Constitutive modelling and experimental studies of densification of porous ceramic component

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**CONSTITUTIVE MODELLING AND EXPERIMENTAL
STUDIES OF DENSIFICATION OF POROUS CERAMIC
COMPONENT**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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**CONSTITUTIVE MODELLING AND EXPERIMENTAL
STUDIES OF DENSIFICATION OF POROUS CERAMIC
COMPONENT**

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Abstract

Porous ceramic components have found increasing applications in recent years. These include supports and electrodes for solid oxide fuel cells which require a porous structure to allow gas transport. The fabrication and stability of these porous ceramics have become the immediate challenges as the components are required to operate in harsh environment such as high temperature. Hence, a good understanding of the constitutive law of the porous ceramic will therefore be essential to help in the design and optimization of the sintering process.

In this work, a porous component with a microporous ceramic matrix that contained large macropores, where the size was much larger than the average grain size of the matrix, was considered. The constitutive models for the grain boundary diffusion controlled sintering of macropores in the microporous matrix were first established. In contrast to most of the reported models, the effects of large macropores and small pores on the densification of biporous material were considered separately. A sintering potential arose from the shrinkage of large macropores was introduced in the proposed constitutive laws. Experiments were designed to study the densification of biporous system. The experimental data on the densification of biporous 8YSZ compacts were used to validate the constitutive relationships developed. The theoretical predictions were found to be in good agreement with the experimental data.

The proposed constitutive model of biporous system was further applied to establish a series of constitutive equations to describe the densification of a bi-layered system during co-sintering. The curvature development of bi-layer during co-sintering was estimated and compared with the measured curvature. The established equations were found to be able to provide reasonable prediction for the densification and stress induced in the bi-layer during co-sintering.

The grain growth behaviors were found different when external stress is applied. A term related to the effect of stress was added to the grain growth law by assuming that the external stress affects the grain growth through its effect on densification. The proposed grain growth law was verified by comparing the calculation results with the experimental data of 8YSZ during constrained sintering and co-sintering, as well as experimental results obtained from alumina during sinter-forging. The proposed grain growth law was further applied to calculate the grain growth of a porous 8YSZ with bimodal pore size distribution. The modified grain growth law was found to be able to provide a reasonable prediction of the grain growth of biporous 8YSZ.

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Nomenclature

$\dot{\varepsilon}_{ij}$	:	Strain rate tensor
σ_{ij}	:	Stress tensor
σ_m	:	Main stress
S_{ij}	:	Deviatoric stress tensor
δ_{ij}	:	Kroneker delta ($\delta_{ij}=0$ when $i \neq j$, and $\delta_{ij}=1$ when $i=j$)
μ	:	Shear viscosity
κ	:	Bulk viscosity
ν	:	Poisson's ratio
$\dot{\varepsilon}_0$	:	Strain rate constant of densification
L	:	Grain size
L_0	:	Initial grain size
$f(\rho)$ and $c(\rho)$	:	Dimensionless functions of the relative density
ϕ	:	Strain rate potential
ψ	:	Stress potential
V	:	Total volume
V_m	:	Volume of the microporous matrix
$\sigma_s (\sigma_{s\rho})$	:	Sintering potential (associated with small micropores)
σ_{sR}	:	Sintering potential associated with large macropores
a	:	Diameter of large pores
$\dot{\rho}$	:	Densification rate
ρ	:	Relative density
ρ_0	:	Initial relative density

$\dot{\epsilon}_v$	:	Volumetric strain rate
γ_s	:	Surface energy
$\dot{\epsilon}_{00}$	:	Material constant
Q	:	Activation energy
R	:	Ideal gas constant
T	:	Absolute temperature
f_v	:	Volumetric fraction of large pores

Chapter 2 Introduction

1.1 Background

Ceramic materials play an important role in modern industrial technologies due to their beneficial properties. Apart from applying the material in a monolithic manner, various configurations, such as layered systems, are also widely used in many applications. For layered structures, such as low temperature co-fired ceramics (LTCC) for electronic packaging, Solid Oxide Fuel Cells (SOFC), and gas sensors etc, co-sintering has been a widely applied process which provides a low cost route to combine different materials in a single or reduced step. However, due to different shrinkage behaviour of different layers, the layers can be constrained by each other during the co-sintering. Stresses (tensile or compressive) will hence be induced due to the mismatch, and lead to defect and/or warpage of the multilayer component. The processing challenges of layered ceramics have attracted huge attentions from scientists and engineers. It is also noticed that the sintering behavior of co-sintered layers could affect the densification of the compact [1-3]. It has been reported that films on a co-shrinking substrate were noted to be able to achieve a higher density than free sintered samples [4, 5]. As a result, it is reckoned that the level of induced stresses can influence the sintering behavior of the co-sintered layers significantly. Thus, to achieve a successful process design, good understanding of co-sintering process is essential. This, in turn, requires a good understanding of the sintering behaviour in each individual layer.

In recent years, porous ceramics were applied in an increasing number of advanced applications including Solid Oxide Fuel Cells (SOFCs). The advantages of using ceramics with functionalized porosities are usually the tailored electronic properties, high surface area, and high specific strength, which can be achieved by controlling the composition and microstructure of porous ceramics for each specific application. The performance of

these ceramics depends on their microstructure including their porosity, pore size, etc. In order to tailor the level of porosity, pore forming agents are used. The size of the pores left by the pore forming agents is generally much larger than both the average particle size and the natural pores formed between the particles. It is hence noted that during the sintering process, the strength of the component may be limited by high residual stresses and density inhomogeneities. In porous components with bimodal pore size distribution, the interactions between different type of pores and the matrix will further complicate the situation. Experimental results show that the densification behavior of large pores is different from that of the small pores. The sintering of porous ceramics where both small pores and large pores exist is reckoned to be not fully represented by the average porosity, but influenced largely by the different interactions between different pore types and the ceramic matrix.

In view of vast range of parameters during sintering, it is desirable to use constitutive models to assist the understanding and hence prediction of the sintering process of porous ceramic components. The construction and experimental verification of a more appropriate material constitutive law governing the sintering process for porous ceramic components will be essential to facilitate and improve the co-sintering process.

Despite considerable efforts have been made to understand the sintering of porous ceramic materials [6-16], very few published models study the sintering of a porous body where large and small pores coexist [17, 18]. As a result, the present work attempts to establish a series of constitutive relationships for porous ceramic with bimodal pore size distribution. In this model, unlike the existent approaches, the contribution of large macropores will be considered separately from that of small pores in an interconnected microporous matrix.

1.2 Objectives

In the present work, the main objective is to establish the constitutive relationships for the densification of a porous ceramic body where both small and large pores exist. The relationship will integrate the interaction of the void inclusions and the matrix with density and grain size as the state variables. The models developed will also be validated through experimental results. The study will be limited to the Stage 1 of sintering, which is an essential stage when most rapid shrinkage occurs.

The proposed constitutive model of porous ceramic will be further applied to establish a series of constitutive equations for the co-sintering of a bimodal pore distribution layered structure. The applicability of the model is tested by predicting the induced stress and estimating the curvature development of a co-sintered ceramic bi-layer system.

1.3 Scopes

The present work consists of six chapters. In Chapter 2, a literature survey related to sintering of ceramics and constitutive model is given. The sintering concepts, sintering stages, sintering mechanisms and fundamental parameters in sintering and constitutive model are included in this part.

In Chapter 3, the constitutive model for a porous ceramic is discussed in detail. This chapter gives the description of constitutive modelling of the densification of a porous ceramic with bimodal pore size distribution controlled by grain-boundary diffusion. The establishment of specific forms of several other essential sintering parameters is discussed. The experimental procedure based on porous ceramic is also presented. The results obtained are used to verify the proposed constitutive models. The models are further applied to describe the evolution of large pores during the sintering in Chapter 4.

In Chapter 5, the specific expressions of constitutive laws of biporous material proposed in Chapter 3 and constitutive model of dense ceramic are combined to establish a series of constitutive relationships to describe the co-sintering behavior of a bi-layered system. The constitutive relationships are validated using experimental data obtained, and further evaluated by estimating the warpage development of a ceramic bi-layer system.

Densification and grain growth are two main phenomena during the sintering. Reports have shown that the external stress will significantly influence the grain growth rate. Hence, it is reckoned that it is essential to investigate the grain growth behavior under external stress field. In Chapter 6, the influence of external stress, both tensile and compressive, on grain growth characteristic is studied. Grain growth law is proposed to describe the grain growth behavior with external stress, and the modelling results are compared with experimental data. Parameters related to the effect of external stress are also introduced. The proposed grain growth law is further applied to large pores which are much larger than the grain size.

Lastly, Chapter 7 presents the conclusions and recommended future works.

Chapter 3 Literature review

2.1 Sintering of ceramics

Sintering (firing) is the most widely used technique to fabricate ceramic components in modern industry. Normally, it is a heat treatment process at 0.7~0.8 of the melting temperature ($^{\circ}\text{C}$) of the materials. During the sintering process of bulk ceramic materials, densification and grain growth (coarsening) are two major phenomena (Figure 3.1). The densification rate depends significantly on the grain size; on the other hand, the grain growth rate is influenced by the density. Thus, the interplay between the densification and grain growth is complex.

Figure 3.1 Basic phenomena occurring during sintering [19]

The driving force for the sintering comes from the reduction of the total interfacial energy [19]. The total interface energy of a powder compact can be represented as γA , where γ is the specific surface energy and A is the total surface area of the compact [19]. The reduction of the total energy can be expressed as $\Delta(\gamma A) = A\Delta\gamma + \gamma\Delta A$ [19]. The change in interfacial energy ($\Delta\gamma$) is due to densification and the change in interfacial area (ΔA) is

due to grain growth [19]. Beside densification and grain growth, recrystallization and phase transformation may also happen during the sintering process.

In densification, the density of the powder compact increases by eliminating the pores inside the compact. Densification stops when the porosity is vanished.

Grain growth happens in both dense and porous body during heat treatment process with an increase of average grain size accompanied by the disappearance of some grains. The driving force of grain growth comes from the lowering of the free energy of grain boundary related to the reduced grain boundary area [20].

Generally, sintering occurs in stages according to the sequence of the physical changes that occur in the compact as the particles bond together and the porosity disappears.

Based on the experimental observation of Coble [21], four stages were defined during the sintering process, denoted as Stages 1a, 1b, 2 and 3 [22, 23].

The definitions of the stages are described as follows [22, 23]:

Stage 1a represents the early stages of sintering for powder compact with low relative densities, and the pores form an interconnected network through the material. The grain growth can be generally ignored during this stage.

Stage 1b starts at a relatively low relative density of the order of 0.6. The pore structure is the same as during Stage 1a, but grains begin to growth.

Stage 2 occurs during the later stage of sintering process when the pores become isolated. During this stage, the grains continue to grow as densification proceeds. The transition from Stage 1b to 2 generally occurs at a relative density of about 0.95 [23].

Stage 3 occurs when the pores break away from grain boundaries and become isolated within grains. Densification virtually ceased during this stage, but grain growth continues, often at an accelerated rate.

Stages 1 and Stage 2 are considered as the general stages of the sintering of ceramic materials.

2.2 Constitutive modelling

The sintering of a powder compact is driven by the diffusion of atoms along definite paths. In the work of Ashby and co-workers [24-26], different mechanisms of sintering for the full range of processing routes were identified. The schematic of different mechanisms is displayed and listed in Figure 3.2 and Table 3.1. All the six mechanisms lead to neck growth, but only mechanisms 4, 5 and 6 cause densification.

Figure 3.2 Schematic of six mechanisms of sintering [20]

Table 3.1 Mechanisms of sintering

	Transport path	Source	Sink	Contribution to densification
1	Surface diffusion	Surface	Neck	No
2	Lattice diffusion	Surface	Neck	No
3	Vapour transport	Surface	Neck	No
4	Boundary diffusion	Boundary	Neck	Yes
5	Lattice diffusion	Boundary	Neck	Yes
6	Plastic flow	Dislocation	Neck	Yes

It is noted that for densification, the dominant mechanism depends on the sintering temperature and external loading, and also material parameters such as grain size and purity. Diffusional mechanisms (grain boundary diffusion and lattice diffusion from boundary) tend to be favoured at low pressures and in fine grained materials, particularly in ceramic systems, where the dominant path for diffusion is usually along the grain boundary [27].

In view of the large number of sintering parameters, the study of ceramic sintering can hardly be limited to experimental approaches. It is hence desirable to use constitutive models to theoretically understand the basis of ceramic sintering. Constitutive modelling can be used to study the sintering parameters, describe the densification and grain growth process, and identify the sintering mechanism. The results obtained from constitutive modelling can be applied to design, control and optimize sintering process.

Generally, constitutive models can be divided into two groups: empirical and micromechanical models. The empirical models are first assumed and determined by suitable experiments. Micromechanical models, on the other hand, originate from simple models which the microstructure evolves during the sintering process, provide quantitative relationship of the state variables involved.

Frenkel [28] first proposed a model for the sintering of viscous materials in 1945, since then, many approaches to understand the constitutive relationship have been developed. Ashby and co-workers ([22, 24, 25]) have obtained micromechanical models for the densification under simple applied stress states. The works contributed by Ashby and co-workers have since provided a good basis for the micromechanical constitutive models for sintering.

Apart from the work done by Ashby and co-workers, considerable works have also been reported by many other researchers to improve the constitutive relationships for the sintering process governed by different densification mechanisms such as viscous

sintering [14-16], plastic yielding and power-law creeping controlled densification with the application of external pressure [29-33] as well as grain boundary diffusion [23, 25, 34, 35]. It is also found that when the particle size decreases to nanoscale, the diffusion can be limited by interface reaction [36-42]. However, it is noted that there exists challenges in the processing of nanomaterials, particularly, in the situation of mass production. In addition, nano-powders are also more costly. As a result, micron and submicron sized ceramic powders are still the most popular choice world-wide. In these systems, grain boundary diffusion is found to be the dominant mechanism.

