited by the six samples. The coarser as-received powder (A-42-2) can be seen to have a higher green density in comparison to the finer as-received powder (A-43-M). This difference in green density can be attributed to the increase in friction within the fine particle system. Through the refinement of A-43-M, large particles are removed from the system so increasing the level of frictional forces present and hence further reducing the green density. When the two powders are
combined an increase in density is observed which can be attributed to the smaller particles sitting within the interstitial sites between the large particles. Larger green densities are observed as a greater number of interstitial sites are made available with the addition of increased numbers of large particles. Examination of the final densities shows that the density increases with increased levels of small particles as a result of the greater sinterability of the smaller particles.

### 4.3.2 Sintering curves

The density-time curves obtained from this study all exhibited the same generic behaviour. As an example, figure 4.2 shows the results from unrefined A-43-M where six distinguishing regions can be identified.

![Sintering Curve](image)

**Figure 4.2 - Sintering curve obtained for unrefined A-43-M with results from interrupted tests**

- The density of the compact initially decreased at a slow rate with increases in temperature as would be expected from thermal expansion data.
- At approximately 600 °C the density dropped abruptly by a small amount and then continued to decrease at the previous steady rate.
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- At temperatures between 1300 °C and 1400 °C the density began to increase rapidly.
- As the temperature approached the isothermal sintering temperature the densification rate increased.
- During the isothermal sintering regime the densification rate gradually decreased with time.
- On cooling to room temperature a density increase greater than predicted from thermal expansion data was observed.

Differences between the results were evident in the degree of densification and the temperature at which sintering was initiated. Lower degrees of densification and later initiation became more prevalent with increased amounts of A-42-2 (the coarser of the two powders).

The accuracy of the in situ technique can be determined by comparing final densities measured from the sample with those determined from the in situ technique, and by comparing the in situ data with data obtained from a series of interrupted tests. The independently measured end densities were found to be in good agreement with those determined from the in situ study as shown in table 4.1. The agreement between interrupted and in situ data is not as good. It can be seen in figure 4.2 that the densities obtained from the interrupted sintering tests are consistently higher than those observed in the in situ study. The difference between the in situ and interrupted results and the rate at which the interrupted and in situ test densities vary with time are comparable indicating that there is a constant discrepancy.

4.4 **CORRECTION FOR RADIANCE**

From figure 4.2 it can be seen that the results obtained from interrupted tests do not agree with those obtained from the in situ study. The sudden abrupt drop in density at
approximately 600 °C and the excessive shrinkage on cooling are also of interest as they cannot be explained by conventional sintering theory. There are two possible explanations to account for the differences between the two sets of results and the abnormal density changes that occur at approximately 600 °C and on cooling.

The decrease in density at approximately 600 °C could be a result of the release of residual stresses introduced during uniaxial pressing. Examination of the variation in sample height and diameter during the course of the experiments showed that the sample height increased suddenly at 600 °C (t ~ 100 mins) which was not evident in the corresponding measurements of the diameter (figure 4.3). If residual stresses were present in the compact following pressing it is reasonable to assume that they would be greater in the direction of pressing such that the sample height would be predominantly affected by the release of stresses. The subsequent excessive increase in density on cooling could be a result of continued sintering as the samples cooled. Continued sintering on cooling would also result in the discrepancies between the density of the in situ sample and that of the interrupted test samples.
Figure 4.3 – Variation in sample height (h) and diameter (d) during sintering with subscript i indicating initial dimensions

The second explanation for the discrepancies observed is the phenomenon of radiance, where the sample radiates light at elevated temperatures causing the sample to appear larger than it is and an error to be introduced into the measured dimensions. This effect would lead to an overestimation of the sample volume and hence a lower apparent density. Figure 4.3 shows an apparent increase in the sample height after approximately 100 minutes (corresponding to 600 °C) which correlates with the point at which the samples begin to glow during testing. A corresponding increase in sample diameter is not observed as the effect of radiance results in a constant increase in dimensions and so becomes less significant as a fraction of a larger, initial diameter. The effect of radiance can account for all three of the discrepancies observed in the results as at temperatures above 600 °C the apparent density would be suppressed.

In order to ascertain which of the two possible effects was the cause of the deviations it was necessary to conduct a further set of experiments. The in situ tests were
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repeated after the sample had been thermally cycled to 1000 °C so as to remove any thermal stresses that may be present. It can be seen from figure 4.4 that the decrease in density is observed on both the initial cycle to 1000 °C and also the subsequent sintering cycle. It is also shown that on cooling from 1000 °C the density change was fully recovered indicating a reversible process which cannot be accounted for by residual stress release. The initial thermal cycle of 1000 °C did not eliminate the abnormal density change at approximately 600 °C indicating that the effect was not a result of the release of residual stresses resulting from green body formation.

Continued sintering can be dismissed as a cause of the discrepancy between interrupted tests and in situ tests, and the excessive densification on cooling, by examining the rate of cooling and the corresponding densification rates at reduced temperatures. In situ sintering studies of A-43-M at 1300 and 1400 °C showed that negligible densification occurred at these temperatures over a period in excess of 150 minutes. It can, therefore, be assumed that the excess densification would have to occur in the time taken to cool from 1560 to 1400 °C. Observations of the cooling times have shown that the samples cool to 1400 °C within 15 minutes. There is insufficient time during the cooling down to account for the degree of densification observed which is in excess of that occurring in the preceding 1 hour of sintering at 1560 °C.
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![Sintering curve](image)

Figure 4.4 - Sintering curve obtained for unrefined A-43-M incorporating an initial 1000 °C thermal cycle designed to eliminate pressing stresses

Thermal cycling of the green body samples prior to testing and considerations of the cooling rates and densification indicate that the discrepancies in the results are not caused by either the release of residual stresses or continued sintering. To verify the radiance theory further an *in situ* analysis was conducted on a fully dense alumina sample. The fully dense sample should only undergo volume change due to thermal expansion effects. It can be seen from figure 4.5 that an apparent decrease in density at approximately 600 °C (the same as in previous experiments) is observed. No permanent dimensional change is observed during the experiment as can be seen by the end density returning to that observed prior to heating.
Figure 4.5 - Sintering curve obtained for fully dense alumina showing an abrupt decrease in density at approximately 600 °C

Using the results from the *in situ* analysis of the fully dense alumina sample it is possible to determine a 'correction' factor to eliminate the radiance effect from the results. The effect of radiance causes the dimensional measurements to be overestimated by an amount that increases with temperature. At the point of maximum discrepancy this results in an error of approximately 4 % in measurements of sample height and 1 % in measurements of sample diameter. This 1 % error is too small to be resolved by the current technique and hence was not evident in the results shown in figure 4.3. Figures 4.6 a) to f) show the corrected sintering curve for the six powders examined.
Figure 4.6 a) - Corrected sintering curve of as-received A-42-2 with results from interrupted tests

Figure 4.6 b) - Corrected sintering curve of as-received A-43-M with results from interrupted tests
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Figure 4.6 c) - Corrected sintering curve of refined A-43-M

Figure 4.6 d) - Corrected sintering curve of powder blend with A-43-M : A-42-2 ratio of 3:1
Figure 4.6 c) - Corrected sintering curve of powder blend with A-43-M : A-42-2 ratio of 1:1

Figure 4.6 f) - Corrected sintering curve of powder blend with A-43-M : A-42-2 ratio of 1:3

The corrected in situ results show good agreement with results obtained from the interrupted tests as can be seen in figures 4.6 a) and b). As with the uncorrected

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results, the corrected results show the start of densification occurring at temperatures below the isothermal sintering temperature. The exact temperature at which densification starts to occur depends on the amount of A-42-2 present in the powder blend. With increased levels of large particles the start of densification can be seen to occur at higher temperatures. As the sample temperature approached the isothermal sintering temperature the rate of change of density increased sharply as the diffusion of atoms increased. On attaining the isothermal sintering temperature the rate of densification decreases with time. The sample density increases, as predicted by thermal expansion data, on cooling to room temperature.

Comparison of the density change observed during heating and cooling with that predicted by thermal expansion data from fully dense alumina, indicates that porosity has little, or no, effect on the thermal expansion characteristics of a compact. This observation agrees with observations in the literature that porosity has no effect on thermal expansion of a porous body as long as the matrix remain continuous (section 2.3.7).

4.5 SINTERING MODEL

4.5.1 Experimental verification

Much theoretical work has been aimed at modelling the initial stage of the solid state sintering behaviour of powders. Initial attempts were concerned with powders composed of particles of a single size. Recently, equation 4.1 has been developed by Pan et al. (1998) to describe the degree of densification occurring in a powder compact composed of particles of two sizes (section 2.2.4.4).

$$1 - \left( \frac{\rho_i}{\rho} \right)^\frac{1}{3} = \frac{1}{2} \chi(R_t, V_{fR}) A_p \left( \frac{t}{R^4_L} \right)^\frac{1}{n_p}$$

Eqn. 4.1
where \( A \) is a function of material properties and temperature, \( R_L \) is the size of the large particles, \( n \) is a constant predicted to have a value between 3 and 4, and \( \chi(R_r,V_f R_s) \) is a constant defined by:

\[
\chi(R_r,V_f R_s) = \frac{R_r^3 (1 - V_f R_s)^2 + V_f R_s (1 - V_f R_s)(1 + R_r)R_r + V_f R_s^2}{R_r^3 (1 - V_f R_s)^2 + 0.5V_f R_s (1 - V_f R_s)(1 + R_r)R_r + V_f R_s^2 R_r} \quad \text{Eqn. 2.25}
\]

where \( R_r = R_s/R_L \), \( R_s \) is the size of the small particles, and \( V_f R_s \) is the volume fraction of small particles. By taking natural logarithms of both sides, equation 4.1 can be arranged to a form which when plotted appropriately should give a straight line of slope \( 1/n \) i.e.

