Effect of additives on sintering and conductivity of yttria-stabilized zirconia

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**NANYANG
TECHNOLOGICAL
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**EFFECT OF ADDITIVES ON SINTERING AND
CONDUCTIVITY OF YTTRIA-STABILIZED ZIRCONIA**

Dissertation for Doctor of Philosophy

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Abstract

The effect of additives on sintering and functional properties of ceramics is one of the on-going interests in the fabrication of high performance advanced components for novel applications. In the present work, the effect of additives on yttria-stabilized zirconia (YSZ) was studied. YSZ is a well accepted electrolyte material used in solid oxide fuel cell (SOFC) system. In the multi-layer SOFC system, YSZ is sandwiched between the anode (Ni/YSZ cermet) and cathode (Sr-doped LaMnO₃). There are several practical concerns in the co-sintering of this system, such as the higher sintering temperature of YSZ than that of the electrodes, unavoidable interdiffusion of NiO from anode, and ubiquitous presence of SiO₂ impurity. The present work focuses on the understanding of the influence of the additives, either in the form of purposely added Al₂O₃ or inevitably existed NiO, SiO₂, on sintering and conductivity of YSZ. The study aims to clarify the sintering mechanisms, hence shed light to the lowering of the sintering temperature, and to improve the conductivity of YSZ. Through the study, we also established models that provide prediction on the microstructural evolution during sintering, which could support the design of new material system in co-sintering and other application.

It has been reported that a small amount of Al₂O₃ or NiO could enhance the densification of YSZ, however, it was found in the present work that in the heavily doped YSZ samples, there exists an optimal additive amount for the densification. Grain growth of YSZ was also found to be initially advantageous by Al₂O₃ or NiO addition, but showed deteriorating effect upon further addition. In the present work, densification and grain growth kinetics of YSZ with/without additives were studied via the proposed master curve approach, which consists of Master Densification Curve (MDC)

and Master Grain Growth Curve (MGGC) approach. During the first-stage sintering ($\rho = 60\%$), the abnormally higher activation energy (620–730 kJ/mol) was observed, which was attributed to the contribution from interface reaction and surface diffusion. For the second stage of sintering ($60\% \leq \rho \leq 95\%$), lattice diffusion was proposed as the dominant mechanism for undoped 8YSZ. However, upon 1.0 wt.% Al_2O_3 , or 0.28 wt.% NiO addition, grain boundary diffusion was found to significantly contribute to the densification, where the activation energy was noted to decrease about 250 kJ/mol. The proposed MDC as well as MGGC were found to be able to facilitate prediction of microstructural evolution with good accuracy for a wide range of sintering profiles.

In order to further reduce the sintering temperature of YSZ, the approach of co-addition of Al_2O_3 and SiO_2 was evaluated. The lowest temperature for maximum densification rate (T_{max}) has been achieved at 1210°C in YSZ with 0.5 wt.% Al_2O_3 and 0.05 wt.% SiO_2 co-additives. The improved densification behavior is ascribed to the enhanced grain boundary diffusivity and liquid phase sintering.

Finally, the conductivity of YSZ with additives was examined, with respect to its application as electrolyte for SOFC. In contrary to the prevailing thought that SiO_2 contamination should be especially avoided, the present work demonstrated that co-addition of Al_2O_3 and SiO_2 could not only further enhance densification, but also could improve the conductivity of YSZ, provided a careful manipulation of additive content and suitable heat treatment temperatures. The optimum concentration of co-addition of Al_2O_3 and SiO_2 was identified via carefully designed experiments.