In the present work, we will focus on grain boundary diffusion controlled densification. The constitutive laws will be developed based on expansion of the models proposed by Du and Cocks [23]. The models of Du and Cocks are micromechanical models developed from both macroscopic and microscopic approaches. The advantage of the selected models is that they are simple in structure, but provide a detailed description of the development of the microstructure in the material. Another feature of the presented models is that the state variables are related to physically measurable quantities, such as relative density and grain size, allowing a direct comparison to be made between theory and experiment.

2.2.1 Constitutive laws for densification

The constitutive law is a series of mathematic equations which can be used to describe the relationship between stress, strain, strain rate, and other sintering state variables. In this section, general presentation and definition of constitutive laws will be given.

The densification of a ceramic compact at a high temperature is driven by time dependent power-law creep or diffusional creep.

When a material suffers an external uniaxial stress, the relationship between strain rate, $\dot{\epsilon}$ and external loaded uniaxial stress, σ can be written as

$$\dot{\epsilon} = \dot{\epsilon}_0 \left(\frac{\sigma}{\sigma_0} \right)^n \quad (3-1)$$

where $\dot{\epsilon}_0$ is the strain rate at a given stress σ_0 , n is creep exponent, which depends on the dominant mechanism of densification.

Generalized to multi-axial stress state, the equation of strain rate (equation (2-1)) becomes

$$\dot{\epsilon}_{ij} = \frac{3}{2} \dot{\epsilon}_0 \left(\frac{\sigma_e}{\sigma_0} \right)^{n-1} \frac{S_{ij}}{\sigma_0} \quad (3-2)$$

with σ_e and S_{ij} are effective stress and deviatoric stress tensor, respectively, and σ_e can be expressed as

$$\sigma_e = \sqrt{\frac{3}{2} S_{ij} S_{ij}} \quad (3-3)$$

deviatoric stress tensor S_{ij} can be expressed as

$$S_{ij} = \sigma_{ij} - \sigma_m \delta_{ij} \quad (3-4)$$

with σ_m the mean stress.

The volumetric strain rate is

$$\dot{\epsilon}_v = (\dot{\epsilon}_1 + \dot{\epsilon}_2 + \dot{\epsilon}_3) \quad (3-5)$$

The densification rate, $\dot{\rho}$, can then be determined from the volumetric strain rate as

$$\dot{\rho} = -\rho \dot{\epsilon}_v \quad (3-6)$$

with ρ the relative density.

2.2.2 Sintering potential σ_s

A porous powder compact will densify during sintering, even without an externally applied load or chemical reaction, due to the effect of sintering potential (also known as sintering stress). Sintering potential is an apparent stress that could lead to the similar strain rate as an externally applied mechanical stress. It arises from the curvature of the

pore surface, and is related to the changes of internal surface and grain-boundary energy as the material densifies.

Sintering potential is a fundamental intrinsic parameter in constitutive relationship. Different theoretical expressions of sintering potential have been established using energy difference method, curvature method, and force balance method [21, 22, 27, 32, 43-50]. These proposed theoretical expressions related the sintering potential to different variables, such as porosity, mean curvature of pore surface [46], grain size [48] as well as dihedral angle [49, 50]. However, parameters such as curvature of the pore surface, dihedral angle are difficult to obtain which complicated the application of proposed expressions of sintering potential. To simplify the expression as a function of easily quantified state variables, Ashby [22] suggested a relationship of the form for sintering potential, σ_s :

$$\sigma_s = \frac{\gamma_s}{L} g(\rho) \quad (3-7)$$

where $g(\rho)$ is a density function, γ_s is the surface free energy per unit area and L is the grain size. He further suggested that different sintering stages require different functions due to the different structure of porosity. Hence the specific forms of sintering potential for the different stages are:

Stage 1

$$\sigma_s = \frac{6\gamma_s}{L} \rho^2 \left(\frac{2\rho - \rho_0}{1 - \rho_0} \right) \quad (3-8)$$

where ρ_0 is the initial relative density

Stage 2:

$$\sigma_s = \frac{4\gamma_s}{L} \left(\frac{6\rho}{1 - \rho} \right)^{1/3} \quad (3-9)$$

The above expressions proposed by Ashby et al. [22] have been further modified by Cocks [27] by introducing the term related to the increase in grain boundary area as:

$$\sigma_s = \frac{3(2\gamma_s - \gamma_b)}{L} \rho^2 \left(\frac{2\rho - \rho_0}{1 - \rho_0} \right) \quad (3-10)$$

In the present work, we will apply the expression of sintering potential improved by Cocks [27] since it is simple in structure and with measurable variables.

2.3 Sintering of porous body

As mentioned in Chapter 1, in order to reach the acceptable level of porosity, pore forming agents are commonly used to create additional porosity. The pore forming agents create voids where the size is generally much larger than the average particle size. In the present work, ‘macropore’ refers to a situation where the pore diameter is much larger than the average grain size. When the pore diameter is the same or smaller than the grain size, the pore will be defined as ‘micropore’.

Lange et al. [8-10] have proposed in their earlier work that during the sintering process, a pore can only shrink if it has a coordination number which is lower than the critical coordination number. Furthermore, for the large pores, shrinkage will only occur when grain growth takes place [8-10, 51, 52]. De Jonghe and Rahaman [53], on the other hand, took the ratio of pore size to grain size as the criterion for the stability of large pores, and proposed that when the pores are much larger than the grain size, shrinkage can occur even if grain growth is minimal or absent. And in a later work of Slamovich and Lange [11, 12], they observed that the shrinkage behaviors of large pores were not controlled by coordination number, but by the characteristic diffusion distance. On the other hand, in the situation where the size of pores is much larger than the mean grain size, Cocks and Searle [7] reported that the shrinkage of large pores were not from the direct diffusion from matrix to pores, but resulted from the deformation of surrounding grains.

Considerable efforts have been made to understand the constitutive laws for the sintering of porous ceramic materials [7-12, 14-16]. In most of the works published, only the average porosity is considered. However, in the situation of a porous material with bimodal pore size distribution, small pores in the microporous and large macropores may have different sintering behaviour which will affect significantly the densification of ceramic components. Thus, it is reckoned that the densification of a porous material with bimodal pore size distribution is not governed so much by the average porosity, but influenced largely by the interactions between different pore types and the ceramic matrix. By combining the large amount of experimental data on porous body densification, Cocks [6] proposed that the sintering of the micropores and macropores have to be considered separately. This idea is also supported by the numerical study of Pan et al. [54].

Slamovich and Lange [12] and Pan et al. [13] established a kinetic analysis of densification for the situation where closed and isolated large pores are surrounded by a dense polycrystalline material. The computational simulation of Pan et al. [13] showed that during the densification of the large pore, the shorter facet of the pore surface tends to disappear and cause the smallest grains to meet each other, and new grain-boundaries are formed between them which are oriented in the radial direction. This is similar to the mechanism of “neighbor-switching” which maintains the equiaxed structure during superplastic deformation proposed by Ashby and Verrall [55]. Lin and German [52] proposed an expression of removal stress for large pores in a fine grain matrix by combining the effects of pore size, ratio of pore size to grain size, and coordination number of the pore. However, the coordination number of the pore is not practical to obtain. Recently, a model of sintering for porous material with the presence of both small and large pores is developed by Shtern et al. [56]. Two parameters related to small and large pores are introduced to the model respectively. However, they did not propose detailed expression of sintering potential of large pores.

Based on the above literature review, the present work will start by examining the constitutive relationship for the grain boundary diffusion controlled porous ceramic component with bimodal pore size distribution, i.e. both small micropores and large macropores co-exist. The sintering potentials associate with microporous matrix and large pores will be studied. The contribution of these two parts to the densification will then be investigated.

Chapter 3 Development of Constitutive Model for the Sintering of Porous Ceramics with Bimodal Pore Size

In this chapter, a porous ceramic material, which consists of both small pores and big pores, is considered (Figure 3.1). The size of the large pores is much bigger than the average grain size of the matrix. These pores will be defined as ‘macropore’. On the other hand, the size of the small pores in the matrix is approximately the same or smaller than the grain size, which normally formed naturally between the particles of good packing are termed as ‘micropore’. The porous system where both large macropores and small micropores are present will be called as ‘biporous system’.

Figure 3.1 Representation of a biporous system

Grain-boundary diffusion model will be used as grain-boundary diffusion is well accepted to be the governing mechanism for the densification of fine-grained ceramic material. And the study will be limited in the Stage 1 of sintering.

3.1 Establishment of constitutive laws of a porous material bimodal pore size

3.1.1 Constitutive laws of microporous matrix

The general constitutive law of grain boundary diffusion controlled densification can be written as

$$\dot{\epsilon}_{ij} = \frac{1}{2\mu} s_{ij} + \frac{1}{3\kappa} \sigma_m \delta_{ij} \quad (3-1)$$

where μ and κ are the shear viscosity and the bulk viscosity, respectively, and they satisfy the relationship [23, 34]:

$$\mu = \frac{\frac{\sigma_0}{\dot{\epsilon}_0} \left(\frac{L}{L_0}\right)^3}{3c(\rho)} \quad (3-2)$$

$$\kappa = \frac{\frac{\sigma_0}{\dot{\epsilon}_0} \left(\frac{L}{L_0}\right)^3}{9f(\rho)} \quad (3-3)$$

where $\dot{\epsilon}_0$ is the uniaxial strain rate at a given stress σ_0 for a fully dense material of grain size L_0 , $f(\rho)$ and $c(\rho)$ are dimensionless functions of the relative density. The other symbols in the equation (3-1) have the same definition as used in Chapter 2.

For the case of a biporous system, Eshelby [57] has examined from the angle of a general problem of an ellipsoidal inhomogeneity, Hashin and Shtrikman [58] have also developed an upper bound by applying a variational principal for anisotropic nonhomogenous elasticity.

In the following section, a thick-walled shell analysis is also used to obtain the volumetric strain rate of a body under hydrostatic stresses, followed by the discussion of the explicit solution from Eshelby.

3.1.2 Thick-walled shell analysis

A thick-walled hollow shell is used here to simulate the situation of a biporous body subjected to hydrostatic stresses with a macropore in the center.

Figure 3.2 (a) shows the cross section of the macropore in the center of microporous matrix, with a is the macropore radius and $2b$ is the mean spacing between the macropores. The body is experiencing a uniform external pressure, σ_m , and the principal stresses are shown in Figure 3.2 (b).

Figure 3.2 (a) Cross section of the spherical shell with a large macropore in the centre
(b) Principal stress acting on an element

The thick-walled shell analysis demonstrates that the macroscopic volumetric strain rate is from two fields: dilatational and deviatoric fields.

For the dilatational part:

$$\dot{\epsilon}_r = \dot{\epsilon}_\phi = \dot{\epsilon}_\theta = A \quad (3-4)$$

$$\dot{\epsilon}_m = \frac{1}{3}(\dot{\epsilon}_r + \dot{\epsilon}_\phi + \dot{\epsilon}_\theta) = A \quad (3-5)$$

and for the deviatoric part:

$$\dot{\epsilon}_r = -2\dot{\epsilon}_\phi = -2\dot{\epsilon}_\theta = -\frac{2B}{r^3} \quad (3-6)$$

where r is the radial distance from the centre of the cell. A and B represent the magnitudes of the two fields. The macroscopic volumetric strain rate can be obtained by combining these two fields:

$$\dot{\epsilon}_{kk} = 3(A + \frac{B}{b^3}) \quad (3-7)$$

Considering equilibrium, the stresses in the shell are

$$\sigma_r = \frac{\sigma_m}{1-f_v} \left(1 - \frac{a^3}{r^3}\right) \quad (3-8)$$

and

$$\sigma_\theta = \frac{\sigma_m}{1-f_v} \left(1 + \frac{a^3}{2r^3}\right) \quad (3-9)$$

where $f_v = \frac{a^3}{b^3}$, is the volume fraction of macropores in the matrix. Substituting

equations (3-4) and (3-5) into Hooke's stress strain relationship

$$\dot{\epsilon}_\theta = \frac{\dot{u}}{r} = \frac{1}{\eta} [\sigma_\theta - \nu(\sigma_\theta + \sigma_r)] \quad (3-10)$$

and differentiating u with respect to r , we can obtain the volumetric strain expression as follows:

$$\dot{\epsilon}_{ij} = \frac{1}{\eta} \frac{\sigma_m \delta_{ij}}{(1-f_v)} \left[1 - 2\nu + (1+\nu) \frac{f_v}{2} \right] \quad (3-11)$$

The strain rate field within the system can be divided into two characteristic fields: a pure dilatational field, $\dot{\epsilon}^v$; and a pure deviatoric field, $\dot{\epsilon}^d$.

$\dot{\epsilon}^v$ is the volumetric strain rate of the microporous matrix; $\dot{\epsilon}^d$ is the deviatoric field under pure hydrostatic loading resulting from the uniform expansion of the macropores.

The expressions of $\dot{\epsilon}^v$ and $\dot{\epsilon}^d$ are given as follows:

$$\dot{\epsilon}^v = \dot{\epsilon}_{kk} = \frac{1}{3\kappa} \frac{\sigma_m \delta_{ij}}{(1-f_v)} \quad (3-12)$$

and

$$\dot{\epsilon}^d = \dot{\epsilon}^r \left(\frac{a}{r} \right)^3 = \frac{1}{4\mu} \frac{f_v \sigma_m \delta_{ij}}{(1-f_v)} \quad (3-13)$$

where $\dot{\epsilon}^r$ is the magnitude of the radial strain rate adjacent to the macropore and a is the radius of the macropore.

3.1.3 Inhomogeneity approach of Eshelby

Eshelby [57] has obtained an explicit solution of the situation that spherical inhomogeneities are present in a homogeneous linear elastic matrix, which is identical to the situation of the biporous system. Odqvist [59] indicated that the results from an elastic analysis can be used to evaluate the response of a linear viscous material via the analogue, where the strains evaluated for the elastic material are simply taken as strain rates for the linear viscous material. The expression for the strain rate potential of a homogeneous material in the absence of inhomogeneity as proposed by Eshelby [57] is:

$$\phi = \frac{1}{6\mu} \sigma_e^2 + \frac{1}{2\kappa} \sigma_m^2 \quad (3-14)$$

where $\sigma_e^2 = \frac{3}{2} S_{ij} S_{ij}$ is the effective stress, $\sigma_m = \frac{1}{3} \sigma_{kk}$ is the mean stress. Equation (3-14)

can be applied to describe the strain rate potential of a microporous body.