\[
\ln \left[ 1 - \left( \frac{\rho_i}{\rho} \right)^{3/2} \right] = \ln \left[ \frac{1}{2} \chi(R_r,V_f R_s) A_n \right] + \frac{1}{n} \ln \left[ \frac{t}{R_L^{4/3}} \right] \quad \text{Eqn. 4.2}
\]

The ratio of initial density to instant density, \( \rho_i/\rho \), can be obtained from sintering curves with \( t = 0 \) taken as the time at which densification first started. For this study \( R_L \) was taken as 2.75 \( \mu \text{m} \) (the mean particle radius obtained from particle size analysis of the large (A-42-2) powder) and the values of time and \( \rho_i/\rho \) used are given in table 4.2. The results are shown in figure 4.7.
Table 4.2 - Shrinkage data for bimodal powders

<table>
<thead>
<tr>
<th>powder</th>
<th>A-42-2</th>
<th>A-43-M</th>
<th>3:1</th>
<th>1:1</th>
<th>1:3</th>
</tr>
</thead>
<tbody>
<tr>
<td>time (min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.93</td>
<td>0.73</td>
<td>0.78</td>
<td>0.83</td>
<td>0.95</td>
</tr>
<tr>
<td>70</td>
<td>0.90</td>
<td>0.64</td>
<td>0.72</td>
<td>0.77</td>
<td>0.91</td>
</tr>
<tr>
<td>90</td>
<td>0.88</td>
<td>0.60</td>
<td>0.68</td>
<td>0.75</td>
<td>0.88</td>
</tr>
<tr>
<td>110</td>
<td>0.87</td>
<td>0.58</td>
<td>0.68</td>
<td>0.73</td>
<td>0.87</td>
</tr>
<tr>
<td>130</td>
<td>0.86</td>
<td>0.57</td>
<td>0.67</td>
<td>0.73</td>
<td>0.88</td>
</tr>
<tr>
<td>150</td>
<td>0.85</td>
<td>0.57</td>
<td>0.65</td>
<td>0.71</td>
<td>0.87</td>
</tr>
<tr>
<td>170</td>
<td>0.86</td>
<td>0.56</td>
<td>0.66</td>
<td>0.71</td>
<td>0.86</td>
</tr>
<tr>
<td>190</td>
<td>0.83</td>
<td>0.56</td>
<td>0.64</td>
<td>0.70</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Figure 4.7 - Variation in density with time for the various powder blends. Dashed lines represent lines of best fit for the initial and final sections of the curve.
Chapter 4 - In Situ Observations of Sintering

It can be seen that each data set presented in figure 4.7 does not lie on a straight line over the entire range as would be expected from equation 4.2. The curves can be regarded as consisting of two linear sections with the change in slope occurring at the same point irrespective of powder system. This consistency in the change of slope indicates the action of an effect that is constant throughout the powder systems. Examination of the microstructure of the sample containing only small particles (figure 4.8) indicates that interactions between the neighbouring necks of small particles have begun to occur at a time corresponding to the time when the slope of the lines change.

![SEM Photomicrograph of small particles (refined A-43-M) sintered for 70 minutes showing interaction of necks](image-url)

Figure 4.8 - SEM Photomicrograph of small particles (refined A-43-M) sintered for 70 minutes showing interaction of necks

All powder systems contain a proportion of these small particles, therefore, it is reasonable to assume that the small particles will begin to form interacting necks at approximately the same time leading to a reduction in the densification rate. Due to the interaction of particle necks, the initial section of the curves can be regarded as
more representative of the conditions described by the model proposed by Pan et al.

Table 4.3 gives details of both values of $n$ (i.e. $1$/slope) calculated for each powder.

<table>
<thead>
<tr>
<th>Powder</th>
<th>n (initial)</th>
<th>n (final)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-received A-42-2</td>
<td>0.70</td>
<td>3.82</td>
</tr>
<tr>
<td>refine A-43-M</td>
<td>1.23</td>
<td>6.81</td>
</tr>
<tr>
<td>A-43-M 3:1 A-42-2</td>
<td>1.42</td>
<td>5.44</td>
</tr>
<tr>
<td>A-43-M 1:1 A-42-2</td>
<td>1.41</td>
<td>3.83</td>
</tr>
<tr>
<td>A-43-M 1:3 A-42-2</td>
<td>1.23</td>
<td>2.59</td>
</tr>
</tbody>
</table>

Pan et al. predicted that $n$ would have a value between 3 and 4. It can be seen from the results presented in table 4.3 that this value of $n$ is not attained for the initial slopes. Only in the final sections of the curves are $n$ values attained that agree with those predicted. However, during this latter stage the microstructure is not consistent with that used to develop the model.

**4.5.2 Model limitations**

**4.5.2.1 Introduction**

To address fully the discrepancy between predicted and experimental values of $n$, the limitations of the model must be considered. The three main conditions imposed by the model that must be considered are that the model is only valid: (i) during the initial stages of densification when there is no interaction between neighbouring particle necks, (ii) when the contact number is not affected by densification changes, and (iii) where the ratio of the sizes of the small and large particles exceeds 0.5. Each of these limitations, and their effect on the value of $n$, are addressed separately.
4.5.2.2 Interaction between neighbouring particle necks

The shrinkage rates determined through computer simulations are based on the assumption of two interacting spheres where the surface curvatures within the system control the rate at which matter is distributed and hence the rate of shrinkage. When two or more neighbouring necks begin to interact with each other the surface curvature is reduced and the rate of shrinkage decreases. The model developed by Pan et al. does not account for such reductions in shrinkage rates and will predict higher than observed levels of densification. Figure 4.9 demonstrates schematically how a reduction in shrinkage rate can give rise to a decrease in the slope (and hence an increase in n).

![Graph showing interaction between particle necks](image)

Figure 4.9 – Schematic representation of how particle neck interaction (reduction in shrinkage rate) gives rise to a decrease in the slope.

4.5.2.3 Change in contact number with densification

The term $\chi(R_c, Vf_{Rs})$ in equation 4.3 describes the number of contacts between the particles within the compact. This function is strictly only valid for situations where there are particles of only two sizes present. For a real system, composed of a variety of particle sizes, it can be assumed that the term $\chi(R_c, Vf_{Rs})$ would still be a function of the sizes and amounts of the various particles present. If the particles do not grow in size, or are not removed from the system, then it is reasonable to assume that the term $\chi(R_c, Vf_{Rs})$ would remain constant as necessitated by the model. Figure 4.10
shows the evolution of the microstructure of the compact containing large particles. It can be seen that the number of small particles decreases with time. Due to the large size difference between the small and large particles it can be assumed that resultant redistribution of matter would cause a negligible increase in the size of the large particles.

Figure 4.10 - SEM photomicrograph showing microstructural changes of compact composed of large particles (A-42-2)

A reduction in the number of small particles will result in a change in the value of \( \chi(R_s, Vf_{Rs}) \). If the term \( \chi(R_s, Vf_{Rs}) \) for real powders is considered to behave in a similar manner to the term \( \chi(R_s, Vf_{Rs}) \) used to describe a system composed of particles of two sizes only, then it becomes possible to surmise what the effect would be of removing the small particles from the system.

The removal of small particles would be expected to result in a reduction in the proportion of smaller particles and a decrease in the size difference between the largest and smallest particles remaining within the system. Examination of equation 2.25 shows that a reduction in the volume fraction of small particles and a reduction in the size difference of the particles both have the effect of reducing the value of
\( \chi(R_r, Vf_{Rs}) \). Figure 4.11 demonstrates how a reduction in \( \chi(R_r, Vf_{Rs}) \) can give rise to a decrease in the slope of the curve.

![Figure 4.11 - Schematic representation of how removal of small particles (reduction in \( \chi(R_r, Vf_{Rs}) \) term) gives rise to a decrease in the slope](image)

4.5.2.4 *Ratio of the size of small and large particles*

Computer simulations on the effect of the ratio of the sizes of the small and large particles within the system (Pan *et al.*, 1998) revealed that for \( R_s/R_L \) ratios greater than 0.5 the results fell on parallel lines. For \( R_s/R_L \) ratios less than 0.5 the normalised shrinkage rate was shown to decrease more rapidly than predicted (figure 4.12).

![Figure 4.12 - Schematic representation of relationship between shrinkage rate and contact radius for various values of \( R_s/R_L \) (after Pan *et al.*, 1998)](image)
If the initial powder compact contains a large number of particle pairs where $R_S/R_L < 0.5$ then the observed normalised shrinkage rate will be greatly reduced in comparison to that predicted by the model. When the smallest particles are removed, it is reasonable to assume that the average $R_S/R_L$ value will increase and hence the shrinkage rate will increase. Continued removal of the smallest particles will lead to a continuous increase in the normalised shrinkage rate. The density increases observed following the removal of the small particles will have the effect of increasing the apparent densification rate with respect to that expected had the small particles remained. It is unlikely that the gradual increase in $R_S/R_L$ would result in a slope that exceeded that predicted for a case of $R_S/R_L > 0.5$ (figure 4.13).

![Diagram](image)

Figure 4.13 – Schematic representation of how removal of small particles (gradual increase in shrinkage rate) gives rise to an apparent decrease in the slope.

The removal of small particles will also have another effect in that it will create new particle-particle contacts. It can also be seen from figure 4.12 that the formation of new contacts (low contact radii) will result in a large increase in the rate of shrinkage. Hence the removal of particles (and the corresponding formation of new contacts) will greatly increase the rate of densification.

### 4.5.3 Variation in the slope of the curves

The results obtained in section 4.5.1 can now be re-examined in light of the limitations of the model. During the early stages of sintering, prior to the interactions
of particle necks, the factor that will affect the slope of the curves will be the removal of the small particles. This has been shown to give rise to a reduction in the slope due to changes in the terms $\chi(R_r, Vf_{Rs})$ and $R_s/R_L$. However, these changes are expected to be small in comparison to the effect of creating new particle-particle contacts which will greatly increase the normalised shrinkage rates and lead to increases in the slope of the curve. During the latter stages the factor that will control the slope of the curve will be the removal of small particles and the particle-neck interactions. The increases in densification that are attained through the removal of the small particles will be reduced due to the reduction in densification rates elsewhere in the system.