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Symbols and abbreviation

δ_{gb}	Thickness of grain boundary	Q	Activation energy of densification
δL	The change of sample length	R	Universal gas constant
Ω_a	Volume of atom	T	Temperature
ρ_0	Green density of sample	t	Time
ρ	Density of sample; or resistivity	3Y-TZP	3 mol% Yttria-stabilized Zirconia Polycrystals
σ^{sp}	Specific conductivity	8YSZ	8 mol% Yttria-stabilized Zirconia Master Densification Curve
σ_{gb}	Conductivity of grain boundary	CIP	Cold Isostatic Pressing
σ_{gi}	Conductivity of grain interior	CRH	Constant Rate of Heating
Θ	Thermal history	GB	Grain Boundary
A	Area	GBD	Grain Boundary Diffusion
C	Capacitance	GI	Grain Interior
D	Diffusion coefficient	H.R	Heating Rate
D_{gb}	Grain boundary diffusion coefficient	LD	Lattice Diffusion
D_l	Lattice diffusion coefficient	LSGM	Strontium/Magnesium-doped Lanthanum Gallate
E	Activation energy of conductivity	MGGC	Master Grain Growth Curve
G	Grain size	MRS	Mean Residual Square
k	Boltzmann's constant	MSC	Master Densification Curve
K_0	Pre-exponential factor	ScSZ	Scandia-Stabilized Zirconia
L	Thickness	SEM	Scanning Electron Microscopy
L_0	Original length of sample	SOFC	Solid Oxide Fuel Cell
max	Maximum	STEM	Scanning Transmission Electron Microscopy
min	Minimum	TEC	Thermal Expansion Coefficient
n	Mechanism-controlled constant	TEM	Transmission Electron Microscopy
Q_G	Activation energy of grain growth	TEOS	Tetraethyl Orthosilicate
		TGA	Thermal Gravimetric Analysis
		XRD	X-ray Diffraction
		Y-TZP	Yttria-stabilized Tetragonal Zirconia Polycrystals
		YSZ	Yttria-Stabilized Zirconia

1

Introduction

1.1 Background

The utilization of additives for tailoring of the sintering behavior and functional properties of various ceramic materials has been practiced for many years [1–3]. When a small amount of additives is introduced into the host material, they can be present as (1) a single solid/liquid phase, (b) a solid solution within the matrix, or (3) segregation along interfaces (surface/grain boundaries) [4]. The presence and interaction of additives with the host material could significantly influence the sintering kinetics and microstructural development, and thus is possible to achieve unique or outstanding functionality [5]. For these reasons, the effect of additives on processing and properties of ceramic materials is still one of the on-going interests in the fabrication of high performance components for advanced applications.

8 mol% yttria-stabilized zirconia (8YSZ) is a well known ceramic material which finds wide applications such as oxygen gas sensor and electrolyte for solid oxide fuel cell (SOFC) [6], owing to its good conductivity and excellent chemical stability under both oxidizing and reducing environment. In recent years, with the advances of SOFC technology, extensive studies have been carried out on processing and properties of the 8YSZ electrolyte, and one of the essential focuses is to lower the fabrication cost and to enhance reliability of the SOFC system. SOFC is an energy conversion de-

1.1 Background

vice that comprises all solid-state components, in which the electrolyte is sandwiched between anode (Ni/YSZ cermet) and cathode (Sr-doped LaMnO_3) [7]. SOFC possesses the main advantages of high efficiency and environmental friendliness, which has the potential applications as both auxiliary power unit as well as stationary power generator.

To fabricate the multi-layered SOFC system, co-sintering is acknowledged to be the most suitable and cost-effective technique [8, 9]. Nevertheless, the optimization of co-sintering temperature profile is usually difficult. A sintering process at temperatures of $\geq 1350^\circ\text{C}$ is always required to obtain gastight 8YSZ electrolyte. On the other hand, to avoid unfavorable interface reaction between component layers as well as coarsening of the porous electrodes microstructure, the performing of co-sintering at temperatures below 1250°C is desirable [10, 11].

To densify 8YSZ electrolyte at a reduced temperature, the addition of sintering aids has been widely adopted [12, 13]. Among various additives, a small amount of Al_2O_3 is found to not only effectively reduce the sintering temperature, but also beneficial to the ionic conductivity and toughness of YSZ [12, 14, 15]. Therefore, small amount of Al_2O_3 is always purposely added into YSZ when applied as electrolyte for SOFC.

A second important issue pertaining to the co-firing process, yet has been given little attention, is the inter-diffusion of Ni element. NiO/YSZ cermet is currently the most common anode material for SOFC. During co-sintering, the diffusion of Ni from anode side towards the electrolyte is frequently observed [16, 17]. Nevertheless, the influence of NiO on sintering behavior of YSZ and the mechanism remains unclear, particularly when NiO exists as impurities.