Ignoring the interactions between the macropores, Eshelby's expressions can be used to express the strain rate potential of a biporous system as:

$$\phi = \frac{1}{6\mu}(1 + Bf_v)\sigma_e^2 + \frac{1}{2\kappa}(1 + Af_v)\sigma_m^2 \quad (3-15)$$

where $A = \frac{1}{1 - \frac{1}{3}(1+\nu)}$, $B = \frac{1}{1 - \frac{2}{15}(4-5\nu)}$ and f_v is the void volume fraction.

Using $\dot{\epsilon}_{ij} = \frac{\partial \phi}{\partial \sigma_{ij}}$, the strain rate expression is:

$$\dot{\epsilon}_{ij} = \frac{\sigma_m \delta_{ij}}{2\mu(1+\nu)} \left[(1-2\nu) + \frac{3}{2}f_v(1-\nu) \right] + \frac{s_{ij}}{2\mu(7-5\nu)} [(7-5\nu) + 15f_v(1-\nu)] \quad (3-16)$$

It is noted that the strain rate field under pure hydrostatic loading can be divided into relatively simple fields which are orthogonal to each other. Since the material response is linear, we can write the strain rate potential in the form of:

$$\phi = \frac{1}{2\mu_n}\sigma_e^2 + \frac{3}{8\mu}\frac{f_v\sigma_m^2}{(1-f_v)} + \frac{1}{2\kappa}\frac{\sigma_m^2}{(1-f_v)} \quad (3-17)$$

where

$$\mu_n = \mu \frac{7-5\nu}{(7-5\nu) + 15f_v(1-\nu)} \quad (3-18)$$

Equation (3-17) is obtained from the superposition of three fields: the first is due to the pure shear element of the macroelement; the second is from the deviatoric field of the equation (3-13), and the last part results from the dilatational field of equation (3-12).

3.1.4 Introduction of the sintering potentials

It is noted that the volumetric strain rate given by equation (3-17) is mainly due to the mean stress, σ_m , and deviatoric stress, S_{ij} . However, in practice, a porous powder compact will sinter even without an externally loading. Thus, the sintering potentials which act as the driving force for densification need to be introduced to the equation.

We begin by looking at the potential expressions, where the strain rate potential and stress potential can be related as follows:

$$\sigma_{ij} \dot{\epsilon}_{ij} = \phi + \psi \quad (3-19)$$

where ϕ is a function of stress and ψ is a function of strain rate. From the stress potential and strain rate potential the stress σ_{ij} and strain rate $\dot{\epsilon}_{ij}$ at a material point can then be obtained, respectively, in the following manner:

$$\dot{\epsilon}_{ij} = \frac{\partial \phi}{\partial \sigma_{ij}}; \quad \sigma_{ij} = \frac{\partial \psi}{\partial \dot{\epsilon}_{ij}} \quad (3-20)$$

The situation where a porous body subjected to a stress σ_{ij} and creeps at a rate $\dot{\epsilon}_{ij}$ is considered, an element of material within a grain experiences a stress σ_{ij} . Following the expression proposed by Cocks [27] where the convexity condition was used

$$\phi \geq \sigma_{ij} \dot{\epsilon}_{ij} - \Psi^c \quad (3-21)$$

with the stress potential associated with the porous body as:

$$\Psi^c = \frac{1}{V} \int_{V_m} \psi^c dV = \frac{1}{V} \left(\int_{V_m} \psi dV + \int_{V_m} \sigma_s \dot{\epsilon}_{kk} dV \right) \quad (3-22)$$

and

$$\psi = \frac{3}{2} \mu \dot{\epsilon}_e^2 + \frac{9}{2} \kappa \dot{\epsilon}_m^2 \quad (3-23)$$

where σ_s is the sintering potential arose from the shrinkage of the pores in the porous body. V is the total volume of the porous body, and V_m is the volume of the microporous matrix.

Combining equation (3-4) to (3-7), (3-21) and (3-22), the strain rate potential can be written as

$$\phi = 3\sigma_m \left(A + \frac{B}{b^3} \right) - 6\mu B^2 \frac{(1-f_v)}{a^3 b^3} - \frac{9\kappa}{2} A^2 (1-f_v) - 3\sigma_s (1-f_v) A \quad (3-24)$$

Optimizing equation (3-24) with respect to A and B , we obtain

$$A = \frac{\sigma_m - \sigma_s (1-f_v)}{3\kappa(1-f_v)}$$

$$B = \frac{\sigma_m a^3}{4\mu(1-f_v)}$$

Substituting A and B back to equation (3-24) and combine with the deviatoric strain rate gives:

$$\phi = \frac{1}{2\mu_n} \sigma_e^2 + \frac{1}{2\kappa} \frac{(\sigma_m - \sigma_s)^2 - \sigma_s^2 f_v^2}{1-f_v} + \frac{3}{8\mu} \frac{\sigma_m^2 f_v}{1-f_v} \quad (3-25)$$

$$\text{with } \mu_n = \mu \frac{7-5\nu}{(7-5\nu)+15f_v(1-\nu)}$$

using $\dot{\varepsilon}_{ij} = \frac{\partial \phi}{\partial \sigma_{ij}}$ [27], the strain rate expression for the grain-boundary diffusion

controlled densification of a biporous body is:

$$\dot{\varepsilon}_{ij} = \left[\frac{S_{ij}}{2\mu(7-5\nu)} [(7-5\nu)+15f_v(1-\nu)] + \frac{1}{3\kappa} \frac{\sigma_m - \sigma_s}{1-f_v} + \frac{1}{4\mu} \frac{\sigma_m f_v}{1-f_v} \right] \quad (3-26)$$

3.2 Experimental procedure

In previous sections, the constitutive models for the densification of a biporous material were discussed. In this section, experiments are designed based on biporous structure to obtain the necessary data to validate the constitutive relationships proposed.

3.2.1 Starting Materials

Commercial 8 mol% yttria-stabilized zirconia (8YSZ) powder (Tosoh, Japan) which is a material widely used for advanced applications, such as, Solid Oxide Fuel Cells as electrolyte, thermal barrier coating for turbine blades and refractory in jet engines, etc., was used as raw material. The measured mean particle size was 0.1 μm . Poly (methyl methacrylate), PMMA microspheres (Struers, Singapore) with a mean particle size of 50-70 μm were used as pore former to produce large macropores. The volume fraction of PMMA used to produce porous 8YSZ was 20%.

Figure 3.3 Microstructure of 8YSZ powder

3.2.2 Production of green body

The two-roll compaction technique [60] was used to fabricate the ceramic green bodies. An important feature of the two-roll compaction method is that the two rollers are not rolling at the same speed. This provides a shear effect on the dough during rolling, which will provide a better mix of the mixture.

Beside biporous 8YSZ, microporous 8YSZ was also prepared as reference. In the subsequent text, “8YSZ/20%” will be used to refer to the biporous 8YSZ sample, and “8YSZ” refers to the microporous 8YSZ sample.

Initially a dough was made by weighing out the 8YSZ powder, methylcellulose, glycerol, distilled water. The roll compaction formulations of the microporous and biporous 8YSZ systems are listed in Table 3.1. The well mixed dough was then rolled on a two-roll-mill until a moist tape was obtained. The tape was then removed from the machine and cut into 15 mm×15 mm.

Table 3.1 Composition of biporous 8YSZ system (where X% is volume fraction of PMMA)

Materials	Composition (wt %)
8YSZ powder	59
PMMA powder	$18.1307X/(100-X)$
Methylcellulose	6
Glycerol	2
Distilled water	33

3.2.3 Sintering schedule

The 8YSZ samples, both macro- and microporous, were heated to 150°C with a heating rate of 0.5°C/min and were held for 1 hour to get rid of all the water in the samples. They were then heated to 600°C at a heating rate of 1°C/min, and held for 1 hour to eliminate the polymers. The green density of the samples was measured only after the polymers had been burnt out. Then, the samples were heated 2°C/min to 1350°C, and held for different holding times.

3.2.4 Characterization Methods

The mass and volume of sintered samples were measured in order to calculate their density, $D_{measured}$. The relative density ρ is then obtained by:

$$\rho = \frac{D_{measured}}{D_{theoretical}} \quad (3-27)$$

where the theoretical density ($D_{theoretical}$) of 8YSZ is taken as 5.95 g/cm³.

Cross-section images of sintered samples were obtained using Scanning Electron Microscope (SEM, JSM-6340F JEOL company, Japan) after polishing and thermal etching.

The grain size was determined by straight lines method on the micrograph. About 150 ~ 200 grains were measured for each sample. The final mean grain size was obtained as 1.56 times the average intercept length [61]. A schematic illustration of determination of grain size is shown in Figure 3.4. The size of the large pores was also measured. About 100-200 pores were measured to obtain the mean pore size.

Figure 3.4 Schematic illustration of calculation of grain size

The volume fraction of large pores in the overall biporous body, f_v , was obtained using equation (3-28) (see Appendix A):

$$f_v = 1 - \left(1 + \frac{1 - \rho_m}{\rho_m}\right) \rho \quad (3-28)$$

where ρ_m and ρ are the relative density of the microporous matrix and the overall biporous body, respectively. ρ_m cannot be obtained directly, but it can be obtained via image analysis of the SEM images of the cross-section of the specimens..

3.3 Results and discussion

3.3.1 Sintering results

The SEM images of typical sintered 8YSZ/20% samples are displayed in Figure 3.5. The microstructure shows that the large macropores are distributed evenly throughout the 8YSZ microporous matrix.

(a)

(b)

Figure 3.5 SEM images of sintered biporous 8YSZ/20%
(a) Biporous structure (b) Microporous matrix

As a result, from the experiment, the relative density, grain size, diameter of the macropores and volumetric fraction of large macropores for the samples sintered at 1350°C, can be determined and are shown in Figure 3.6 to Figure 3.8. The relative density and grain size of sintered microporous 8YSZ are also plotted for a better comparison.

Figure 3.6 Relative density of samples sintered at 1350°C

Figure 3.7 Grain size of samples sintered at 1350°C

Figure 3.8 Diameter and volumetric fraction of macropores of biporous 8YSZ/20% sintered at 1350°C

During the experiments, the biporous 8YSZ/20% showed a relatively slower grain growth rate than that of microporous 8YSZ, the grain size of biporous 8YSZ/20% after 2h sintering at 1350°C reached 1.2 μm compared with 1.9 μm of microporous 8YSZ. And the large pores of 8YSZ/20% were found to be shrinking continuously throughout the sintering process in the present work.

The experimental results obtained will be used to validate the model established in Section 3.1.

3.3.2 Modelling results

The specific equation of strain rate for grain boundary diffusion controlled densification is given by equation (3-26), and the densification rate can be obtained from the strain rate expression as

$$\dot{\rho} = -\rho \dot{\epsilon}_v \quad (2-8)$$

For free sintering, the mean stress σ_m and deviatoric stress S_{ij} are equal to zero since there is no external stress applied on the samples. Thus, the densification rate for biporous systems during free sintering becomes as:

$$\dot{\rho} = \rho \left(\frac{1}{\kappa} \frac{\sigma_s}{1 - f_v} \right) \quad (3-29)$$

Substituting equations (3-2) and (3-3) to equation (3-29), the densification rate turns out to be

$$\dot{\rho} = 9\rho \frac{\dot{\epsilon}_0}{\sigma_0} \left(\frac{L_0}{L} \right)^3 f(\rho) \left[\frac{\sigma_s}{1 - f_v} \right] \quad (3-30)$$

In equation (3-30), the sintering potential σ_s and dimensionless function $f(\rho)$ of sintering Stage 1 are [62]:

$$\sigma_s = \frac{4.5\gamma_s}{L} \rho^2 \left(\frac{2\rho - \rho_0}{1 - \rho_0} \right) \quad (3-31)$$

$$f(\rho) = \frac{0.54(1 - \rho_0)^2}{\rho(\rho - \rho_0)^2} \quad (3-32)$$

and σ_s and $f(\rho)$ of sintering Stage 2 are [62]:

$$\sigma_s = \frac{4\gamma_s}{L} \left(\frac{\rho}{6(1 - \rho)} \right)^{1/3} \quad (3-33)$$

$$f(\rho) = \frac{0.5}{1 - 2.5(1 - \rho)^{2/3}} \quad (3-34)$$

The σ_0 in equation (3-30) can be written as [23]

$$\sigma_0 = \frac{\gamma_s}{L_0} \quad (3-35)$$

Equation (3-30) can then be expressed as

$$\dot{\rho} = 9\rho \dot{\epsilon}_0 \left(\frac{L_0}{\gamma_s} \right) \left(\frac{L_0}{L} \right)^3 f(\rho) \left[\frac{\sigma_s}{1 - f_v} \right] \quad (3-36)$$

After substituting expressions of $f(\rho)$, σ_s into equation (3-34), the densification rate equation contains the relative density, grain size, volume fraction of large macropore as variables, which can be obtained directly from experiments.

Programming language *Java* was used to perform the modelling with a simple Euler scheme to calculate the relative density after a time step, Δt ,

$$\rho_{t+\Delta t} = \rho_t + \dot{\rho}_t \Delta t \quad (3-37)$$

During modelling, the value of γ_s was taken as 1 J/m² [63], the grain size, diameter of macropore and macropore volume fraction were converted to the function of the relative density in order to avoid added complication. The strain rate constant of densification, $\dot{\epsilon}_0$,

is temperature dependent, and can be expressed as: $\dot{\epsilon}_0 = \frac{\dot{\epsilon}_{00}}{T} \exp(-\frac{Q}{RT})$ [64], where $\dot{\epsilon}_{00}$

is a material constant, Q is the activation energy, R and T are the ideal gas constant and absolute temperature respectively. When evaluating the constitutive model proposed, data is needed for the value of $\dot{\epsilon}_0$. Appropriate value of $\dot{\epsilon}_0$ is determined from the modelling process by comparing the prediction of proposed equation to the experimental results obtained.

Figure 3.9 shows the modelling results for the densification (relative density versus holding time) of microporous and biporous systems. For comparison, the experimental data are also plotted in the figure.