These controlling factors have the effect of initially increasing the slope of the curve such that $n$ is underestimated. Once particle pairs begin to interact an additional slope reducing effect will cause the value of $n$ to increase. The apparent agreement between the values of $n$ observed during the later stages of sintering and those predicted by Pan et al. is coincidental and results from combinations of the various contributing factors producing slopes similar to those predicted by the model.

### 4.5.4 Variation in the intercept of the curve

Along with predicting values of $n$, Pan et al. suggested further that the relative positions of the sintering curves could be predicted by considering the relative values of $\chi(R_r, Vf_{Rs})$. The term $\ln[1/2 \chi(R_r, Vf_{Rs}) A]$ represents the point at which the experimental curve intercepts the y-axis and therefore details the separation between the various sintering curves. The term $A$ is dependent on material and temperature, and hence is constant for a given system. Therefore, the value of $\chi(R_r, Vf_{Rs})$ should give an indication of the relative positions of the curves. Table 4.4 shows a comparison of calculated $\chi(R_r, Vf_{Rs})$ values and y-axis intercept values obtained from the initial section of the sintering curves.
Table 4.4 – Comparison of extrapolated intercept values and calculated $\chi(R_0, V_f R_0)$ values.

<table>
<thead>
<tr>
<th>Small to large blend ratio</th>
<th>y-axis intercept values</th>
<th>ln [calculated $\chi(R_0, V_f R_0)$] (using equation 4.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All small</td>
<td>-2.19</td>
<td>1.90</td>
</tr>
<tr>
<td>3:1</td>
<td>-2.43</td>
<td>1.76</td>
</tr>
<tr>
<td>1:1</td>
<td>-2.69</td>
<td>1.55</td>
</tr>
<tr>
<td>1:3</td>
<td>-3.55</td>
<td>1.18</td>
</tr>
<tr>
<td>All large</td>
<td>-3.81</td>
<td>0.0</td>
</tr>
</tbody>
</table>

It can be seen from the results presented in table 4.4 that it is possible to predict the relative order in which the various experimental curves will appear. A more accurate prediction is not possible due to the difficulty in defining the term $\chi(R_0, V_f R_0)$. Equation 2.25 can only be used for situations where the compact is composed of particles of two sizes. Real powder systems are composed of powders that contain particles that vary in size over an order of magnitude.

4.6 SUMMARY

A technique for continuously monitoring the densification of powder compacts has been presented. Accurate densification data for powders with different size distributions has been obtained from these in situ studies. A disparity between the in situ and interrupted test sintering data was attributed to the effect of radiance and effectively eliminated following an in situ study of the sintering of fully dense alumina. The ‘corrected’ results showed that as the green body temperature increased the thermal expansion of the sample was identical to that measured from fully dense samples confirming that thermal expansion is independent of porosity. The corrected in situ results were used to provide experimental verification of a model proposed by Pan et al. to describe the sintering of a powder compact composed of particles of two sizes. It was shown that the model correctly predicted that the results would fall on a
series of straight, parallel lines. The model also correctly predicted the relative position of the lines based on the proportions of small and large particles. The predictions of the slope, n, could not be verified due to the particle size distribution exceeding the $\frac{R_o}{R_i} > 0.5$ limit and interactions between the necks of the small particles resulting in a decrease in the value of n observed.
Chapter 5 - Behaviour of Large Pores during Sintering

CHAPTER 5

BEHAVIOUR OF LARGE PORES DURING SINTERING

5.1 INTRODUCTION

The final stage of sintering is often modelled assuming an ideal system composed of equisized grains and small pores. However, real systems often include large pores formed by poor agglomerate packing. This chapter will examine the shrinkage behaviour of large pores and compare it with model predictions. Large pores were introduced by adding starch to the powder blend. During the sintering process the starch particles are expected to burn off resulting in a body containing isolated large pores. Measurements of sample density are used to determine the level of absolute porosity and the amount of deliberately introduced large pores. A technique is then presented that enables the degree of pore shrinkage to be calculated by comparing the observed density changes with those predicted using a rule of mixtures. Previous work by Slamovich and Lange (1992) calculated the percentage volume reduction of the large pores during matrix densification to be identical to that exhibited by the matrix phase. The current method is capable of determining changes in the size of the pores other then that expected from matrix densification.

Details of the ceramographic techniques used to obtain microstructural information on the porous bodies are also presented and the results used to corroborate calculations of pore shrinkage and levels of porosity. These techniques are also used to determine the mean grain size and porosity of the matrix phase and to characterise the large pores. This is required to enable full analysis of the subsequent mechanical tests as both the amount and form of porosity is known to affect the mechanical properties of ceramics.
5.2 EXPERIMENTAL METHODOLOGY

5.2.1 Ceramographic preparation

Both fractography and sectioning were utilised to obtain information on the microstructure of the samples. Sectioning and polishing allows a random cross-section of the sample to be examined. The section should be representative of the sample assuming that there is a random distribution of phases. When examining sections from polished samples it is important to consider the possible effects of grain growth and grain pullout that can occur during sample preparation. This is not an issue when examining fracture surfaces as polishing and thermal etching are not required for sample preparation. However, non representative surfaces may be obtained if the sample preferentially fractures along a line of weakness i.e. an area of high porosity. The use of both techniques ensures that the microstructure is characterised accurately.

Sectioning of samples was conducted using a diamond cut-off saw (Struers Accutom and Accutom 5). Cutting rates of 0.2 mm/min and wheel rotation speed of 3000 rpm were employed throughout preparation. Grinding and polishing were conducted following the schedule described in Table 5.1 using the Struers Planopol-2/Pedemax-2 polishing wheel and holder.
Table 5.1 – Polishing schedule for 6 cylindrical samples or 15 test bars

<table>
<thead>
<tr>
<th>Polishing wheel/cloth</th>
<th>Time (mins)</th>
<th>Pressure (1 = 30N)</th>
<th>Speed (rpm)</th>
<th>Lubricant</th>
</tr>
</thead>
<tbody>
<tr>
<td>125 µm</td>
<td>until plane</td>
<td>3</td>
<td>300</td>
<td>water</td>
</tr>
<tr>
<td>75, 40, 30, 20, 10 µm</td>
<td>10</td>
<td>3</td>
<td>300</td>
<td>water</td>
</tr>
<tr>
<td>6, 3 µm</td>
<td>10</td>
<td>3</td>
<td>300</td>
<td>Struers blue</td>
</tr>
<tr>
<td>1 µm</td>
<td>5</td>
<td>2</td>
<td>300</td>
<td>Struers blue</td>
</tr>
</tbody>
</table>

5.2.2 Thermal etching

To facilitate the measurement of grain size, samples were thermally etched at 1450 °C for 20 minutes in a tube furnace (Lenton 1850 High Temperature Tube Furnace) with an air atmosphere. Comparison of etched and unetched samples indicates that thermal etching does not affect the grain size significantly.

5.2.3 Microscopy

5.2.3.1 Reflected light microscopy

Prior to examination with the reflected light microscope it was necessary to polish the samples to 1 µm to obtain a flat and optically reflective surface. The microscope used was a Ziess Axiophot equipped with a digital camera (Pixera PVC 100C).

5.2.3.2 Scanning electron microscopy

The insulating nature of ceramics leads to sample charging during examination with a scanning electron microscope (SEM). Incident electrons are not conducted away and result in a negative charge on the surface of the sample which deflects the electron beam. To eliminate this problem, non-conducting samples are sputter coated.
with gold (Edwards sputter coater S150B) to form a conducting surface layer. SEM photomicrographs were obtained from Cambridge Instruments S100 and Hitachi S-3200N scanning electron microscopes operating in secondary electron imaging mode.

5.2.4 Density measurement

Two techniques were used to determine the density of samples. With the presence of open porosity or where degradation was likely to occur with water contact (i.e. green bodies) the density was determined using direct dimensional and mass measurements. All other sample densities were determined using a water immersion technique based on the Archimedes' principle. Samples were thoroughly dried and initially weighed in air and then in water. Equation 5.1. was then used to calculate the density of the samples.

\[
\rho = \frac{m_a \rho_n}{\Delta m}
\]

Eqn 5.1.

where \(\rho\) is the density of the ceramic sample, \(m_a\) is the mass of the sample measured in air, \(\rho_n\) is the density of the immersion fluid (water) and \(\Delta m\) is the difference between the mass of the ceramic measured in air and measured in water. Prior to measurement of sample densities, the density of the water was determined by measuring the mass of 50 ml of water that had been held at the ambient temperature for 30 minutes.

5.2.5 Determination of volume fraction of porosity

5.2.5.1 Density method

The density of the porous body was used to determine the volume fraction of total porosity present using equation 5.2.
\[ V_{fp} = 1 - \frac{\rho}{\rho_{th}} \quad \text{Eqn. 5.2} \]

where \( \rho_{th} \) is the theoretical density of the material (taken to be 3.97 g/cm\(^3\) for alumina) and \( V_{fp} \) is the volume fraction of porosity. To determine the level of added porosity it is necessary to assume that the matrix phase has a constant level of porosity. The porous matrix can then be regarded as constant and the density of the pore free material, \( \rho_{th} \), can then be replaced by the density of the material with no added porosity, \( \rho_0 \).

5.2.5.2 Pore area fraction method

For a composite containing uniformly distributed constituents the area fraction of each phase bisected by a plane passing through the body is equal to the volume fraction present within the body as a whole (Haynes, 1986). To determine the area fraction of porosity the samples were sectioned and polished to 1 \( \mu \)m as described in section 5.2.1. SEM images were then examined using an image analysis package (Image Tool v2.0, University of Texas Health Science Centre in San Antonio) to measure the area fraction of the pores and hence determine the volume fraction of porosity.