For the densification, it can be seen that the proposed expression of densification rate (equation (3-34)) underestimated the densification of the biporous 8YSZ/20%.

Figure 3.9 Modelling results of densification at 1350°C

3.4 Modification of proposed model for biporous material

It can be seen that the small pores within the microporous matrix can sinter quickly and disappear, however, the large pores were observed shrinking throughout the sintering process despite the large coordination number of large pores and were presented at the end of sintering process (Figure 3.8). The large pores and small pores showed different shrinking characteristics, thus, the densification of the porous body with bimodal pore size is not governed by the average porosity. The contributions from large pores and small pores to the densification have to be considered separately.

In the following section, the effect of the large macropores to the densification of a biporous body will be treated separately from that of the small micropores in the matrix.

We will use the kinematic bounds proposed by Cocks [27] again:

$$\phi \geq \sigma_{ij} \dot{\epsilon}_{ij} - \Psi^c \quad (3-21)$$

with

$$\Psi^c = \frac{1}{V} \left[\int_{V_m} \psi^c dV + \gamma_s \dot{A}_s^c + \gamma_b \dot{A}_b^c \right] \quad (3-38)$$

$\dot{A}_s^c$ and $\dot{A}_b^c$ are the rates of change of surface area and grain-boundary area, respectively, and the superscript c represents an assumed compatible strain rate field within the macroscopic element. The first term of right hand side related to shrinkage of small pores in microporous matrix, and the last two are resulted from the shrinkage of macropores.

Then, the sintering potentials will be introduced to the models.

The stress potential associated with the microporous matrix (the first term of right hand side of equation (3-38)) can be incorporated as:

$$\frac{1}{V} \int_{V_m} \psi^c dV = \frac{1}{V} \left(\int_{V_m} \psi dV + \int_{V_m} \sigma_{sp} \dot{\epsilon}_{kk} dV \right) \quad (3-39)$$

and

$$\psi = \frac{3}{2} \mu \dot{\epsilon}_e^2 + \frac{9}{2} \kappa \dot{\epsilon}_m^2 \quad (3-40)$$

where σ_{sp} is the sintering potential arose from the shrinkage of small micropores in the microporous matrix.

The computational simulation of Pan et al. [13] showed that during the densification of the large pore, the shorter facet of the pore surface tends to disappear and cause the smallest grains to meet each other, and new grain-boundaries are formed between them which are oriented in the radial direction. This is similar to mechanism of “neighbor-switching” which maintains the equiaxed structure during superplastic deformation proposed by Ashby and Verrall [55]. One feature of the neighbor-switching events is that if the pore surface area is changed by an amount of $d\dot{A}_s$, then this must be accompanied by a change in the grain boundary area by an amount of $-\frac{d\dot{A}_s}{2}$.

The rate of change of surface area of the macropore can be expressed in terms of the field quantities A and B :

$$\dot{A}_s = 8\pi a \left(Aa + \frac{B}{a^2} \right) \quad (3-41)$$

Then,

$$\gamma_s \dot{A}_s^c + \gamma_b \dot{A}_b^c = \left(\gamma_s - \frac{1}{2} \gamma_b \right) \cdot 8\pi a^2 \left(A + \frac{B}{a^3} \right) \quad (3-42)$$

Combine equations (3-36) to (3-40) with (3-21) gives

$$\phi = 3\sigma_m \left(A + \frac{B}{b^3} \right) - 6\mu B^2 \frac{(1-f_v)}{a^3 b^3} - \frac{9\kappa}{2} A^2 (1-f_v) - 3\sigma_{s\rho} (1-f_v) A - 3f_v \sigma_{sR} \left(A + \frac{B}{b^3} \right) \quad (3-43)$$

where

$$\sigma_{sR} = \frac{2\gamma_s}{a} \left(1 - \frac{\gamma_b}{2\gamma_s} \right) \quad (3-44)$$

σ_{sR} will be defined as the sintering potential arose from the shrinkage of the macropores.

We can see that it is related to the surface and grain-boundary energies and influenced by the size of the large macropore. Mackenzie and Shuttleworth [65] proposed that the shrinkage of the large pores was equivalent to the application of a traction on the surface

of the large pore with a value of $2\frac{\gamma_s}{a}$, where γ_s is the surface energy and a is the radius of

large pore. Slamovich and Lange [12] showed that the driving stress of shrinkage of the

closed large pore in a dense polycrystalline material approached $\frac{2\gamma_s}{a} \sin \frac{\theta}{2}$ with

increasing grain size, with θ is the dihedral angle. In the present work, the assumption of

“neighbor-switching” in the vicinity of the large pore was employed, and the expression of sintering potential of the large pore (equation (3-42)) is obtained by using the ratio of

$-\frac{1}{2}$ between the change in surface area and that in grain boundary area. The contribution

of grain boundary energy was added to the sintering potential of the large pores compared with the expression proposed by Mackenzie and Shuttleworth [65].

The volume fraction of the large pores can be expressed by f_v which equals to a^3/b^3 .

Optimizing equation (3-43) with respect to A and B , we can have

$$A = \frac{\sigma_m - \sigma_{sp}(1 - f_v) - \sigma_{sR}f_v}{3\kappa(1 - f_v)}$$

$$B = \frac{3(\sigma_m - \sigma_{sR})f_v b^3}{12\mu(1 - f_v)}$$

Finally by substituting A and B back into equation (3-43) and combining with the deviatoric strain rate term proposed by Eshelby, the expression for the strain rate potential of a biporous body is:

$$\phi = \frac{1}{2\mu_n} \sigma_e^2 + \frac{1}{2\kappa} \frac{[\sigma_m - \sigma_{sp}(1 - f_v) - \sigma_{sR}f_v]^2}{1 - f_v} + \frac{3}{8\mu} \frac{(\sigma_m - \sigma_{sR})^2 f_v}{1 - f_v} \quad (3-45)$$

$$\text{with } \mu_n = \mu \frac{7 - 5\nu}{(7 - 5\nu) + 15f_v(1 - \nu)}$$

using $\dot{\epsilon}_{ij} = \frac{\partial \phi}{\partial \sigma_{ij}}$ [27], the strain rate expression for grain-boundary diffusion controlled

densification of a biporous body is obtained as:

$$\dot{\epsilon}_{ij} = \frac{S_{ij}}{2\mu(7 - 5\nu)} [(7 - 5\nu) + 15f_v(1 - \nu)] + \frac{1}{3\kappa} \frac{\sigma_m - \sigma_{sp}(1 - f_v) - \sigma_{sR}f_v}{1 - f_v} + \frac{1}{4\mu} \frac{(\sigma_m - \sigma_{sR})f_v}{1 - f_v} \quad (3-46)$$

In the above equation, sintering potentials associated with both large and small pores are considered. This equation will be used to model the densification of biporous body and the modelling results will be compared with the results obtained by model with consideration of average porosity.

Figure 3.10 shows the comparison of calculation results between models with and without consideration of sintering potential associated with the large macropores, equations (3-36) and (3-46), respectively. The results show that the model, which considers separately the large pores and small pores, provide a better description of the densification of the

biporous 8YSZ/20%; during the densification, the shrinkage of the macropores will provide an additional driving force for the densification of porous body. The sintering potential contributed from the macropores could be reasonably significant and needs to be considered in order to give a more accurate prediction to the densification behaviors of the biporous material system. Value of strain rate constant of densification, $\dot{\epsilon}_0$, is determined from the modelling process as $1.38 \times 10^{-4} \text{ s}^{-1}$.

Figure 3.10 Model calculation of densification of biporous 8YSZ/20%: comparison of models with σ_{SR} (equation (3-46)) and without σ_{SR} (equation (3-36))

3.5 Concluding remarks

In this chapter, constitutive models for determining grain-boundary diffusion controlled sintering characteristics of a porous body with bimodal pore size were studied. Experiments were design based on biporous structure from a submicronic 8YSZ.

The model for the porous structure which considers only the average porosity was first established and was found underestimating the densification of biporous body. The established model was further modified by introducing separately the sintering potential

associated with small pores and large pores. The expression of the sintering potential associated with large macropores was verified.

The experimental results obtained were compared with theoretical prediction of the modified model. The comparison shows that the modified constitutive model of biporous material can give good prediction for the densification of biporous 8YSZ used in the present work.

The results indicated that the densification of a porous body with bimodal pore size distribution was not governed so much by the average porosity, but influenced by the shrinkage behaviours of different pore types. By introducing the sintering potential associated with the macropores, the constitutive model gave a more accurate prediction of the densification of a porous material that consists of both micro- and macropores. It is further noted that the shrinkage of large pores provided an additional driving force for the densification of the porous material with bimodal pore size distribution.

Chapter 4 Evolution of Large Pores during Densification

It is noted that the porosity and dimension of the pores essential parameters to the properties and performance of the porous components in advanced applications, such as Solid Oxide Fuel Cells (SOFCs), high-temperature thermal insulators, filters and membranes for high temperature gas cleaning or molten metal filtration, and gas burner media, etc. There exists several reported models on the densification behaviour of isolated large pores in a fully densified matrix [12, 13], for example, Pan et al. [66] have performed a computer simulation on this problem, and observed that the shrinkage rate of large pores in a fully dense solid was slower than that in a porous matrix.

In this chapter, we aim to establish the relationships for the evolution of the large pores separated by a matrix material containing small pores during densification.

4.1 Model for the evolution of large pores

As described in Chapter 3, the thick-walled shell model is used to simulate the situation of a large pore in a microporous matrix. Figure 3.2 (a) shows the cross section of a macropore in microporous matrix. The porous body is subjected to a uniform external hydrostatic stress, σ_m . a is the radius of large macropore and $2b$ is the mean spacing between the macropores. The volume fraction of large pore f_v is written as:

$$f_v = \frac{a^3}{b^3} \quad (4-1)$$

The expression for the strain rate potential of a porous body with bimodal pore size distribution, when the densification was controlled by grain-boundary diffusion, has been established in Chapter 3 as:

$$\phi = \frac{1}{2\mu_n} \sigma_e^2 + \frac{1}{2\kappa} \frac{[\sigma_m - \sigma_{s\rho}(1-f_v) - \sigma_{sR}f_v]^2}{1-f_v} + \frac{3}{8\mu} \frac{(\sigma_m - \sigma_{sR})^2 f_v}{1-f_v} \quad (3-45)$$

$$\text{with } \sigma_s = \sigma_{s\rho}(1-f_v) + \sigma_{sR}f_v$$

The symbols in the above equations have the same definition as in Chapter 3.

The first term of right hand side of equation (3-45) is from a pure shear field, the second term is from the dilatational field, and the last part results from the deviatoric field.

During sintering, the small pores in the microporous matrix will first shrink to reduce surface energy. In this chapter, the expression of sintering potential arose from the shrinkage of small pores in the microporous matrix, and sintering potential associated with the shrinkage of large pores, will follow the same expressions used in Chapter 3, i.e.,

$$\sigma_{s\rho} = \frac{4.5\gamma_s}{L} \rho_m^2 \left(\frac{2\rho_m - \rho_{m0}}{1 - \rho_{m0}} \right) \quad (3-33)$$

and

$$\sigma_{sR} = \frac{2\gamma_s}{a} \left(1 - \frac{\gamma_b}{2\gamma_s} \right) \quad (3-44)$$

The effects of the sintering potentials arose from the shrinkage of the small pores in the microporous matrix, and the large pore, are equivalent to the effect of applying a uniform pressures on the surface of the shell and large pore, respectively.

From the thick-walled shell analysis, the equation of displacement of the material contained within the microporous matrix at location r , $a \leq r \leq b$, can be obtained as:

$$U_r = Ar + \frac{B}{r^2} \quad (4-2)$$

From the boundary conditions of the stress tensor σ_r at location r :

$$\begin{aligned} \sigma_r(r=a) &= \sigma_{sR} \\ \sigma_r(r=b) &= \sigma_m \end{aligned} \quad (4-3)$$

The values of A and B in equation (4-2) can be determined as:

$$A = \frac{\sigma_m - \sigma_{s\rho}(1 - f_v) - \sigma_{sR}f_v}{3\kappa(1 - f_v)} \quad (4-4)$$

$$B = \frac{a^3(\sigma_m - \sigma_{sR})}{4\mu(1 - f_v)} \quad (4-5)$$

By differentiating both sides of equations (4-1), the rate of change of the volumetric fraction of large pores can be presented as:

$$\dot{f}_v = 3f_v \left(\frac{\dot{a}}{a} - \frac{\dot{b}}{b} \right) \quad (4-6)$$

Using the elastic analogue, we can obtain

$$\dot{a} = A \cdot a + \frac{B}{a^2} \quad (4-7)$$

and

$$\dot{b} = A \cdot b + \frac{B}{b^2} \quad (4-8)$$

By combining equations (4-5) to (4-8), we have the expression for the rate of change of f_v as

$$\dot{f}_v = -\frac{\partial \phi}{\partial \sigma_{sR}}(1 - f_v) \quad (4-9)$$

From equation (4-2), the relative velocity of the material at location r can be written as:

$$\dot{r} = \frac{\sigma_m - \sigma_{s\rho}(1 - f_v) - \sigma_{sR}f_v}{3\kappa(1 - f_v)} \cdot r + \frac{a^3(\sigma_m - \sigma_{sR})}{4\mu(1 - f_v)} \cdot \frac{1}{r^2} \quad (4-10)$$

Hence, the shrinkage rates for the large pore can then be obtained as:

$$\dot{a} = \frac{\sigma_m - \sigma_{s\rho}(1 - f_v) - \sigma_{sR}f_v}{3\kappa(1 - f_v)} \cdot a + \frac{a^3(\sigma_m - \sigma_{sR})}{4\mu(1 - f_v)} \cdot \frac{1}{a^2} \quad (4-11)$$

4.2 Experimental procedure

8 mol% yttria-stabilized zirconia (TZ-8Y, Tosoh, Japan) of 0.1 μm of mean particle size was used as raw material. Different amount (20 and 45 vol%) of starch microspheres

with a mean particle size of 20 μm were added to 8YSZ powder as pore forming agent. In the subsequent text, we will use “YSZ-P20” to refer to the porous 8YSZ with 20 vol% of pore former, and “YSZ-P45” to refer to the porous 8YSZ with 45 vol% of pore former. Tape casting was applied to prepare the samples. The mixture of 8YSZ powders and pore former was first ball milled for 24 hours with ethanol as solvent and triethanolamine as dispersant. Polyvinyl butyral and polyethylene glycerol were then added to the slurry and ball milled for another 24 hours before pouring into the tape caster. The green samples were then punched into 25 mm $\times$ 25 mm square samples for sintering experiments. After burning out the binder at 500°C for 1h, the samples were then heated to 1350°C at a heating rate of 2°C/min, and held for different holding times. The densities of sintered samples were measured using Archimedes method. The relative density was calculated by dividing the measured density by the theoretical density of 8YSZ. In the present work, the theoretical density of 8YSZ is taken as 5.95 g/cm³. The microstructures of the sintered samples were observed at their cross-section by using Field Emission Scanning Electron Microscope (FESEM, JSM-7600F, JEOL Company, Japan) after polishing and thermal etching. The grain size and radius of large pores were determined as described in Chapter 3. The volume fraction of large pores, f_v , in the porous body was obtained by equation (3-28).