5.2.6 Pore size determination

5.2.6.1 Sectioning method

Two techniques were employed to measure the pore size from sectioned samples. The first method used techniques described in section 2.5.5.2 to obtain measurements of mean pore area which were then used to calculate the mean pore diameter assuming a circular pore geometry. The second technique was based on a linear
intercept method as described in section 5.2.7 with the porous phase regarded as the primary phase.

5.2.6.2 Density method

If the resultant pore size is equal to that of the size of the starch particles then there should be a linear relationship between density and volume fraction of starch addition such that:

$$\rho = \rho_0 (1 - V_{fs})$$  \hspace{1cm} \text{Eqn. 5.3}$$

where $\rho_0$ is the density of the ceramic with no added porosity, $\rho$ is the density of the porous ceramic and $V_{fs}$ is the volume fraction of starch added. If the pores shrink, the density will increase relative to that predicted by the rule of mixtures. To determine the degree of pore shrinkage it is necessary to express the predicted density in terms of the volume of the original pores and solid material present. If the pores are assumed to be identical then:

$$\frac{\rho}{\rho_0} = 1 - \frac{N_p V_p}{V_e + N_p V_p}$$  \hspace{1cm} \text{Eqn. 5.4}$$

hence:

$$\frac{\rho}{\rho_0} = \frac{V_e}{V_e + N_p V_p}$$  \hspace{1cm} \text{Eqn. 5.5}$$

where $N_p$ is the number of pores, $V_p$ is the original volume of one pore (also equal to the volume of the starch particle) and $V_e$ is the volume of ceramic. An expression for the number of pores present in the porous body can then be obtained by rearranging equation 5.5:
The relative density of the body containing pores smaller than the original starch particles can be given by:

\[ N_p = \frac{V_c}{V_p} \left( \frac{\rho_0}{\rho} - 1 \right) \]  
Eqn. 5.6

where \( \rho^* \) and \( V_p^* \) is the new density and pore volume assuming shrinkage. During pore shrinkage only the pore volume decreases and the number of pores remains constant but the volume decreases, hence:

\[ \frac{\rho^*}{\rho_0} = \frac{V_c}{V_c + N_p V_p^*} \]  
Eqn. 5.7

A series of 'shrinkage curves' can be calculated by varying the volume ratio of the shrunken and original pore \((V_p^*/V_p)\). If the volume ratio is equal to 1 (i.e. no pore shrinkage) then the relative density calculated will agree with that predicted by the rule of mixtures. Figure 5.1 shows one possible modified curve \((V_p^*/V_p = 0.30)\) where the size of the pores, but not their number, has decreased. As the pores decrease in size the deviation from the 'no pore shrinkage' curve becomes more pronounced.
Chapter 5 – Behaviour of Large Pores during Sintering

Figure 5.1 - Variation of sintered body density with starch additions showing case of no pore shrinkage and one possible result of pore shrinkage ($V_p^*/V_p = 0.30$)

The calculated shrinkage curves can be fitted with a third order quadratic equation to give an excellent fit over the entire porosity range. However, over the range of interest (volume fraction of starch additions < 0.2) the curve is approximated well by a straight line. By plotting experimentally determined density data versus the volume fraction of starch present in the original powder, and applying a line of best fit to the data, it is possible to determine the change in slope from that predicted by the rule of mixtures. Theoretically determined curves can then be used to relate the change in slope observed to the degree of pore shrinkage and hence the mean pore size using a knowledge of the size of the initial starch particles.

A similar technique can also be applied to measurements of green body density. Equation 5.3 must be modified to account for the presence of the starch particles in the green body as shown by:

$$\rho = \rho_{Ge}(1 - V_{f_s}) + \rho_{Gs}V_{f_s}$$

Eqn. 5.9
where \( \rho_{G} \) and \( \rho_{G} \) represent green densities of alumina and starch. Equations 5.5 and 5.6 then become:

\[
\frac{\rho}{\rho_0} = \frac{V_{Ge} + N_p V_p (\rho_{Gs}/\rho_{Ge})}{V_{Ge} + N_p V_p}
\]

Eqn. 5.10

\[
N_p = V_e \left( \frac{\rho_{Ge}}{\rho} - 1 \right) / \left( 1 - \frac{\rho_{Gs}}{\rho} \right) V_p
\]

Eqn. 5.11

where \( V_{Ge} \) is the volume of the ceramic green body. The green body analysis is based on the assumption that \( \rho_0 \) and \( \rho_s \) refer to the density of the respective green bodies and that the packing efficiency does not change significantly with composition.

5.2.7 Grain size determination

A modified linear intercept technique proposed by Wurst and Nelson (1972) was used to determine the mean grain size. An overlay, containing one or more test lines of known length, was fixed over a photomicrograph of a polished section. The number of interceptions between test lines and grain-grain boundaries were then counted. For the case of a homogenous single phase materials the standard linear intercept equation (equation 5.12) was used to determine the mean grain size.

\[
GS = 1.56 - \frac{C}{M N}
\]

Eqn. 5.12

where \( GS \) is the mean grain size, \( C \) is the total length of test line, \( M \) is the magnification and \( N \) is the number of intercepts. A constant of 1.56 is incorporated as a correction factor to account for the probability of the line not encountering the maximum diameter of the grain. To account for the presence of second phases (e.g. porosity) the length of the test line must be reduced by the amount that lies on the second phase. It is also necessary to recognise the different types of intersections.
(grain-grain and grain-pore). The effective number of intercepts with grain boundaries of the primary phase is given by:

\[ N_{\text{eff}} = N_{aa} + \frac{1}{2} N_{ab} \]  
Eqn. 5.13

where \( N_{\text{eff}} \) is the effective number of intercepts, \( N_{aa} \) is the number of intercepts with a grain-grain interface and \( N_{ab} \) is the number of intercepts with a grain-pore interface.

The modified linear intercept equation is thus given by:

\[ GS = 1.56 \frac{C_{\text{eff}}}{MN_{\text{eff}}} \]  
Eqn. 5.14

where \( C_{\text{eff}} \) is the effective length of the test line.

An overlay grid containing 14 lines of known length was placed over a SEM photomicrograph of the sample. The number of points where a line intersected a grain-grain boundary or a grain-pore boundary were counted and used to calculate the mean grain size using equation 5.14. A minimum of 3 photomicrographs were used to obtain the grain size for a given sample. To confirm a consistent matrix grain size, the matrix phase of each sample type (different volume percent starch) was measured.

5.3 RESULTS

5.3.1 Density measurements

Table 5.2 gives details of the volume fraction of starch added with the corresponding green and final density and volume fraction of porosity present in the sintered bodies. As expected, the density of the sintered body decreases with increased starch addition.
Table 5.2 – Variation in final density with starch addition

<table>
<thead>
<tr>
<th>Volume fraction of starch added</th>
<th>Green density (g/cm(^3))</th>
<th>Final density (g/cm(^3))</th>
<th>Volume fraction of added porosity following sintering</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2.11</td>
<td>3.81</td>
<td>0.0</td>
</tr>
<tr>
<td>0.044</td>
<td>2.06</td>
<td>3.71</td>
<td>0.026</td>
</tr>
<tr>
<td>0.098</td>
<td>2.00</td>
<td>3.61</td>
<td>0.054</td>
</tr>
<tr>
<td>0.130</td>
<td>1.94</td>
<td>3.51</td>
<td>0.080</td>
</tr>
<tr>
<td>0.181</td>
<td>1.84</td>
<td>3.36</td>
<td>0.119</td>
</tr>
</tbody>
</table>

Figures shown are to 2 significant figures.

To verify the results of the porosity volume fraction calculated from density measurements the results were compared with those obtained from measurements of porosity area fractions of polished sections. Figure 5.2 shows a comparison between the results obtained using image analysis and those from density measurements.

Figure 5.2 - Comparison of volume fraction porosity determined from density measurements and image analysis of sample sections
It can be seen that the two sets of results are in good agreement. There is a degree of scatter associated with the results from the image analysis technique arising from local inhomegeneities in the pore distribution that are detected due to the finite size of the sampling area. Measurements of the area fraction of porosity present within the matrix phase shows that the level of porosity to be approximately constant. This is confirmed by the good agreement between the values of volume fraction of added porosity determined from density measurements and those obtained using area analysis. If the matrix phase did not exhibit a constant density then the volume fraction of added porosity determined by density measurements would exhibit a deviation from that shown by area analysis.

5.3.2 Pore size determination

Figures 5.3 and 5.4 show the density-starch addition curves relating to green bodies and sintered bodies respectively. The dashed lines represent the model predictions assuming no starch/pore shrinkage while the solid line represents a line of best fit relating to the experimental data. Data relating to green and final density are presented in table 5.2. The density of starch was taken as 0.75 g/cm³ which takes into account a 50 % packing efficiency, similar to that observed in the alumina green body.
Figure 5.3 - Density-starch addition relationship for green bodies containing starch particles (a line of best fit is not included as it coincides with the theory line)

Figure 5.4 - Density-starch addition relationship for sintered bodies containing pores

It can be seen that the experimental density data relating to the green body corresponds with that predicted by the rule of mixtures indicating that the starch particles do not decrease in size during pressing. The corresponding experimental data relating to the sintered samples clearly illustrates a marked deviation from that predicted by the rule of mixtures. Application of a line of best fit shows that the experimental data can be described by a straight line with a slope relative to that of
the no shrinkage prediction of 0.65. Comparison with the theoretically derived curves indicates that a decrease in the slope by a factor of 0.65 relates to a pore shrinkage factor of 0.85. Particle size analysis of corn starch particles determined the mean particle diameter to be approximately 15 μm (section 3.3.1). Hence the mean pore diameter is approximately 12.8 μm.

Examination of polished sections of the porous samples indicates that the mean pore diameter as determined by area analysis is approximately 14.0 μm, while that determined using the linear intercept technique is about 11.9 μm. It can be seen that all three sets of results show that the pores shrink during processing. There is some degree of disagreement between the sets of results due to the different techniques used to obtain them. No correction factor has been applied to the results obtained from examination of polished sections. When considering a composite composed of two solid phases a correction factor of 1.56 is usually applied to data obtained using the linear intercept technique (a slightly reduced factor would be used for the case of area intercept technique) to account for the sampling line (or area) not bisecting the grain at its maximum diameter. For the case of a porous body the standard conversion factor is not applicable due to the possible enlargement of pores during sample preparation. This is demonstrated in figure 5.5 which shows how fracture around some pores can lead to pore enlargement. Further compounding the issue is the charging effect associated with sharp edges when using a SEM. The charging effects at the edge of pores makes it difficult to accurately define the edge of a pore when examining images obtained using a SEM. Both of these factors lead to an overestimation of the pore size if conventional conversion factors are applied. Examination of the fracture surface of a porous ceramic (figure 5.8) shows the mean pore size to be approximately 10 μm. However, quantitative size analysis is not possible due to the varying levels of pore bisection exhibited by the fracture surface.
Both density measurements and microstructural studies have shown that the pores found in the sintered bodies are smaller than the starch particles used to introduce them indicating that a degree of pore shrinkage has occurred during the sintering process. Analysis of pore shrinkage has generally only examined the case of pores surrounded by grains of a uniform size and concluded that shrinkage of large pores does not occur. Experimental observations, however, have shown that that samples containing large pores surrounded by many small grains densify at a faster rate than samples containing large pores surrounded by large grains (Slamovich & Lange, 1992). These experimental observations, and those observed in this work, appear to be in contradiction with the analysis of shrinkage of large pores. Pan et al. (1999) have shown that large pores surrounded by many small, equisized grains are not expected to shrink (agreeing with previous work). However, a real system is not composed of grains of one size. Pan et al. showed that the presence of a variation in the size of the grains surrounding the pore facilitates shrinkage of the pore. Finite difference analysis of pore shrinkage showed that pore shrinkage could occur either via neighbour shrinkage when the small grains move towards the pore, or by grain growth where the small grains are consumed by the larger ones. Both techniques lead to a change in the number of grain surrounding the pore. Which process dominates was shown to be a function of the grain boundary and surface diffusivities and the
Chapter 5 – Behaviour of Large Pores during Sintering

grain boundary mobility with the grain growth mechanism favours by high grain boundary migration and surface diffusion.

5.3.3 Grain size determination

Sample grain sizes are given in table 5.3. It can be seen that the matrix grain size is comparable in all samples indicating that the addition of starch did not affect the sintering of alumina. A representative photomicrograph of the matrix phase of sintered AKP30 is shown in figure 5.6.

Table 5.3 – Matrix grain size measurements

<table>
<thead>
<tr>
<th>Porosity volume fraction</th>
<th>Mean grain size (μm)</th>
<th>Mean grain size (μm) (from all samples)</th>
<th>Standard deviation (from all samples)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.13 ± 0.53</td>
<td>2.18</td>
<td>0.39</td>
</tr>
<tr>
<td>0.026</td>
<td>2.35 ± 0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.054</td>
<td>2.08 ± 0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.080</td>
<td>2.20 ± 0.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.119</td>
<td>2.12 ± 0.25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.6 - Representative photomicrograph of matrix phase of alumina-pore composite

The photomicrograph shows that some areas of the microstructure are fully dense while others have not yet densified fully. This form of microstructure is probably a result of the differential sintering characteristics of inter and intra-agglomerate zones.

5.3.4 Pore distribution

Examination of polished sections and fracture surfaces shows that there was a degree of pore clustering that became more pronounced with increased levels of starch addition. Figure 5.7 demonstrates the variation of clustering with increased starch content.
Figure 5.7 – Reflected light photomicrographs showing the variation in pore microstructure with increased starch addition [where added porosity for A, B, C and D is 2.6%, 5.4%, 8.0% and 11.9% respectively]

With increased pore clustering, areas of low porosity between the clusters become more pronounced. Pore clustering of this nature is thought to occur due to the presence of large alumina agglomerates. The agglomerates form areas of no added porosity and subsequently cause an increase in the level of porosity in the surrounding material.

There is also evidence that alumina particles become embedded in the softer starch particles to form a coating as demonstrated by the presence of ‘husks’ within the pores of a fracture surface shown in figure 5.8. The husks have a thickness of one grain indicating that the grains were separated from the matrix during the sintering process. Such debonding could be a result of the grains of alumina closest to the
starch particle being pulled away as the starch particle shrank during pyrolysis. Alternatively, the first layer of alumina grains may have sintered more rapidly as a result of having a level of packing efficiency. The more rapid sintering would result in a greater shrinkage rate causing the layer to separate from the matrix phase.

Figure 5.8 - SEM photomicrographs of fracture surface showing alumina husks within pores

Husks are not evident in all pores. As there is not extensive bonding between the husks and matrix, husks may become dislodged during fracture and sample handling. It is uncertain whether these coatings were formed during powder processing or during the green body formation process. It is conceivable that if the coatings were formed during processing then they could also lead to a degree of pore clustering when neighbouring starch particles share a common particle. The formation of such coatings around the starch particle may also explain why pore combination is not
observed. This point favours the formation of coatings during the processing stage when large scale movement of particles is still possible.

5.4 SUMMARY

Measurements of sample density have been used to determine both the absolute level of porosity and the level of deliberately introduced porosity. Analysis of the area fractions of porosity has confirmed measurements made using sample densities. The variation in sample density following sintering has also been used to calculate the mean pore size by comparing observed density changes with those calculated for a model system. By assuming an initial pore size of 15 μm, the technique indicates that the starch particles are not compacted during pressing and that the pore size following sintering is approximately 12.8 μm. Microstructural analysis of sections through the material indicate the pore size to be between 11.9 and 14.0 μm. Without an accurate conversion factor to account for pore enlargement during polishing it is not possible to make a direct comparison between the two sets. Both techniques, however, indicate that pore shrinkage occurs, confirming predictions of large pore shrinkage made following computer simulations of the sintering process (Pan et al., 1999).

Subsequent characterisation of the sample microstructure indicates that the matrix phase has a mean grain size of approximately 2.18 μm and 3.8 % porosity irrespective of the amount to starch addition. Increased levels of starch addition cause an increase in the degree of pore clustering (i.e. pore free areas are surrounded by relatively highly porous material). The pore clustering was attributed to presence of agglomerates of alumina powder.
CHAPTER 6

EFFECT OF POROSITY ON
MATERIAL PROPERTIES

6.1 INTRODUCTION

This chapter aims to examine the effect of porosity on the strength, Young’s modulus and work of fracture which in turn affect the thermal shock resistance of the material. The extent of this effect is dependent on the amount of porosity present and the nature of the pores. The experimental techniques used to obtain strength and Young’s modulus data are presented in conjunction with the experimental results obtained. The results are then analysed with reference to the Spriggs’ empirical equation and compared with results predicted by the theoretical minimum solid area model. The discrepancies between model and experimental results are explained with reference to the microstructure and pore distribution within the bodies with particular reference to the role that pore clustering plays in the different behaviour of strength and Young’s modulus.

6.2 MECHANICAL TESTING

6.2.1 Strength and Young’s modulus measurement

Strength and Young's modulus values of non-ceramic materials can normally be obtained from load and displacement measurements taken during tensile tests. This technique is unsuitable for testing ceramics due to their brittle nature which leads to difficulty in gripping the sample and a need for very accurate alignment of the
sample and load train to prevent premature failure. To obtain strength and Young's modulus values for a ceramic body a convenient technique to use is flexure testing where a sample is loaded using either a 3 or 4 point bend rig. Bending of the sample results in tensile stresses being generated on the outside surface of the sample while compressive stresses are generated on the inside surface. The magnitude of the stresses generated can be calculated from the applied load. Young's modulus can be determined from the load and associated deflection.

Following sintering, the samples were ground to produce specimens of width 4.0 mm ± 0.13 mm and thickness 3.0 mm ± 0.13 mm in accordance with ASTM C 1161-90. Samples were ground to shape using a diamond embedded grinding wheel attached to a flat bed grinder. The test samples were ground longitudinally such that no more than 0.03 mm of material was removed per pass. Final grinding and polishing of the tensile surface, to 1 μm, was conducted using the ceramographic preparation techniques described in section 5.2.1. To reduce the risk of sample failure initiating from an edge, the sample edges were chamfered at 45° using a 10 μm polishing wheel. Figure 6.1 shows the sample dimensions employed with the polished face marked in bold.

![Figure 6.1 - Test sample geometry](image)

The bend rig was arranged as shown in figure 6.2 with the polished surface of the sample (lower face) in contact with the bottom two rollers so that it would be subjected to a tensile stress. To prevent pre-loading of the sample, the top roller was secured to the upper cross-head. Machine stiffness was eliminated by obtaining
deflection data using an extensometer mounted between points A and B. This ensured that the deflection measured was the deflection of the sample and did not include elastic strains associated with the bend rig or testing machine. The samples were loaded at a constant cross-head displacement rate of 0.5 mm/min until failure.

![Three point flexure test rig](image)

**Figure 6.2 – Schematic of the three point flexure test rig used to obtain strength and Young’s modulus data**

Sample dimensions were measured following testing to prevent strength limiting flaws from being introduced. Width and thickness values were taken as the mean of the values measured on either side of the point of failure. Equations 6.1 and 6.2 were used to determine strength ($\sigma_f$) and Young’s modulus ($E$) values from load-displacement curves and sample dimension measurements (ASTM C 1161-90, ASTM C 674-88).

$$\sigma_f = \frac{3P_{\text{max}}L_B}{2bd^2} \quad \text{Eqn. 6.1}$$

$$E = \frac{P}{\delta} \frac{L_B^3}{4bd^3} \quad \text{Eqn. 6.2}$$
where $P_{\text{max}}$ is applied load at failure, $L_d$ is the span between the bottom two rollers, $b$ and $d$ are specimen cross-section width and thickness respectively and $P/\delta$ is the slope of the linear section of the load-displacement curve.