4.3 Results and discussion

Figure 4.1 show the typical microstructures of sintered YSZ-P20 and YSZ-P45. The microstructures show that the large pores are distributed evenly throughout the 8YSZ matrix.

Figure 4.1 Typical SEM images of overall sintered YSZ-P20 and YSZ-P45

Figure 4.2 Microstructure of microporous matrix of samples sintered at 1350°C YSZ-P20 sintered (a) 30 min (b) 2 h, and YSZ-P45 sintered (c) 30 min and (d) 2 h

The evolutions of microstructure of microporous matrix of YSZ-P20 and YSZ-P45 were shown in Figure 4.2. From the microstructure, it can be found that the amount of micropores decreased with increasing sintering time. And YSZ-P45 contains relatively less small pores than YSZ-P20.

For free sintering, the mean stress σ_m and deviatoric stress S_{ij} are zero. The equation for densification rate equation (3-46) was numerically integrated together with the rate of change of volumetric fraction of the large pores (equation (4-9)) and shrinkage rate of large pores (equation (4-11)). To take care of the grain growth, the grain size was converted to function of relative density with equations fitted from experimental data.

The modelling results for the relative density, volumetric fraction and radius of large pores are shown in Figure 4.3 to Figure 4.5. Experimental data is plotted together with the modelling results (discrete symbols represent the experimental data, and solid lines for calculated results from model), and good agreement was found between the two.

Figure 4.3 Relative densities as a function of time of porous bodies with different initial volumetric fraction of large pores

The equation of shrinkage rate of large pore (equation (4-11)) indicates that the densification of microporous matrix plays an important role on the shrinkage of the large macropores. In a microporous matrix which densifies faster, the material surrounding the large pores diffuse faster to the surface of large pores, hence promoted the shrinkage of large pores. When the microporous matrix approaches full density, the large pores will still continue to shrink with a relatively slower shrinkage rate despite without the

contribution from the densification of microporous matrix. The present result is also found to be consistent with the simulation performed by Pan et al. [66]. On the earlier expression (equation (3-46)), the densification rate of the bimodal porous body includes the contribution from the shrinkage of large pores. The results have shown that the sintering stress contributed from the large macropores could be reasonably significant. As a result, consideration of the shrinkage of large macropores can provide a more accurate prediction for the densification of a porous body with bimodal pore distribution. At a given pore size, the densification rate, rate of change of volumetric fraction of large pores and shrinkage rate of large pores are also the function of the amount of large pores. The macropores shrink faster in the materials with a greater amount of large pores at a given time; hence exhibit a faster densification rate. It is consistent with the experimental observations (Figure 4.2) and the modelling results of the present work (Figure 4.3 to Figure 4.5), and that reported by Slamovich and Lange [11]. Slamovich and Lange have indicated that a greater number of large pores resulted in a smaller average distance between pores, i.e. a shorter diffusion distance for mass transport. Consequently, a faster densification rate was observed for the compact with larger amount of large macropores. Figure 4.4 and Figure 4.5 have also further shown that it is not practical to eliminate the large macropores. Despite the large pores shrink fast at the beginning of the sintering, they become extremely stable at the later phase of the sintering process.

Figure 4.4 Evolutions of volumetric fraction of large pores as a function of time of porous bodies with different initial volumetric fraction of large pores

Figure 4.5 Shrinkage of large pores as a function of sintering time of porous bodies with different initial volumetric fraction of large pores

4.4 Concluding remarks

The model for the sintering of porous material with bimodal pore size distribution was established and utilized to calculate the shrinkage rate of large pores. The results of modelling agree well with the experimental data. The calculations from the model and the experimental observations in this chapter show that the large macropores in a microporous matrix shrink continually, and provide an additional driving force to the densification of porous material. On the other hand, both the calculations from the model and the experimental results show that it is difficult to remove the large pores even with extended sintering time.

The expressions of shrinkage rate of large pores established in this chapter can help to understand the parameters which affect the shrinkage of large pores, and the expressions can be further combined with densification equations to obtain a more complete series of constitutive model to predict the sintering behavior of a porous material with bimodal pore size distribution.

Chapter 5 Development of Sintering Model for multilayer system

In this chapter, the model of the biporous system developed in Chapter 3 together with the model of the microporous material will be used to establish a series of constitutive relationships for the co-sintering of a bi-layer system. This will provide a theoretical method for the study of co-sintered bodies. It should be noted that during co-sintering, the mismatch stress as induced by the differential shrinkage rate will not only affect the densification behavior, but also the microstructure evolution of the layers. As densification is sensitive to grain size [23, 67, 68], the densification rate of the layers under co-sintering could be largely affected if grain growth effect is not considered. Hence, in the current approach, the effect of grain size, as well as relative density and stresses, are included. The model is validated by predicting the induced stress, and hence, the curvature developed during the co-sintering of a ceramic bi-layer system.

5.1 Co-sintering model

In the present work, the co-sintering of a bi-layer system was considered. This bi-layer system consists of a microporous layer which contains only small pores and a biporous layer which consists of both small pores and big macropores.

Figure 5.1 presents a simple geometry of bi-layer structure, layer 1 is a microporous layer and layer 2 is a biporous layer. The layers have different thicknesses of t_1 and t_2 respectively. When these different layers are adhered together, constraints arise at the layers' interfaces due to the shrinkage rate mismatch between the different layers. The layer which shrinks faster will experience a tensile stress; and the adjacent layer will experience a compressive stress. $\dot{\varepsilon}_i$ and σ_i are the in-plane strain rate and stress developed

in the layers; 1 and 2 refer to layer 1 and layer 2, respectively. $\dot{\epsilon}_{ii}$ and σ_{ii} represent the through thickness strain rate and stress in the layers.

Figure 5.1 Schematic of stress and strain rate analysis of two layers

We assume that there is no sliding at the interface, hence the in-plane strain rates and stresses of the two layers could satisfy the following compatibility and equilibrium conditions

$$\dot{\epsilon}_1 = \dot{\epsilon}_2 \quad (5-1)$$

$$\sigma_1 t_1 = -\sigma_2 t_2 \quad (5-2)$$

The negative sign in right term of equation (5-2) denotes the mismatch stresses in layer 1 and layer 2.

The strain rate of a microporous body can then be expressed as [23]

$$\dot{\epsilon}_{ij} = \frac{S_{ij}}{2\mu} + \frac{1}{3\kappa}(\sigma_m - \sigma_{sp}) \quad (5-3)$$

Recall that the expression for the strain rate of a biporous body is

$$\dot{\epsilon}_{ij} = \frac{S_{ij}}{2\mu} \left[1 + \frac{15f_v(1-\nu)}{7-5\nu} \right] + \frac{1}{3\kappa} \left(\frac{\sigma_m - \sigma_s}{1-f_v} \right) + \frac{1}{4\mu} \left(\frac{\sigma_m - \sigma_{sR}}{1-f_v} \right) f_v \quad (3-46)$$

$$\text{and } \sigma_s = \sigma_{sp}(1-f_v) + \sigma_{sR}f_v$$

The symbols in the expressions have the same definition as in the earlier sections.

Using the constitutive equations of the microporous and biporous compacts (equations (5-3) and (3-46)), the in-plane strain rates of layer 1 and layer 2 can be written as

$$\dot{\epsilon}_1 = \frac{S_1}{2\mu_1} + \frac{1}{3\kappa_1}(\sigma_{m1} - \sigma_{s\rho1}) \quad (5-4)$$

$$\dot{\epsilon}_2 = \frac{S_2}{2\mu_2} \left[1 + \frac{15f_v(1-\nu_2)}{7-5\nu_2} \right] + \frac{1}{3\kappa_2} \left(\frac{\sigma_{m2} - \sigma_{s2}}{1-f_v} \right) + \frac{1}{4\mu_2} \frac{(\sigma_{m2} - \sigma_{sR2})f_v}{1-f_v} \quad (5-5)$$

And the through thickness strain rate in layer 1 and layer 2 can be obtained as

$$\dot{\epsilon}_{t1} = \frac{S_{t1}}{2\mu_1} + \frac{1}{3\kappa_1}(\sigma_{m1} - \sigma_{s\rho1}) \quad (5-6)$$

$$\dot{\epsilon}_{t2} = \frac{S_{t2}}{2\mu_2} \left[1 + \frac{15f_v(1-\nu_2)}{7-5\nu_2} \right] + \frac{1}{3\kappa_2} \left(\frac{\sigma_{m2} - \sigma_{s2}}{1-f_v} \right) + \frac{1}{4\mu_2} \frac{(\sigma_{m2} - \sigma_{sR2})f_v}{1-f_v} \quad (5-7)$$

where S_{ti} is the through thickness deviatoric stress

Assuming there is no through thickness stress developed in the layers, we have

$$\sigma_{mi} = \frac{1}{3}(\sigma_i + \sigma_i + 0) = \frac{2}{3}\sigma_i \quad (5-8)$$

$$S_i = \sigma_i - \sigma_{mi} = \frac{1}{3}\sigma_i \quad (5-9)$$

and

$$S_{ti} = 0 - \sigma_{mi} = -\frac{2}{3}\sigma_i \quad (5-10)$$

Substituting equations (5-5) to (5-10) into compatibility condition (equation (5-1)):

$$\frac{1}{3}\frac{\sigma_1}{\kappa_1} + \frac{1}{3\kappa_1} \left(\frac{2}{3}\sigma_1 - \sigma_{s\rho1} \right) = -\frac{1}{3\kappa_2} \frac{m\sigma_1}{1-f_v} \left[1 + \frac{15f_v(1-\nu_2)}{7-5\nu_2} \right] + \frac{1}{3\kappa_2} \left(\frac{-\frac{2}{3}m\sigma_1 - \sigma_{s2}}{1-f_v} \right) + \frac{1}{6\kappa_2} \frac{(-\frac{2}{3}m\sigma_1 - \sigma_{sR2})f_v}{1-f_v} \quad (5-11)$$

where m is the thickness ratio of two layers, $m = \frac{t_1}{t_2}$

From equation (5-11), we can then obtain the value for mismatch stress in layer 1, σ_1

$$\sigma_1 = \frac{\frac{1}{\kappa_1}\sigma_{s\rho1} - \frac{1}{\kappa_2} \frac{2\sigma_{s\rho2}(1-f_v) + 3\sigma_{sR2}f_v}{2(1-f_v)}}{\frac{1}{\kappa_1} + \frac{1}{\kappa_2} \frac{m}{3} \left[1 + \frac{15f_v(1-\nu_2)}{7-5\nu_2} \right] + \frac{2+f_v}{1-f_v}} \quad (5-12)$$

The equation (5-12) can be simplified as:

$$\sigma_1 = \frac{\Delta \dot{\epsilon}}{\frac{1}{\kappa_1} + \frac{1}{\kappa_2} \frac{m}{3} \left[1 + \frac{15f_v(1-\nu_2)}{7-5\nu_2} + \frac{2+f_v}{1-f_v} \right]} \quad (5-13)$$

with

$$\Delta \dot{\epsilon} = \frac{1}{\kappa_1} \sigma_{s\rho 1} - \frac{1}{\kappa_2} \frac{2\sigma_{s\rho 2}(1-f_v) + 3\sigma_{sR2}f_v}{2(1-f_v)} \quad (5-14)$$

and the stress in layer 2 can then be obtained as

$$\sigma_2 = -\sigma_1 \cdot m = \frac{\Delta \dot{\epsilon}}{\frac{1}{\kappa_1 m} + \frac{1}{\kappa_2} \frac{1}{3} \left[1 + \frac{15f_v(1-\nu_2)}{7-5\nu_2} + \frac{2+f_v}{1-f_v} \right]} \quad (5-15)$$

The volumetric strain rate of the layers can be written as

$$\dot{\epsilon}_{vi} = 2\dot{\epsilon}_i + \dot{\epsilon}_{ii} \quad (5-16)$$

Substituting equations (5-5) - (5-9) to equation (5-16), we can obtain

$$\dot{\epsilon}_{v1} = \frac{1}{\kappa_1} \left(\frac{2}{3} \sigma_1 - \sigma_{s1} \right) \quad (5-17)$$

$$\dot{\epsilon}_{v2} = \frac{\frac{2}{3} \sigma_2 (2+f_v) - 2\sigma_{s\rho 2}(1-f_v) - 3\sigma_{sR2}f_v}{2\kappa_2(1-f_v)} \quad (5-18)$$

From equations (5-17) and (5-18), it can be seen that a tensile stress will inhibit the densification of the ceramic layer; on the contrary, a compressive stress can accelerate the densification. As a result, during the co-sintering process, the sintering behavior of two layers will be controlled by the strain rate mismatch between them, i.e. $\Delta \dot{\epsilon}$.

5.2 Experimental procedure

In the present work, a thin microporous 8 mol% yttria-stabilized zirconia (8YSZ) layer was laminated on a biporous 8YSZ layer to form a bi-layer system, and co-sintering was then performed.