6.2.2 Work of fracture measurement

Samples were prepared as described in section 6.2.1. To eliminate the effect of crack initiation, a sharp pre-crack was introduced into the sample by applying a series of Vickers indents (2 kg load) along a line such that they acted as a macro crack of uniform depth. The samples were then tested in three point bending as described in section 6.2.1. The resultant load-displacement curves were then used to determine the work of fracture of the sample by calculating the area under the curves.

6.3 RESULTS

Analysis of the sample microstructure showed that there was a constant degree of porosity present in the matrix phase of the samples as a result of incomplete sintering (section 5.3.1). Porosity arising from incomplete sintering affects the mechanical properties to a different extent to porosity introduced via a fugitive phase. Thus, it was necessary to separate the two effects by considering the porous matrix as the base material. The strength and modulus measurements obtained were then compared to the results obtained from samples containing no added porosity (i.e. the porous alumina matrix was considered as a homogenous material of strength, $\sigma_0$, and Young’s modulus, $E_0$). Volume fractions of added porosity were determined as described in section 5.2.5.

Figures 6.3, 6.4 and 6.5 show the results for strength, Young's modulus and work of fracture as a function of volume fraction of added porosity. It can be seen that the strength and Young’s modulus decrease with increased levels of porosity while work of fracture increases slightly.
Figure 6.3 – Variation of strength with added porosity
(at least 3 samples were used per data point with the error bars representing 1 standard deviation)

Figure 6.4 – Variation of Young’s modulus with added porosity (at least 3 samples were used per data point with the error bars representing 1 standard deviation)
Figure 6.5 – Variation in work of fracture with added porosity (at least 2 samples were used per data point with the error bars representing 1 standard deviation)

6.4 **POROSITY DEPENDENCE OF STRENGTH AND YOUNG’S MODULUS**

6.4.1 Comparison with model data

Strength and Young’s modulus data for samples containing a homogenous distribution of pores has been shown to be accurately described by a Spriggs type equation where the empirical constant, $b$, is equal to 2.8 (equation 6.3).

$$X = X_0 \exp(-bX V_{fp})$$  \hspace{1cm} \text{Eqn 6.3}

where $X$ is the material property with the subscript 0 representing the condition of no added porosity. Application of the Spriggs type equation to the available data for strength and Young’s modulus (figures 6.3 and 6.4) results in $b$ values of 5.22 and 3.60 respectively. Both strength and Young’s modulus results exhibit a porosity dependence that is greater than that predicted and previously observed.
6.4.2 Effect of pore morphology

Work conducted on alumina containing isolated spherical pores introduced in an identical manner (Chen, 1999) has shown the porosity dependence of both strength and Young’s modulus to be described using a b value of 2.8. The study reported pore distribution to be homogenous with no obvious pore clustering. The minimum solid area predictions are also based on the assumption that the distribution of pores is homogenous. However, examination of a fracture surface of a porous sample with 0.121 volume fraction porosity (figure 6.6) shows that this is not the case and that a degree of pore clustering has occurred.

Figure 6.6 - Photomicrograph of fracture surface showing pore clustering whereby the local volume fraction of porosity is altered
Pore clustering appears to result in some areas of the structure being devoid of pores while other areas show an increase in the level of porosity above that associated with the bulk. Such a microstructure is probably a result of agglomerates of alumina powder failing to break up so preventing the starch particles from mixing thoroughly.

The effect of such a microstructure is to cause the material as a whole to act as a composite composed of one phase which is pore free and another phase which is pore rich. The pore free phase should exhibit the same material properties as the material with no added porosity. The pore rich phase should exhibit a porosity dependence that can be described by the minimum solid area model. The complex nature of the pore clustering makes predictions of material properties difficult. However, an approximate description of the porosity behaviour should be obtainable if the material is considered as a particulate composite.

By examining the nature of a particulate composite it can be seen that pore clustering should result in the material exhibiting a different porosity dependence for strength and Young’s modulus. Young’s modulus is expected to show porosity dependence where the net porosity dependence is between that predicted for the two extremes. However, strength is likely to exhibit weak link behaviour. If the weaker phase fractures then the size of the flaw created is likely to exceed the critical flaw size so leading to failure of the sample as a whole.

The Young’s modulus behaviour should be classified with the bounds established using the Voigt and Reuss equations given by equations 6.4 and 6.5 respectively.

\[
X_e = X_1 Vf_1 + X_2 (1 - Vf_1)
\]

Eqn. 6.4

\[
\frac{1}{X_e} = \frac{Vf_1}{X_1} + \frac{(1 - Vf_1)}{X_2}
\]

Eqn. 6.5
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where X is the material property and V_f is the volume fraction. Subscripts T, 1 and 2 relate to the total, phase 1 and phase 2. Conversely strength behaviour should be described by that of the weakest phase where failure of the weakest phase is expected to result in a flaw of size in excess of the critical flaw size. Hence, failure of the weakest phase should result in catastrophic failure of the composite.

Figure 6.7 demonstrates how pore clustering can lead to variations in the porosity dependence of the material on a macroscopic scale. To construct the curves phase 1 was considered to be pore free at all times and phase two was described using the Spriggs equation such that \( b = 2.8 \). The volume fraction of porosity within the clusters and the volume fraction of the clusters were adjusted subject to the limitation that the macroscopic volume fraction of porosity did not change. To simplify matters it was assumed that pore clustering only resulted in an increase in the volume fraction of porosity within the clusters and that the volume fraction of clusters did not change with increased degrees of pore clustering. This is a reasonable assumption if the clustering is a result of the formation of alumina particle agglomerates.

Figure 6.7 – Variation in porosity dependence showing homogenous pore distribution (\( b = 2.8 \)), upper and lower bounds for Young’s modulus and the weak link (behaviour of weakest phase) representative of the strength dependence
Application of the Spriggs equation to the predictions for the lower limit and the weak link result in b values of 3.55 and 5.6 respectively. Values of b can be increased by decreasing the volume fraction of clusters and so increasing the level of porosity within the clusters. The predictions shown were obtained using a value of 0.5 for the volume fraction of clusters. These values are in reasonable agreement with those observed from experimental observations. In reality the effect of pore clustering will be more complex as the concentration of pores within the clustered zones will not be constant leading to a range of material properties throughout the body. However, the simplification demonstrates how pore clustering can lead to a different porosity dependence being exhibited by strength and Young’s modulus.

6.5 POROSITY DEPENDENCE OF THE WORK OF FRACTURE

The energy required to create a fracture surface will not be affected by the presence of porosity (i.e. the bond energy is unaffected). The presence of porosity will, however, reduce the amount of energy required to propagate a crack as the amount of material in the crack path is reduced. Hence the fracture energy term used can be described as the effective fracture energy and is expected to show a similar porosity dependence to that exhibited by strength.

Analysis of the results shows that the work of fracture increases slightly with increased additions of porosity. Literature data relating to samples containing a homogenous distribution of porosity indicates that the effective fracture energy decreases with increased levels of porosity such that the application of the Spriggs equation results in a b value of approximately 2.8. A slight initial increase in effective fracture energy has also been reported (Chen, 1999). With increased additions of porosity above 0.2 volume fraction the effective fracture energy was
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shown to again decrease such that the Spriggs equation can again be used to describe the porosity dependence.

Observations of the porosity dependence of the work of fracture agree with those of the effective fracture energy which exhibited a maximum value at approximately 0.1 volume fraction porosity. It is thought that with increased additions of porosity the porosity dependence of the work of fracture would also begin to decrease. Work by Chen was concerned with alumina containing a homogenous distribution of pores and the maximum factor of improvement in fracture energy was approximately 1.1. Examination of the results for samples containing pore clusters indicates that an improvement factor of approximately 1.5 is obtained. This indicates that pore clustering further increases the effective fracture energy of the material. It is thought that the additional improvement is a result of increased crack branching caused by the dual effect of pores and clusters.

6.6 SUMMARY

The experimental techniques for determining strength, Young's modulus and work of fracture values from 3 point bend tests have been described. To eliminate the effect of matrix porosity the matrix was considered to be constant with characteristic properties. Results of mechanical properties as a function of added porosity show a reduction in strength and Young's modulus as the level of porosity is increased. By fitting a previously developed empirical equation to the results it was shown that the material exhibited a higher porosity dependence for strength and Young's modulus than that previously reported for similar materials. Strength was also found to exhibit a higher porosity dependence in comparison to Young's modulus. The discrepancy between predicted and observed results was attributed to the occurrence of pore clustering that locally altered the volume fraction of porosity present. This local variation in the volume fraction of porosity caused the material to behave as a
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composite and hence exhibit an increase in porosity dependence. The increased porosity dependence of strength was attributed to the weak link theory whereby strength would be controlled by the weakest part of the material (i.e. the high porosity areas). Young’s modulus would be expected to exhibit a porosity dependence between the two extremes and hence would show a reduced porosity dependence with respect to strength.

Observations of work of fracture indicate that there is a slight increase in the energy requires to fracture the samples with increased levels of porosity. Comparison with data obtained from samples containing a homogenous distribution of porosity indicates that pore clustering leads to an even greater rise in the energy required to fracture a sample.
7.1 INTRODUCTION

A method for subjecting samples to rapid cooling rates is presented along with the results of residual strength measurements for samples containing various amounts of porosity and subjected to increased temperature changes. The results from the thermal shock tests are then compared with predictions of thermal shock resistance made using thermal shock resistance parameters and observations of the porosity dependence of material properties.

7.2 THERMAL SHOCK TESTING

Test bars were prepared as described in section 6.2.1. The samples were held at an elevated temperature for 30 minutes, to ensure a homogenous temperature distribution, and then cooled rapidly to 22 °C by immersion into water. The soak temperatures were selected to produce temperature changes of 150, 200, 350 and 450 °C on quenching. Following quenching the samples were dried thoroughly at 75 °C for 24 hours prior to mechanical testing. Flexure tests were conducted as described in section 6.2.1.