5.2.1 Fabrication of bi-layer

8 mol% yttria-stabilized zirconia (Tosoh, Japan) was used as raw material. The biporous 8YSZ layer was made by adding starch microspheres with a mean particle size of 20 μm as pore former to 8YSZ powder. The weight percentage of starch powder was 20 wt%, and ~ 45 vol% porosity was created. In the subsequent text, we will use “8YSZ/45%” to refer to the biporous 8YSZ layer, and “8YSZ” to refer to the microporous 8YSZ layer. Tape casting was applied to the fabrication of both layers. 8YSZ powder with and without pore former were first ball milled for 24 hours with ethanol as solvent and triethanolamine as dispersant. Polyvinyl butyral and polyethylene glycerol were then added to the slurry and ball milled for another 24 hours before pouring into the tape caster. After drying overnight at room temperature, the green 8YSZ and 8YSZ/45% tapes of average thickness of ~ 80 μm and ~ 400 μm , respectively, were cut into size of 50 mm $\times$ 50 mm for subsequent lamination.

The bi-layer system was prepared by lamination of one thin 8YSZ layer and three 8YSZ/45% layers in a 50 mm $\times$ 50 mm square stainless-steel mold at 70°C for 5 mins with a pressure of 20 MPa. The bi-layers were then punched into 25 mm $\times$ 25 mm square samples for sintering experiments. Rectangle samples of 20 mm $\times$ 5 mm with a thickness ~ 1.2 mm were also prepared for curvature study.

5.2.2 Co-sintering and characterization of bi-layers

After burning out the binder at 500°C for 1h, bi-layers were then heated to 1350°C at a heating rate of 2°C/min, and held for different holding times. A porous Al₂O₃ loading plate which has a weight of 7 g was placed on top of the 25 mm×25 mm bi-layers to prevent bending. The porous Al₂O₃ plate will introduce a pressure of ~110 Pa on the co-sintered samples. The pressure resulting from the porous plate was much smaller than internal sintering potential which has a value ~10 MPa. Hence, the pressure introduced by this porous plate can be ignored. In addition to the bi-layers, free-standing 8YSZ and 8YSZ/45% layers were also sintered as reference.

The 20 mm×5 mm rectangle samples for curvature study were sintered without the porous Al₂O₃ loading plate. The images of sintered bi-layers of 20 mm×5 mm rectangle were recorded after the samples cooled to room temperature. The radius of curvature, r , was determined from recorded images by fitting a circle to the middle plane of the bi-layer.

Figure 5.2 Schematic illustration of determination of the radius of curvature, r , of sintered bi-layer (with a dense thin layer on top)

The microstructures of the co-sintered bi-layers and the free-sintered 8YSZ and 8YSZ/45% layers were observed at their cross-section by using Field Emission Scanning Electron Microscope (FESEM, JSM-7600F, JEOL Company, Japan) after polishing and thermal etching. The top surface of co-sintered 8YSZ layer was also observed using FESEM, and the images were used to calculate the grain size. The grain size was

measured by counting the number of grains traversed by straight lines. More than 300 grains were measured for each sample. The final mean grain size was obtained as 1.56 times the average intercept length [61].

The densities of 8YSZ/45% layer in the bi-layer system were calculated by measuring their mass and volume after the 8YSZ top layer was removed by polishing. The densities of the 8YSZ top layer were obtained from image analysis of the fracture surface of 8YSZ layer.

The radius of the large pores in the 8YSZ/45% layer was also measured. About 100-200 pores were measured to obtain the mean pore size.

5.3 Results and discussion

5.3.1 Experimental results

The obtained relative densities of 8YSZ top layer as well as 8YSZ/45% layer were presented in Figure 5.3 (a). The relative densities of free-sintered 8YSZ and 8YSZ/45% were also plotted for comparison.

The relative densities of co-sintered 8YSZ layer in Figure 5.3 display significant retarding on densification. After sintered at 1350°C for 2 h, the relative density of co-sintered 8YSZ layer was only ~85% compared with ~96.4% for the free-sintered 8YSZ. The results of relative density are consistent with microstructure observation: co-sintered 8YSZ showed an interconnected porosity after 2h sintering at 1350°C (Figure 5.4 (b)); on the contrary, only closed pore structure was observed in the free-sintered 8YSZ (Figure 5.4 (a)). In contrast to the retarded densification of 8YSZ layer, the densification of 8YSZ/45% layer in the system was consistently noted to have been enhanced at all holding time comparing to that of the free-sintered 8YSZ/45%. Enhanced densification was also observed for the microporous matrix of 8YSZ/45% after co-sintering (Figure 5.3 (b)). Lower porosity was

found in the matrix of co-sintered 8YSZ/45% (Figure 5.4 (d)) compared to that of the free-sintered 8YSZ/45% (Figure 5.4 (c)).

Figure 5.3 (a) Relative densities of co-sintered and free-sintered 8YSZ and 8YSZ/45% (b) relative densities of microporous matrix of co-sintered and free-sintered porous 8YSZ/45%

Figure 5.4 SEM images of samples sintered 2h at 1350°C (a) free-sintered 8YSZ, (b) co-sintered 8YSZ, (c) microporous matrix of free-sintered 8YSZ/45%, (d) microporous matrix of co-sintered 8YSZ/45%, (e) cross-section of co-sintered sample

The grain sizes of the 8YSZ and 8YSZ/45% layers as a function of relative density are showed in Figure 5.5. The results of free-sintered samples are also plotted.

Different grain size versus relative density trajectories were observed between free-sintered and co-sintered samples for both two layers, i.e., the grain sizes obtained were

different at a given density. He and Ma [69] have reported that during pressure-assisted sintering of Al_2O_3 , the grain size of the samples at a fixed relative density varied with applied pressures. As a result, the grain size is a function of, not only the current relative density and grain size, but also influenced by the densification history. The sintering paths of co-sintered 8YSZ and 8YSZ/45% have also demonstrated that densification and grain growth are two competitive processes. At the same relative density, a slower densification is accompanied by a faster grain growth; whereas on the other hand, an enhanced densification will inhibit grain growth.

Figure 5.5 Grain size of sintered 8YSZ and 8YSZ/45% samples as a function of relative density

5.3.2 Modelling results

In this section, experimental results obtained are applied to validate the constitutive relationships established earlier in Section 4.1. The validated relationships, which are expressed in term of measurable state variables, will be able to provide useful predictions on the parameters, such as the stresses induced during the co-sintering.

Recall the expression of densification rate

$$\dot{\rho} = -\rho \dot{\epsilon}_v \quad (2-8)$$

The densification rate equations of microporous and biporous layer can then be obtained from equations (5-17), (5-18) and (2-8) as follows:

$$\dot{\rho}_1 = -\rho_1 \frac{1}{\kappa_1} \left(\frac{2}{3} \sigma_1 - \sigma_{sp1} \right) \quad (5-19)$$

$$\dot{\rho}_2 = -\rho_2 \frac{\frac{2}{3} \sigma_2 (2 + f_v) - 2 \sigma_{sp2} (1 - f_v) - 3 \sigma_{sR2} f_v}{2 \kappa_2 (1 - f_v)} \quad (5-20)$$

with σ_l derived earlier (equation (5-14)).

The thickness ratio of two layers, m , was noted to be 0.06, which was obtained from SEM image (Figure 5.4 (e)), and it is assumed that m remained constant during the co-sintering.

The Poisson's ratio, ν was calculated by using Scherer's model [70]:

$$\nu = 0.5 \left[\frac{\rho}{3 - 2\rho} \right]^{1/2} \quad (5-21)$$

The sintering potential associated with the microporous body σ_{sp} , and the bulk viscosity κ_i , are expressed as equations (3-36) and (3-3), respectively.

In the present work, the programming language *Java* was used to perform the modelling. The Euler scheme used in Chapter 3 was adopted to calculate the relative density with time step, Δt ,

$$\rho_{i_t+\Delta t} = \rho_{i_t} + \dot{\rho}_{i_t} \Delta t \quad (3-37)$$

As the grain size, diameter and volume fraction of the large pores are functions of relative density and stress (internal and/or external), these parameters were converted to functions of relative density with equations fitted directly to these data.

It is noted that the kinetic constant, $\dot{\epsilon}_0$, is a function of material systems and sintering temperatures. As a result, the value of $\dot{\epsilon}_0$ for 8YSZ sintered at 1350°C obtained in Chapter 3, $1.38 \times 10^{-4} \text{s}^{-1}$, can be applied for the calculation in current chapter. The

densification results of the microporous 8YSZ layer and biporous 8YSZ/45% co-sintered at 1350°C were computed using equations (5-19) and (5-20), and the results are presented in Figure 5.6. It can be seen that the theoretical predictions agree well with the experimental data.

Equations (5-15) and (5-16) are applied to estimate the mismatch stresses arose in the co-sintered layer which are induced by the differential shrinkage rate of two layers, and the results are shown in Figure 5.7. The stresses in the two layers are of opposite signs. In the beginning of co-sintering at 1350°C, the 8YSZ layer was in tension, and 8YSZ/45% layer was in compression. It agrees with the observed retarded densification in 8YSZ layer and enhanced densification in 8YSZ/45% layer. The signs of the mismatch stresses in two layers switch between them at the later stage of co-sintering. The value of sintering potential in the co-sintered 8YSZ layer calculated by the model was also shown in Figure 5.7. The mismatch stresses in the co-sintered layers are of a smaller magnitude than that of the sintering potential. The highest mismatch stresses are noted to occur at the beginning of the co-sintering, and the mismatch stresses decrease as the densification continues. It can be seen that the magnitude of the mismatch stress in 8YSZ/45% layer is much lower than that in the 8YSZ layer. That is attributed to the large thickness difference between 8YSZ and 8YSZ/45% layers (m is ~ 0.06). From the expressions of mismatch stresses (equations (5-14) and (5-15)), we can see that when the thickness ratio, m , is very small, $m \ll 1$, the differential shrinkage rate can induce a high stress in the thinner layer; on the other hand, the influence of the differential shrinkage rate on the densification is relatively insignificant in the layer which is relatively much thicker. This is consistent with the little enhancement of densification observed in the co-sintered 8YSZ/45% layer. The mismatch stresses calculated were further used to estimate the warpage development during the co-sintering.

Figure 5.6 Modelling results of densification process of co-sintering at 1350°C

Figure 5.7 Calculated mismatch stresses in two layers

During the co-sintering, a curvature will be developed due to the mismatch shrinkage rates between different layers. The layer which shrinks faster will suffer a tensile stress, and the bi-layer will warp toward this layer. In Figure 5.8, the curvature development of the bi-layer is shown in a series of images, the thin 8YSZ layer is the top layer and porous 8YSZ/45% layer forms the bottom layer.

Figure 5.8 (a) Pictures of curvature of bi-layer show the curvature development during the co-sintering at 1350C (the thin 8YSZ layer is the top layer) (b) top-view of sintered bi-layer

The rate of curvature change normalized to the total thickness of bi-layer, $\dot{k}$, during co-sintering process can be calculated as [71]:

$$\dot{k} = \frac{d((t_1 + t_2)/r)}{dt} = \left[\frac{6(m+1)^2 mm}{m^4 n^2 + 2mn(2m^2 + 3m + 2) + 1} \right] \Delta \dot{\epsilon} \quad (5-22)$$

where r is the curvature radius of the bi-layer, m is the thickness ratio, n is viscosity ratio between two layers. For a plate geometry [72]

$$n = \left(\frac{E_{p1}}{1 - \nu_1} \right) \left(\frac{1 - \nu_2}{E_{p2}} \right) \quad (5-23)$$

and for a beam geometry [72]

$$n = \frac{E_{p1}}{E_{p2}} \quad (5-24)$$

The samples used for curvature measurement (20 mm×5 mm×1.2 mm) in the present work have the beam geometry (Figure 5.8 (b)), thus, equation (5-24) is used for the calculation.

E_{pi} is uniaxial viscosity which can be related to the bulk viscosity, κ , by:

$$\kappa = \frac{E_p}{3(1 - 2\nu)} \quad (5-25)$$

Figure 5.9 Calculated and measured normalized curvature of bi-layer as function of time at 1350°C

The normalized curvature of bi-layer is simulated using equation (5-22). At every calculation step, $\Delta\dot{\epsilon}$ and n are obtained using equations (5-14), (3-3) and (5-24) with the newly calculated relative density.

Figure 5.9 plots the measured and calculated normalized curvature. The direction toward the thin 8YSZ layer is defined as positive. It can be seen that the measured and calculated normalized curvatures showed good agreement. The result indicates that the model proposed in the present work can provide a reasonably good prediction on the mismatch stresses arose in the co-sintered bi-layers. The calculation results have shown that as 8YSZ layer sinters faster than porous 8YSZ/45% layer, the sample cambers toward 8YSZ layer first. When strain rate of 8YSZ/45% layer exceeds that of 8YSZ layer, the curvature decreases and sample cambers toward 8YSZ/45% layer.

During co-sintering of a bi-layer system, the in-plane strain rate varies along thickness direction. Kanters et al. [5] have defined the in-plane strain rate with kinematic approach as:

$$\dot{\epsilon}(t) = \dot{\epsilon}^0 - tk - ik \quad (5-26)$$

The t direction is perpendicular to the interface, and $\dot{\varepsilon}^0$ is the lateral strain rate in the middle plane of the bi-layer, where $t = 0$; and k is principle curvature of bi-layer. Hence, the in-plane stress along the bi-layer thickness can be expressed as [5]:

$$\sigma_i(t) = \frac{E_i(t)}{1-\nu_i(t)} (\dot{\varepsilon}^0 - t\dot{k} - \dot{k}t - \dot{\varepsilon}_i^{free}(t)) \quad (5-27)$$

From equation (5-27), we can see that for thin 8YSZ layer, the magnitude of in-plane stress near free surface does not differ significantly from that near interface between thin 8YSZ layer and 8YSZ/45% layer. Thus, the densification of thin 8YSZ layer can be considered as homogeneous along thickness. On the other hand, the difference between in-plane stress near interface of two layers in 8YSZ/45% layer and that near free surface of 8YSZ/45% layer can become as high as 50% of sintering potential of microporous matrix of 8YSZ/45% layer after about 6h's sintering at 1350°C. Despite the anisotropic in-plane stress field in the thick 8YSZ/45% layer, the calculation shows that the difference of relative density caused by this anisotropic in-plane stress field is <0.05%, which can be considered as negligible. Hence, in the present work, the in-plane strain rates were assumed as uniform along thickness throughout the modelling calculation.

5.4 Concluding remarks

In this chapter, the constitutive model for the sintering of material with bimodal pore size distribution was applied to establish a series of constitutive relationships for co-sintering of a bi-layer system. The constitutive relationships established were applied to predict the densification of a bi-layer system of 8YSZ/porous 8YSZ. The in-plane stress field was assumed as isotropic along thickness during the calculation, and the result shows that the model can provide a reasonably good prediction on the densification of the co-sintered layers. Both theoretical predictions and experimental observations show that the differential shrinkage rate between two layers will induce mismatch stresses to the co-

sintered layers, and hence result in an enhanced or inhibited densification, which in turn depends on the sign of induced mismatch stress. The development of curvature of bi-layer was also calculated by leveraging the proposed model. The calculated results were in good quantitative agreement with measured curvature. Different sintering paths (grain size vs. relative density) were observed between co-sintered and free-sintered samples, which indicated that the grain growth is influenced by the densification process. Further research is required to provide a detailed model of grain growth, which takes into account not only the current microstructure, but also the effect of densification history.

Chapter 6 Grain Growth Law

6.1 Introduction

The grain growth results during co-sintering obtained in Chapter 5 has shown that the samples displayed different sintering trajectories with the presence of external stress. At a given relative density, the material under tensile stress has a larger grain size than that of the material sintered under free sintering. On the other hand, the materials that were subjected to compression showed a smaller grain size than the free-sintered materials. Reduced grain size at a given relative density with the external applied pressure has also been observed for materials processed by sinter-forging and hot isostatic pressing (HIP) [73, 74]. Grain growth is one of the essential phenomena during the sintering process. As this effect is reckoned to couple with the densification rate, it is hence of huge interest to study the grain growth behavior and its representation in constitutive relationship. However, most of existing models of grain growth don't take into consideration of the effect of external stress on grain growth, and are thus limited for free sintering. To take care of that, Hague and Mayo [73] developed a grain growth model which combined static grain growth and dynamic grain growth during the final stage of sinter-forging. On the other hand, Besson and Abouaf [75, 76] examined the microstructure evolution of alumina during HIPing, and proposed a grain growth law by adding a term related to external pressure. However, both the above existing models tailored towards the handling of compressive applied stress and the grain growth behavior under tensile stress, such as constrained sintering, is still lacking attention.

In the attempt to improve the grain growth law, in this chapter, we start by analysing the effect of stress on grain growth via experimental observation, and then propose a constitutive relationship for coupled grain growth, stress (both compressive and tensile), densification, and state variables.

6.2. Experimental observation

In this section, the grain growth and densification characteristics of materials under various external stresses, both tensile and compressive, will be studied via designed experiments.

6.2.1 Experimental procedures

(a) Compressive stress

For the sintering with external compressive stress, the experimental data reported by Ma and He [69] were used. In their work, the densification and grain growth of α -alumina with an initial grain size of $7\mu\text{m}$ during sinter-forging at 1600°C by applying different level of pressure were studied.

(b) Tensile stress

In this section, the sintering behaviors of 8 mol% yttria-stabilized zirconia (8YSZ) during co-sintering and constrained sintering at 1350°C were studied and compared with that of free-sintered 8YSZ. The results of free-sintering and co-sintering were taken from Chapter 5. The constrained 8YSZ layer was laminated on a rigid 8YSZ substrate. The thin microporous layer and substrate were fabricated by tape casting. Details of the procedure for sample preparation have been described in Section 5.2. The densities of the 8YSZ top layer cannot be obtained directly, but estimated by image analysis of the crossed section surface of 8YSZ layer.

6.2.2 Experimental results

Ma and He [69] have investigated densification and grain growth of alumina under different external stress. Their results were plotted in Figure 6.1. It can see that both

densification and grain growth are enhanced during sinter-forging when compared with that of free sintering (0 MPa), and the enhancement of densification and grain growth increased with the increased applied pressure. The enhanced grain growth of α -alumina during sinter-forging is found to be consistent with the observation of Besson and Abouaf [76], Hague and Mayo [73], and Uematsu et al. [74].

Figure 6.1 Sintering results of α -alumina with an initial grain size of $7\mu\text{m}$ during sinter-forging (replotted using data reported in the work of Ma and He [69]): (a) Densification
(b) Grain growth

In contrary to the accelerated densification and grain growth during sinter-forging, the densifications and grain growth of 8YSZ during constrained sintering (with rigid substrate)

and co-sintering (with porous substrate) are largely retarded compared with that of 8YSZ subjected to free sintering (Figure 6.2).

Figure 6.2 Sintering results of 8YSZ at 1350°C (a) Densification (b) Grain growth

During constrained sintering, the rigid substrate is fully dense and will not shrink; hence the top 8YSZ layer suffers a tensile stress throughout the whole sintering process. It is noted that the tensile stress introduced by the rigid substrate is larger than that of a porous substrate (unlike the dense substrate, the porous substrate layer is also shrinking during

co-sintering, despite at a slower rate). Consequently, 8YSZ during constrained sintering suffers a larger tensile stress compared with 8YSZ during co-sintering and free sintering, and shows the slowest densification rate.

The microstructure of sintered 8YSZ after 2h at 1350°C is shown in Figure 6.3. 8YSZ on rigid substrate showed a continuous, three-dimensional network porosity even after 2h sintering at 1350°C. Co-sintered 8YSZ on porous substrate also has an interconnected pore structure, but with a smaller average pore size. 8YSZ subjected to free-sintering only shows small and isolated pores. The observation is also consistent with the densification results plotted in Figure 6.2 (a).

(a)

(b)

(c)

Figure 6.3 SEM image of (a) constrained sintered, (b) co-sintered and (c) free-sintered 8YSZ after 2h at 1350°C

As mentioned earlier, several grain growth laws have been proposed to simulate the enhancement of grain growth generated during sintering with pressure. In this section, we take a closer examination of their models. Hague & Mayo [73] modeled the grain growth by combining normal grain growth and dynamic grain growth during final stage of sinter-forging (when relative density is higher than 90%), and they assumed that the grain size is a linear function of relative density during early stage of sinter-forging (when relative density is smaller than 90%). Hence, when relative density is smaller than 90%, the samples during sinter-forging have same grain size as the samples during free-sintering. However, it can be seen from Figure 6.1 that there exists a clear difference of grain size between samples with external pressure and free-sintered sample.

Besson and Abouaf [76], on the other hand, developed a model for grain growth during hot isostatic pressing (HIP) by adding a term related to external stress as

$$\dot{L} = \frac{k + C\sigma_{eq}^2}{L^3} \quad (6-1)$$

where k , and C are constants, L is grain size and σ_{eq} is Mises equivalent stress. Their analyst also proposed that the external pressure does not alter the grain growth mechanism.

Besson and Abouaf's model has been widely applied to describe the grain growth during HIP and sinter-forging. Although, the model works well for grain growth behavior during sintering with external pressure (HIP and sinter-forging), the model is not appropriate for the case of constrained sintering (where give tensile stress), since the stress related term in their equation, $C\sigma_{eq}^2$ will always lead to an increase in grain growth, which is contrary to that observed in constrained sintering.

From the experimental results, we can see that the external tensile stress retarded the densification and grain growth; on the other hand, the applied compressive stress accelerated the densification and grain growth. Furthermore, different level of applied stress will induce different level of influence on the densification and grain growth. Hence, in the next section, we will suggest an expression to describe the grain growth during sintering with external stress, both compressive stress and tensile stress.

6.3. Grain growth law

It is noted that there exists classical grain growth representation in the literature [23], such as

$$\dot{L} = \dot{L}_0 \left(\frac{L_0}{L}\right)^3 (1 - \rho)^{-m} \quad (6-2)$$

where m is a dimensionless constant (m was proposed to have a value of 3/2 during Stage 1 and 4/3 during Stage 2 [23]); L_0 is the initial grain size. Same as $\dot{\epsilon}_0$ in the expression of densification rate, $\dot{L}_0$ is a temperature dependent kinetic constant. At a given temperature, $\dot{L}_0$ is fixed for each material system. Equation (6-2) gives a good representation as it relates grain growth to physically measurable quantities, such as relative density and grain size, hence allowing a direct comparison to be made between

theory and experiment. In practice, its state variables are also that of interest for process engineers' input on the manufacturing of ceramic components.

The expression (6-2) is subsequently applied to calculate the grain size of 8YSZ and also that of α -alumina in section 6.2. During the calculation, the relative density was converted to a function of time. The grain growth kinetic constant, $\dot{L}_0$, which possessed a fixed value for a given material system, was determined using the free-sintered data and was applied to calculate the grain size of samples sintered with external stress.

Figure 6.4 Grain size of 8YSZ calculated by equation (6-2) during constrained sintering and co-sintering

Figure 6.5 Grain size of α -alumina calculated by equation (6-2)

The grain size of 8YSZ and α -alumina calculated by equation (6-2) are shown in Figure 6.4 and Figure 6.5, respectively. Experimental results of grain size of 8YSZ and α -alumina were also plotted for a better comparison. It can be seen that equation (6-2) was able to provide a good description of the grain growth process for free sintering. However, the modelling results show that equation (6-2) overestimated the grain growth of 8YSZ during sintering with external tensile stress. On the contrary, the grain growth of α -alumina during sinter-forging was underestimated by equation (6-2). The discrepancies when stresses exist are attributed to the fact that equation (6-2) doesn't take into consideration of the interaction between grain growth and densification evolution, which is a function of the stress state.

It can hence be deduced that external stress influences grain growth indirectly through its effect on densification rate. Thus, grain growth depends not only on microstructure and porosity, but also the densification evolution.

The above findings confirmed that observed by Mayo et al. [73] and Besson et al. [76], where stress component needs to be introduced into the expression. To improve from their proposed expressions where only compressive stress is taken care of, the present

work introduces a parameter related with densification evolution to equation (6-2). The grain growth rate then becomes:

$$\dot{L} = \dot{L}_0 \left(\frac{L_0}{L}\right)^3 (1 - \rho)^{-m} \left(\frac{\dot{\rho}}{\dot{\rho}^f}\right)^\alpha \quad (6-3)$$

where $\dot{\rho}$ is the densification rate at specific time with a relative density ρ and grain size L , and $\dot{\rho}^f$ is the reference densification rate of free sintering at the same relative density ρ ; and α is a dimensionless constant reflecting the sensitivity of grain growth rate to densification rate.

The term $\frac{\dot{\rho}}{\dot{\rho}^f}$ corresponds to densification evolution, indicates the relative speed of densification. When the material is under tensile stress, the densification is inhibited, i.e. $\dot{\rho} < \dot{\rho}^f$, consequently, it results in a smaller grain growth rate than that during free sintering. On the contrary, when a pressure is applied, the densification is enhanced, i.e. $\dot{\rho} > \dot{\rho}^f$, thus, a faster grain growth is observed. During free sintering, equation (6-3) reverts back to equation (6-2), since the term $\frac{\dot{\rho}}{\dot{\rho}^f}$ in equation (6-3) equals to 1. The value of $\dot{L}_0$ remained to be a material system constant and was determined using the free sintering data. The value of α was also be obtained as 1.209.

Figure 6.6 Comparison of grain growth of 8YSZ calculated by equation (6-3) and equation (6-2)

Figure 6.7 Comparison of grain growth of α -alumina calculated by equation (6-3) and equation (6-2)

The variations of grain size of 8YSZ and α -alumina calculated by equation (6-3) are plotted in Figure 6.6 and Figure 6.7, respectively. The modelling results are compared with the grain size obtained by using equation (6-2). The comparison shows that equation (6-3) provides a better description of grain growth of material under stress.

In the modelling of densification, the stress directly influences the densification rate by increasing (under compressive stress) or decreasing (under tensile stress) the sintering driving force, $\sigma_m + \sigma_s$ (with σ_m the mean stress, σ_s the sintering potential). During the early stage of sintering, grain growth is generally inhibited by the pinning effect of pores. When a tensile stress is introduced, and resulted in the retardation of the densification, elimination of pores becomes slower. Consequently, the residual porosity retards the grain growth. On the contrary, when the densification is accelerated by applying external pressure, the pores are eliminated faster, and the grain growth process can become faster. Hence, the assumption which stress is influenced by grain growth indirectly through its effect on densification is reasonable.

6.4 Effect of external stress on sintering trajectory

The experimental results of 8YSZ and α -alumina during sintering with external stress show that the densification and grain growth are retarded/enhanced simultaneity under the effect of external tensile/compressive stress. However, the figures of density and grain size in function of time are not able to reveal the real competing effect between densification and grain growth. Sintering trajectory which describes the sintering evolution using microstructural variable vs another, such as grain size vs. relative density, can best display the competition between densification and grain growth. Thus in this section, the influence of external stress on sintering trajectory will be studied in detail.

Sintering trajectories (grain size versus relative density) of α -alumina and 8YSZ were plotted in Figure 6.8 using the data of section 6.2. When the material is subjected to external stress, the sintering trajectory becomes different from that observed for samples under free sintering. At a given relative density, the increased applied pressures lead to a smaller grain size than that of free-sintered material (Figure 6.8 (a)). For the material

subjected to tensile stress, an opposite trend was observed. At the same relative density, the sample during constrained sintering displayed the largest grain size, followed by the sample for co-sintering, and the free-sintered 8YSZ has the smallest grain size (Figure 6.8 (b)).

Figure 6.8 Sintering trajectories of (a) α -alumina sintered at 1600 °C (b) 8YSZ sintered at 1350 °C

The experimental and modelling results show that the external stress influences both the densification and grain growth. As discussed above that the external stress affects the densification which further influences the grain growth behavior. In order to study the

extent of effect of stress on densification and grain growth process, the densification rate and grain growth rate were calculated. In this section, only the full-scale data of densification rate and grain growth rate obtained for α -alumina were plotted in Figure 6.9, since the external pressure has a more significant effect on densification rate and grain growth rate of α -alumina in the present work. The ratios of densification rate and grain growth rate of α -alumina under sinter forging to free-sintered α -alumina were also inserted in Figure 6.9.