7.3 RESULTS

The results from the thermal shock tests are shown in figure 7.1. It can be seen from the results that increased levels of porosity result in a decrease in the initial strength as discussed in section 6.4. Sample strength is unaffected by increases in the
quenching temperature ($\Delta T$) until the temperature change exceeds 200 °C whereupon all samples exhibit an abrupt decrease in strength. The degree by which the strength decreases depends on the level of porosity, with samples containing the highest levels of porosity exhibiting the lowest degree of strength loss. Further increases in the quench temperature result in a gradual decrease in the retained strength. This decrease in retained strength appears to be lowest for the samples which contain the highest level of porosity.

Figure 7.1 a) - Quench test results from 0 volume fraction induced porosity samples
Figure 7.1 b) - Quench test results from 0.026 volume fraction induced porosity samples

Figure 7.1 c) - Quench test results from 0.054 volume fraction induced porosity samples
Figure 7.1 d) - Quench test results from 0.080 volume fraction induced porosity samples

Figure 7.1 e) - Quench test results from 0.119 volume fraction induced porosity samples
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Thermal shock curves for alumina obtained from the literature show the curves to have a stepped shape. This step can be explained with reference to the crack length-temperature difference curve shown in figure 7.2 (Hasselman, 1969). A minimum temperature difference is required to initiate the growth of a crack of length $c_0$ which will then propagate to a length $c_f$. This new crack will remain stable until a temperature difference of $\Delta T'$ is applied at which point it will advance quasi-statically resulting in a gradual increase in the crack length. The form of the resultant strength curves can then be obtained by noting that strength is inversely proportional to the square root of crack length.

![Crack length as a function of thermal history](after Hasselman, 1969)

The dashed lines included with the results of thermal shock tests in figure 7.1 are speculative in that the location of the step change is not known accurately.

7.4 COMPARISON OF EXPERIMENTAL AND PREDICTED RESISTANCE TO THERMAL SHOCK

7.4.1 Thermal shock resistance parameters

The resistance to thermal shock can be described using a number of parameters as discussed in section 2.4. For convenience these have been repeated below. The
parameters describe the resistance to crack initiation, crack propagation and the stability of large cracks when a body is subjected to rapid changes in temperature. The thermal shock resistance parameters given by equations 2.68 and 2.83 are both used for conditions of rapid cooling while those described by equations 2.71 and 2.84 are used for conditions of slow cooling. The thermal shock studies conducted as part of this study used water quenching which offers relatively fast cooling rates, hence equations 2.68 and 2.83 will be considered primarily. The two parameters describing the resistance to crack propagation can be used both for conditions of rapid and slow quenching as they are not concerned with the maximum level of stress, but instead are based on consideration of the energy required to propagate cracks.

\[
R = \frac{\sigma_f (1 - \nu)}{E \alpha} \quad \text{Eqn. 2.68}
\]

\[
R' = \frac{\sigma_f (1 - \nu) \lambda}{E \alpha} \quad \text{Eqn. 2.71}
\]

\[
R''' = \frac{E}{\sigma_r^2 (1 - \nu)} \quad \text{Eqn. 2.75}
\]

\[
R'''' = \frac{E \gamma_{\text{eff}}}{\sigma_r^2 (1 - \nu)} \quad \text{Eqn. 2.77}
\]

\[
R_{\text{st}} = \left( \frac{\gamma_{\text{eff}}}{\alpha^2 E} \right)^{\frac{1}{2}} \quad \text{Eqn. 2.83}
\]

\[
R_{\text{st}}' = \left( \frac{\lambda^2 \gamma_{\text{eff}}}{\alpha^2 E} \right)^{\frac{1}{2}} \quad \text{Eqn. 2.84}
\]

To describe the effect of porosity on the thermal shock resistance of the material it is useful to examine the effect of porosity on the individual material properties which control the resistance parameters. It has been shown in sections 2.3.7 and 4.4 that one
property, the thermal expansion coefficient, is independent of the amount of porosity present provided that the solid phase is continuous.

For materials containing a homogenous distribution of pores it has been shown that strength and Young’s modulus behaviour can be described using the Spriggs type equation (equation 7.1) where the value of b is approximately 2.8 for both material properties.

\[ X = X_0 \exp\left(-b_x V_{f_p}\right) \]  

Eqn. 7.1

where \( X \) is the material property with the subscript 0 indicating no deliberately introduced pores. Experimental observations in chapter 6 of the porosity dependence of material properties for samples containing clustered porosity show that the Spriggs constant (b) is equal to 5.22 and 3.60 for strength and Young’s modulus respectively.

The effect of porosity on Poisson’s ratio is uncertain with contradictory statements being made in the literature. Poisson’s ratio can be described using two of the three moduli (Young’s, shear and bulk). Consequently, if all of the moduli exhibit the same porosity dependence than Poisson’s ratio should be independent of porosity. Due to slight variations in the measurements of the moduli used to calculate Poisson’s ratio, both increases and decreases in its value have been reported. Over a limited range of porosity (\( V_{f_p} < 0.2 \)) the change in Poisson’s ratio is small and so to a first approximation it can be regarded as constant.

Literature data for samples containing a homogenous distribution of porosity indicates that the effective fracture energy initially increases over the first 0.2 volume fraction of porosity added (Chen, 1999). Subsequent additions of porosity result in a decrease in effective fracture energy such that the application of the Spriggs equation results in a b value of approximately 2.8. Studies of the work of fracture for samples containing clustered porosity indicate that the effective fracture energy also
increases. Samples containing in excess of 0.121 volume fraction porosity were not produced so a drop off in effective fracture energy was not observed.

Changes in thermal conductivity were not measured as part of this study but data relating to homogenously distributed porosity indicates that the porosity dependence can be described using a Spriggs constant of approximately 2.8.

7.4.2 Effect of porosity on the resistance to crack initiation

7.4.2.1 Rapid quench conditions

By convention both R and R’ are used to indicate the resistance to crack initiation. However, ceramic bodies cannot be regarded as defect free and observations of the onset of cracking strictly should be regarded as the point at which existing small defects propagate.

Examination of equation 2.68 shows that the only material properties that exhibit a significant porosity dependence are strength and Young’s modulus. Figure 7.3 shows the porosity dependence of R for samples containing a homogenous pore distribution and for those with pore clustering.
Figure 7.3 – Resistance to crack propagation as a function of porosity

Figure 7.3 shows that for cases of homogenous pore distribution $R$ is not affected by increased levels of porosity as would be expected if strength and Young’s modulus exhibit the same porosity dependence. When strength exhibits a greater porosity dependence compared to Young’s modulus there should be a decrease in $R$ with increased levels of porosity as is shown for the case of pore clustering.

Experimental observations of the thermal shock behaviour of alumina containing clustered pores indicates that the critical temperature to initiate fracture does not decrease below 200 °C. A Study on the thermal shock behaviour of AKP30 (Aldridge, 1996) showed that a critical temperature of approximately 200 °C is required to initiated cracking. If this values of $\Delta T$ is used as a basis for the pore free material, calculated values of $R$ predict a decrease in the critical temperature of approximately 30 °C for the most porous sample ($V_{fp} < 0.121$). It was not possible to detect this change in the critical temperature within the range of conditions examined.
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7.4.2.2 Slow quench conditions

If slower quench rates are utilised then the thermal conductivity of the material must also be considered, necessitating the use of equation 2.71. By accounting for the effect of porosity on the thermal conductivity it can be seen that the resistance to crack initiation \((R')\) will decrease with increased levels of porosity irrespective of the homogeneity of the pore distribution.

7.4.3 Effect of porosity on the resistance to crack propagation

7.4.3.1 Stored elastic energy approach

Equation 2.75 is used to describe the resistance to crack propagation for all quenching conditions as it describes the level of stored elastic energy within the body and is independent of the time effects. Examination of equation 2.75 again shows that the porosity dependence of \(R''\) will be dictated by the effect of porosity on strength and Young’s modulus. The effect of porosity on \(R''\) for conditions of homogenous and clustered pore distributions are shown in figure 7.4.
The resistance to crack propagation can be seen to increase, irrespective of the pore distribution, as a result of the greater dependence on strength. The effect of pore clustering is seen to increase the resistance to crack propagation further due to the increased porosity dependence of strength in comparison to Young’s modulus.

7.4.3.2 Fracture energy approach

The thermal shock resistance parameter $R'''$ only considers the minimisation of the energy stored by a sample and does not examine the energy required to create a crack surface. Hence, the second parameter to describe the resistance to crack propagation ($R''''$), as given by equation 2.77, includes a term for the fracture energy of the material.

The slight increases in the effective fracture energy that occurs with increased levels of porosity will result in further increases in the value of $R''''$ for materials containing homogenous and clustered pore distributions (figure 7.5).
7.4.3.3 Comparison with experimental data

The resistance parameter \( R'''' \) describes the resistance to crack propagation and hence should indicate the degree by which the resultant crack length will change (i.e. a 2 fold increase in resistance parameter should result in a 2 fold decrease in crack length). The resultant strengthening can be related to the reduction in crack length if it is assumed that strength is proportional to the square root of the crack size. Table 7.1 gives details of the retained strength measured from thermal shock tests and the corresponding value of \( R'''' \) and figure 7.6 shows the normalised thermal shock results for the five different levels of porosity.
Table 7.1 – Comparison of predicted and measured decrease in the relative retained strength following crack initiation

<table>
<thead>
<tr>
<th>$V_{fp}$</th>
<th>Prediction ($R'''$)</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>0.20</td>
</tr>
<tr>
<td>0.026</td>
<td>1.21</td>
<td>0.21</td>
</tr>
<tr>
<td>0.04</td>
<td>2.04</td>
<td>0.29</td>
</tr>
<tr>
<td>0.080</td>
<td>2.54</td>
<td>0.32</td>
</tr>
<tr>
<td>0.119</td>
<td>3.25</td>
<td>0.36</td>
</tr>
</tbody>
</table>

It can be seen from table 7.1 that both the predicted and observed values of retained strength show an increase with increased levels of porosity. The observed improvements are generally very close to those predicted. Where the measured
values are higher one possible explanation for this is the formation of a greater number of cracks. The thermal shock resistance parameters were developed based on the assumption that only one crack would propagate. However, if multiple cracks were to advance then it is reasonable to assume that any individual crack would not advance as far.