Figure 6.9 Comparison of (a) densification rate and (b) grain growth rate of α -alumina calculated by models

From the calculation results, we can find that both the densification rate and grain growth rate of α -alumina during sinter forging were faster than α -alumina during free sintering. At the initial stage of sintering where most rapid shrinkage occurs, the densification rate of α -alumina with external pressure of 1 MPa is 7 times faster than that of free-sintered α -alumina, and the α -alumina under 3 MPa pressure densifies 8 times faster than free-sintered α -alumina (Figure 6.9 (a)). On the other hand, the acceleration of grain growth rate of α -alumina under 1 MPa pressure and 3 MPa are ~ 3.2 times and ~ 6.5 times, respectively (Figure 6.9 (b)).

The densification rate and grain growth rate of 8YSZ during constrained sintering were also calculated and results show that at the beginning of constrained sintering, the densification rate decreased 90%, and grain growth rate decreased 70% compared with that of 8YSZ during free sintering.

The experimental and calculation results show that the stress influences both the densification and grain growth, but with different extent. The densification is more sensitive to applied external stress than grain growth. The influences of external stress on densification and grain growth process with different extent further alter the sintering trajectories which can be explained as follows:

We start from the initial point (ρ_0, L_0) . We assume that the free-sintered body uses Δt^f to reach point $(\rho_0 + \Delta\rho, L_0 + \Delta L^f)$ with a densification rate of $\dot{\rho}^f$ and grain growth rate of $\dot{L}^f$. Hence, we have $\Delta\rho = \Delta t^f \cdot \dot{\rho}^f$ and $\Delta L^f = \Delta t^f \cdot \dot{L}^f$.

When a compressive stress is applied, both densification rate $\dot{\rho}^c$ and grain growth rate $\dot{L}^c$ are accelerated. In order to reach the relative density $\rho_0 + \Delta\rho$, Δt^c is needed for the body under compressive stress, and we have

$$\Delta t^c = \frac{\Delta\rho}{\dot{\rho}^c} < \Delta t^f = \frac{\Delta\rho}{\dot{\rho}^f} \quad (6-4)$$

During this period of Δt^c , the increase of grain size is

$$\Delta L^c = \Delta t^c \cdot \dot{L}^c \quad (6-5)$$

Combining equations (6-4) and (6-5), we have

$$\Delta L^c = \frac{\Delta \rho}{\dot{\rho}^c} \cdot \dot{L}^c = \frac{\Delta t^f \dot{\rho}^f}{\dot{\rho}^c} \dot{L}^c \quad (6-6)$$

By putting $\Delta L^f = \Delta t^f \cdot \dot{L}^f$ to equation (6-6), we have

$$\Delta L^c = \left(\frac{\dot{\rho}^f}{\dot{\rho}^c} \cdot \frac{\dot{L}^c}{\dot{L}^f} \right) \Delta L^f \quad (6-7)$$

From Figure 6.9, we know that the increase in grain growth rate due to the introduced compressive stress is smaller than the increase in densification rate, hence, we have

$$\Delta L^c < \Delta L^f .$$

Using the same analysis method, when the relative density of material under tensile stress reaches the relative density $\rho_0 + \Delta \rho$, we will get a bigger extent of grain growth ΔL^t than the extent of grain growth during free sintering ΔL^f .

In other words, when a material is under compressive stress, its densification is enhanced compared with that of free-sintered body. Consequently, it can reach a given relative density ρ faster than free-sintered body. However, during this period, the grains in this material don't have enough time to grow. Hence, the ceramic compact reveals a smaller grain size than that of free-sintered body. On the contrary, when the densification of material under tensile stress is retarded compared with that of free-sintered body, thus, the grains have enough time to reach a larger grain size than that of free-sintered body at a given relative density.

6.5 Application of proposed grain growth law to biporous material

In order to verify the proposed grain growth law and the value of α obtained, the model will be further applied to a biporous material where contains both small and large pores in this section. The experimental data of biporous material are taken from Chapter 4.

Figure 6.10 shows densification and grain growth results of biporous 8YSZ. The relative density of both overall biporous body and microporous matrix were measured and compared with relative density of microporous 8YSZ. From the experimental results, the densification and grain growth of biporous 8YSZ was found to be retarded compared with that of microporous 8YSZ.

Figure 6.10 Sintering of biporous 8YSZ (a) Densification (b) Grain growth

Consider the situation of a large pore in the center of microporous matrix (Figure 3.2). When the large pore is stable and does not shrink, the sintering of the surrounding matrix is mainly from a pure dilatational field. In another situation where the large pore is in the center of a fully dense matrix, the large pore shrinks and a sintering potential arises from the shrinkage of large pore in the interface between large pore and matrix, however, the volume of the dense matrix will not be affected by this stress. In this case, the shrinkage of large macropore induces a deviatoric stress field to the microporous matrix. Hence, for a biporous system where consists of small pores and large pores, the change of stress field of the microporous matrix is not only caused by the external applied stress, but also can arise from the existence of large pores.

Figure 3.2 Cross section of the spherical shell with a large macropore in the centre

Figure 6.11 Sintering trajectory of biporous 8YSZ

During the model calculation of grain size, relative density was converted to function of time in order to simplify the calculation. The variations of grain size of biporous 8YSZ calculated by equation (6-3) are plotted in Figure 6.12, the calculation results are compared with the grain size calculated by equation (6-2). The comparison shows equation (6-2) overestimated the grain size of biporous 8YSZ; on the other hand, the grain size calculated by equation (6-3) shows a good agreement with the measured grain size of biporous 8YSZ in the present work. The retarded densification and grain growth indicate

that the presence of large pores has a similar effect as tensile stress on the microporous matrix and retarded its densification and grain growth.

Figure 6.12 Comparison of grain growth of biporous 8YSZ calculated by equation (6-3) and equation (6-2)

6.6 Concluding remarks

In this chapter, the effect of external stress on grain growth was studied. The results show that the presences of external stress affect not only the densification, but also the grain growth. Retarded grain growth was observed for 8YSZ during constrained sintering, co-sintering compared with free sintered 8YSZ. On the other hand, a α -alumina during sinter forging shows a faster grain growth than α -alumina during free sintering.

We assume that the stress influences the grain growth indirectly through its effect on the densification, and proposed a grain growth law by introducing a parameter related with densification evolution. The proposed grain growth law was applied to predict the grain growth of 8YSZ during constrained sintering, co-sintering as well as α -alumina during sinter forging. The results show that the model predictions were in good agreement with measured grain size. The proposed grain growth law was applied to a biporous 8YSZ in

order to validate the obtained constant, α . Comparison between model calculation and experimental data shows a good agreement. The experimental observation and calculation further indicate that the presence of large pores has a similar effect as tensile stress on the microporous matrix and retarded its densification and grain growth.

It is also found that the stress has a larger effect on densification rate than its effect on grain growth rate. This leads to different sintering trajectories observed for samples during different sintering conditions.

Chapter 7 Conclusion and Future Work

7.1 Conclusions

Based on structure of biporous material where both small and large macropores exist, experiments were carried out to study the densification of biporous material. Different densification behavior was found between small pores and large macropores. It is concluded that the contributions from small pores and large pores have to be considered separately due to their different densification characteristics: small pores shrink and disappear quickly, however, on the other hand, the large macropores shrink slowly and continually during the sintering process. The constitutive laws for grain boundary diffusion governed densification were established to describe the densification of a biporous system where the sintering potentials arose from the shrinkage of both small pores and large macropores were considered and included. The proposed models were validated and shown good agreement to the experimental results of a biporous 8YSZ body. The proposed model has also taken separate consideration for the sintering potential associated with shrinkage of large pores. The model was shown to be able to provide a better description of the densification of biporous material than the model considered only the shrinkage of average porosity. From the findings, it was further deduced that the densification of biporous material cannot be fully represented by the average porosity, the dimension and type of pores are more important parameters. It is observed that the densification rate increases with the increase in the amount of large pores at a given pore size; nevertheless, on the other hand, with same amount of large pores, the larger the macropore, the slower the densification rate. It is also found that the continually shrinkage of large macropores in the microporous matrix observed during sintering provide an additional driving force for the densification of biporous material. A variation of size of

large pores and volume fraction were measured experimentally and compared with that derived from model calculation. The predictions were shown to be in good agreement with the experimental data, hence showing the proposed new model gives good description of the sintering process of a bimodal porous system.

The proposed constitutive model of biporous material was further coupled with model of microporous material to describe the densification behavior of a bilayers structure during co-sintering. The comparison between modelling prediction and experimental results shows that the models are capable to provide a reasonable prediction on the sintering of the co-sintered layers. Stresses arose between different layers during co-sintering could be determined by the presently established models.

Furthermore, it is found that the presence of external stress affect not only the densification, but also the grain growth. With the presence of external stress, the sintering trajectory is altered, i.e., at a given relative density, the ceramic body suffered a tensile stress was found to have a larger grain size than that of freely sintered sample; and on the other hand, the ceramic body under an external compressive pressure has a smaller final grain size than that of freely sintered body. Hence, it can be concluded that the grain growth depends not only on microstructure and density, but also depends on external stress. A grain growth law was then developed in the present work to model the grain growth during sintering under external stress. It is noted that the existing models in the literature can only handle external compressive stresses, to take care of both tensile and compressive external stress, a term related to the densification process was added to the grain growth law by assuming that grain growth and densification are coupling processes. The modified grain growth law was then applied to model the grain growth behavior of materials during co-sintering and sinter-forging. It was found that the expression can provide good predictions on the experimental results. The proposed grain growth law was further applied to predict the grain growth behavior of a biporous 8YSZ. Comparison

between model calculation and experimental data indicates that the presence of large macropores has a similar effect as tensile stress on the microporous matrix and inhibited its densification and grain growth.

7.2 Future work

7.2.1 Bimodal particle size distribution

Sintering behavior of ceramic components depends on powder system, microstructure and sintering conditions. Constitutive models were developed to study the densification and grain growth of ceramics. In these models, the particle is generally assumed as having a mono particle size distribution. However, in practice, in order to have a better control of microstructure and porosity, most powder systems possesses a mixture of powders with different particle size which leads to a wide range of particle size distribution. Microstructure is affected by the particle size distribution, further influence the densification and grain growth behaviors of the ceramic components.

Very little experiments and theoretical models on sintering of ceramic with bimodal particle size distribution have been reported, and results reported are not altogether consistent. In view of this, the development of constitutive model for ceramic compacts with bimodal particle size distribution will complete the current generation of constitutive models and provide a useful tool for process engineers on manufacturing of advanced ceramic components.

7.2.2 Densification and grain growth of submicron ceramic prepared by improved packing method

Wet forming method is able to eliminate forming defaults, such as big voids and agglomeration, and obtain a green ceramic body with a homogeneous initial microstructure with a high green density. The comparison of sintering characteristic

between uniaxial cold pressing prepared ceramic compact and that prepared by wet forming method shows that the samples prepared by later method result in a faster densification with a finer microstructure [77, 78]. This may be caused by the difference in initial relative density and microstructure, such as the distribution of pores in the ceramic compacts. Thus, it is interesting to study the effects of improved initial microstructure on the mechanisms of densification and grain growth, and provide appropriate constitutive relationships of sintering to predict the densification and grain growth of ceramics with different initial relative density.

7.2.3 Sintering map for submicron ceramic material

As mentioned earlier that densification and grain growth are two main phenomena during sintering, and they are influenced by a large number of factors, such as temperature, external stress, particle size, microstructure, etc. The experimental data of densification and grain size are generally plotted in function of time. However, density/grain size versus time is not able to reveal the real sintering process (densification and grain growth). Sintering maps which show at a given temperature, the dominant mechanism and densification [79] can be applied to identify sintering mechanism, interpret experimental data, and provide useful information for industrial processing decisions. Thus, it is necessary to develop the sintering maps for sintering of ceramics with different initial particle size, initial microstructure, sintering temperature and applied pressure by incorporated them into suitable constitutive models of various densification mechanisms.

Appendix A Volume Fraction of Large Pores in A Biporous System

The density of the overall biporous body, ρ , can be obtained by measuring the volume and mass of the samples, and can be written as

$$\rho = \frac{V_d}{V_{bp} + V_{sp} + V_d} \quad (\text{A-1})$$

where V_d is the volume of the dense part, V_{bp} is the volume of the large pores and V_{sp} is the volume of the small micropores.

The density of the microporous matrix in the biporous system, ρ_m , can be expressed as

$$\rho_m = \frac{V_d}{V_{sp} + V_d} \quad (\text{A-2})$$

ρ_m cannot be determined directly, but can be obtained from the image analysis of SEM micrographs of the cross section of the specimens.

The volume fraction, f_v , of the large macropores can be expressed as

$$f_v = \frac{V_{bv}}{V_{sp} + V_d + V_{bp}} \quad (\text{A-3})$$

From equation (A-1) and (A-2), equation (A-3) can be expressed in terms of ρ and ρ_m as

$$f_v = 1 - \left(1 + \frac{1 - \rho_m}{\rho_m}\right)\rho \quad (\text{A-4})$$

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List of Publication

1. **J. Lu**, H.H. Hng, X.C. Song, T.S. Zhang, J. Ma, "Co-sintering of a bimodal pore distribution layered structure: constitutive models and experiments," *Journal of the American Ceramic Society*, vol. 94, pp. 1528-1535, 2011.
2. **J. Lu**, J. Ma. Densification modeling studies on porous Al_2O_3 component. *Powder Metallurgy and Metal Ceramics*, vol. 49(3-4), pp. 55-62, 2010.
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Conference:

1. 'The effect of stress on grain growth of a submicronic zirconia', Poster, International Conference on Sintering, Aug 2011, Jeju, South Korea
2. 'Theoretical And Experimental Study On Densification Of Ceramics With Bimodal Pore Distribution', Oral presentation, 3rd International Congress on Ceramics, Nov 2010, Osaka, Japan
3. 'A constitutive model for ceramics with bimodal pore distribution', Oral presentation, 11th International Conference on Ceramic Processing Science, Aug 2010, Zurich, Switzerland