7.4.4 Effect of porosity on the stability of existing cracks

As stated previously in section 7.4.2, ceramics generally are not free from defects hence the resistance parameters $R_{st}$ and $R_{st}'$ could be applied to the situation of the propagation of very small defects (i.e. what is conventionally regarded as crack initiation). The resistance parameters are equally applicable to situations where large cracks are already present either due to prior thermal shock or through machining damage. For conditions of rapid cooling it can be seen that the porosity dependence of $R_{st}$ will be controlled by effective fracture energy and Young’s modulus. Figure 7.7 shows the effect of increases in porosity on the stability of large cracks during conditions of rapid changes in temperature.
Figure 7.7 – Resistance to crack propagation (R_{st}) as a function of porosity (using experimental data and the minimum solid area model)

The variation in R_{st} with increases in porosity indicates that the resistance to the propagation of very small defects should increase. Analysis of changes in R with increased levels of porosity indicate that the resistance to crack initiation should decrease (or remain constant) with increases in porosity. For a real system it is not necessary to initiate cracks, hence it is reasonable to assume that the resistance to the observed crack initiation (i.e. propagation of small cracks) should increase.

For conditions of slow cooling rates the action of thermal conductivity is expected to cause a reduction in the stability of existing cracks as was shown for the case of resistance to crack initiation.

7.5 SUMMARY

A technique for thermal shock testing ceramic components was presented along with residual strength measurements conducted after subjecting the samples to various degrees of thermal shock. The parameters used to describe the resistance to crack
initiation, crack propagation and the stability of large cracks were then used to predict the effect of porosity on the thermal shock resistance of ceramics. Both literature data for homogenous pore distributions and experimental data for samples containing pore clusters were used to examine the effect of porosity on the thermal shock resistance of porous ceramics. Results obtained from the thermal shock tests were then compared with the predictions made.

For conditions of rapid cooling, homogenous porosity was shown to have no effect on the critical temperature required to initiate cracking. A slight decrease in the resistance to crack initiation was predicted for the case of samples containing pore clusters. No decrease in the critical temperature required to initiate cracking was observed. For conditions of slower cooling rates the reduction in thermal conductivity with increased additions of porosity is expected to result in a decrease in the resistance to crack initiation for both pore distributions.

Both samples containing a homogenous pore distribution and pore clustering were predicted to exhibit increases in the resistance to crack propagation. Samples containing pore clusters were expected to show the greatest degree of resistance to crack propagation. Experimental observations of the retained strength following cracking show that there is an increase in the resistance to crack propagation which can be approximately predicted using the resistance parameter $R''''$.

Existing cracks were shown to be more stable with the addition of porosity during conditions of rapid changes in temperature. Assuming that ceramics contain intrinsic flaws then it can be argued that the resistance to the onset of observed cracking may increase. With slower cooling rates the stability of large crack was shown to decrease due to the reduction of the thermal conductivity with increased levels of porosity.
Chapter 8 - Concluding Remarks

CHAPTER 8

CONCLUDING REMARKS

8.1 CONCLUSIONS

8.1.1 Introduction

This study had three linked aims. They were to provide experimental validation of sintering models in terms of the effects of bimodal distribution of powder sizes and large pores and subsequently to examine the effect of porosity on mechanical properties and thermal shock resistance.

8.1.2 Initial stage sintering study

The initial stage of the densification process has been examined for powders containing a bimodal size distribution. The shrinkage of the powder compacts was monitored using an in situ technique. Experimental shrinkage data were then compared with model densification data predicted using a model from the literature developed to examine the effect of a range of particle sizes on the sintering process.

An experimental technique for obtaining shrinkage data during sintering studies has been developed to account for the effect of sample radiance at elevated temperatures. The technique uses optical dilatometric measurements of sample dimensions and corrects for the apparent increase in size through the use of calibration data. In situ measurements of sample shrinkage, following correction, were shown to be in excellent agreement with measurements of sample shrinkage made using a series of interrupted tests.
Experimental shrinkage data from powders containing different proportions of small and large particles were used to examine predictions made by a theoretical model from the literature developed to describe the sintering of real powders more accurately. Model predictions indicated that normalised density-time curves for the various powders would be parallel, straight lines with a slope between 1/4 and 1/3. The relative positions of the curves were predicted to be a function of the size ratio and relative amounts of the large and small particles. The experimental results showed that the data curves for the various powders were parallel and positioned correctly relative to one another. However, the experimental data curves exhibited a variation in slope with time. This was attributed to the range of particle sizes present in real powders leading to an increase in the degree densification and hence an increase in the slope. Further, particle neck interactions during the latter stages of the study resulted in a decrease in the rate of densification and a reduction in the slope. The apparent agreement between predicted and observed slopes during the latter stages of the study would appear to be fortuitous and a result of the two effects cancelling each other out. The production of accurate shrinkage data has shown that the model developed by Pan et al. (1998) represents a significant advancement in the modelling of the sintering process, but the current limitations restrict its full application.

8.1.3 Large pore study

To study the shrinkage of large pores during sintering, alumina powder was mixed with starch particles. During the heating of the samples to the sintering temperature the starch particles burnt off resulting in large, spherical pores. A technique was presented where density measurements of sintered samples containing isolated spherical pores were used to evaluate the degree of pore shrinkage that occurred during the sintering process. Results were the compared to theoretical model predictions.
Examination of sample density following sintering and comparison with theoretically derived sintering curves indicated that the pores shrink from approximately 15 μm to 12.8 μm in diameter. Analysis of pore size from sectioned samples showed the final pore size to be between 11.9 and 14 μm. Exact agreement was not possible due to pore enlargement and charging effects associated with the SEM operation. The observation of large pore shrinkage is in agreement with predictions (Pan et al., 1999) that indicate shrinkage of large pores is possible provided there is a variation in the size of the grains surrounding the pores.

8.1.4 Effect of porosity on mechanical and thermal shock properties

Samples containing isolated spherical pores were then used to examine the effect of porosity on strength, Young’s modulus and work of fracture. Experimental results were then used to predict the effect of porosity on the thermal shock resistance of porous ceramics. The predictions obtained from this analysis were compared with residual strength measurements of porous samples subjected to varying degrees of thermal shock through water quenching from different temperatures.

Strength and Young’s modulus were shown to decrease with increased additions of porosity. The experimental data was described using the Spriggs equation. Strength was shown to exhibit the greatest porosity dependence with a b value of 5.22, while Young’s modulus showed a slightly lower porosity dependence such that b equalled 3.60. Examination of previously reported data relating to systems consisting of homogenously distributed large pores were shown to exhibit a porosity dependence such that b = 2.8. The increased porosity dependence exhibited by the material used in this study was attributed to the presence of pore clustering. Pore clustering was though to result in a composite type structure of areas of no porosity and areas of high porosity. Young’s modulus would be expected to exhibit a porosity dependence between the two extremes. However, the strength of the composite would be
expected to be controlled by the weakest portion of the structure, hence strength would exhibit a greater porosity dependence.

Analysis of the work of fracture showed an initial increase followed by a plateau region at porosity ranges of 0.054 to 0.119 volume fraction added porosity. No work of fracture measurements were obtained from samples containing a greater level of porosity but it is postulated that there will be a gradual decrease in the work of fracture following observations of literature data.

Predictions of the resistance to crack initiation, using experimental data, indicated that the resistance would decrease with increased levels of clustered porosity. No experimental verification of this was obtained due to the small scale of expected decrease. The resistance to crack propagation was shown to increase with increased additions of porosity. Experimental observations of the retained strength following thermal shock showed relative strength loss was lowest for samples containing the highest level of porosity. Predictions of thermal shock behaviour for conditions of slow quench rates indicate that the presence of porosity is detrimental to the resistance to crack initiation and the stability of large cracks due to the reduction in the thermal conductivity with increased additions of porosity.

8.2 FURTHER WORK

The \textit{in situ} monitoring technique allows complete sintering curves to be obtained from a single sample. Currently the accuracy of the process is limited by the transfer of images from 35 mm negatives to digital format. With the full development of the process using digital technology it will be possible to increase the accuracy and obtain more frequent sampling rates. Through the combination of the \textit{in situ} technique with the pore size determination method it would be possible to monitor
changes in the size of large pores during the entire sintering process to obtain information on the manner in which large pores shrink.

Work conducted on the effect of porosity on the thermal shock resistance of ceramics has shown that low levels ($Vf_p \sim 0.1$) of clustered porosity retard crack propagation while homogenous distributions of porosity do not affect the resistance to crack initiation. It would be of interest to examine the effect of a body containing clustered porosity at the centre and a coating of fully dense material (or a coating containing homogenous porosity). This should provide a body that is both resistant to initial crack initiation and crack propagation. An advantage of this material is that there would be no difference in the thermal expansion coefficient between the two parts so eliminating thermal stresses likely to cause spalling.

Many applications for ceramics involve repeated thermal cycling. It has been shown that the stability of pre-existing cracks is expected to increase with the porosity (for the case of clustered porosity). Further studies to examine the effect of porosity on repeated thermal shock may be of interest.

Work on thermal shock has shown that increases in the level of porosity are expected to cause the resistance to crack initiation ($R$) to decrease and the stability of existing cracks ($R_{st}$) to increase. Ceramics are generally not considered to be defect free which should give rise to an increase in the critical temperature at which retained strength abruptly decreases. A thermal shock study of dependence of the critical temperature would give some insight into what is conventionally regarded as of crack initiation.


References


References


References