To fabricate planar SOFCs with controlled microstructure and flatness, an understanding of the microstructural evolution of the respective layers is necessary. So far, a number of sintering models have been reported with the attempt to predict densification and microstructural evolution [18, 19]. In recent years, master sintering curve

1.2 Objective

(MSC) model has been recognized as a simple yet powerful approach to describe the sintering process [20]. The application of MSC on sintering of YSZ electrolyte with or without additives are both scarce, which however could provide valuable guidance on engineering sintering profiles for the co-sintering process.

Another concern is SOFC electrolyte the ubiquitous presence of SiO_2 impurity. Trace of SiO_2 impurity can be easily introduced from either starting material, processing or sintering environment. Generally, the existence of SiO_2 is undesirable, as it would deteriorate the conductivity of YSZ, especially at the grain boundary conduction route by forming resistive phase along grain boundaries [21, 22]. However, the negative effect of SiO_2 can be eliminated by the addition of Al_2O_3 [14]. On the other hand, it was reported that SiO_2 is helpful for densification of YSZ [23]. In the present work, it is reckoned that, the co-addition of Al_2O_3 and SiO_2 would lead to a synergistic improvement on densification of 8YSZ. Meanwhile, by carefully manipulating the co-additives content, the conductivity of 8YSZ might be also improved.

1.2 Objective

The objective of this work is to understand the sintering behavior of 8YSZ with/without a small amount of Al_2O_3 , NiO addition, and co-presence of Al_2O_3 and SiO_2 . The study will also clarify the fundamental sintering mechanisms as well as determine the important parameters, such as activation energy. More importantly, the sintering behavior will be modeled through the master sintering curve (MSC) approach, from which both densification and grain growth is expected to be predicted with accuracy.

In addition, the electrical properties of YSZ with Al_2O_3 and SiO_2 addition will be investigated. The scavenging of silicious phase by Al_2O_3 has been intensively studied in “pure” YSZ containing only background SiO_2 impurity ($\leq 120\text{ppm}$) [22]. However, we are more interested in how effective Al_2O_3 could mitigating the harmful SiO_2 in impure or highly impure 8YSZ (0.05-0.3 wt.% SiO_2). In terms of both improved densification and conductivity, the optimal content of Al_2O_3 and SiO_2 co-addition in 8YSZ

1.3 Scope

would be determined. Specifically, the objectives expected to achieve throughout the present study are:

- to identify the optimal Al_2O_3 addition as sintering promoters for 8YSZ,
- to study the influence of small amount NiO on sintering behavior of 8YSZ,
- to correlate phase and microstructure change with the effect of NiO and Al_2O_3 addition,
- to establish MSC models for both undoped and doped 8YSZ,
- to shed light on the fundamental understanding of the densification and grain growth mechanisms of both undoped and doped 8YSZ,
- to further enhance the densification of 8YSZ via the synthetic effect of the co-presence of Al_2O_3 and SiO_2 , and to determine the mechanisms for enhanced densification,
- to optimize the content of Al_2O_3 and SiO_2 co-additive in terms of the improved conductivity of 8YSZ

1.3 Scope

The thesis consists of nine chapters. The background, objectives of the present study have been introduced in this chapter. In chapter 2, a comprehensive review was given on the historical development of solid state sintering and various sintering models, especially the master sintering curve theory. The application of additives for improving sinterability and conductivity of the YSZ electrolyte is also reviewed.

In chapter 3, the experimental procedures were presented, covering topics of experimental design, sample preparation and characterization, data collection and analysis.

In chapter 4, the application of master curves on undoped 8YSZ was examined. Both master densification curve (MDC) and master grain growth curve (MGGC)

1.3 Scope

were constructed for undoped 8YSZ, and the effectiveness of the established master curves was verified. Meanwhile, the sintering mechanisms were discussed based on the modeling approach.

In chapter 5, the master curves approach was extended to Al_2O_3 -doped and NiO-doped 8YSZ, where sintering behavior of 8YSZ containing both additives was investigated. The effect of additives were clarified based on various characterization techniques and master curves modeling approach.

In chapter 6, sintering behavior and mechanisms of 8YSZ containing Al_2O_3 and SiO_2 co-additives are studied, with the objective to further lower the sintering temperature of 8YSZ.

In chapter 7, the electrical properties of 8YSZ containing Al_2O_3 and SiO_2 co-additives are investigated. The conduction behavior were addressed by the widely used “brick layer model” and “constriction model”. An optimized content of Al_2O_3 and SiO_2 co-additives was proposed, with respect to both improved densification and conductivity.

In chapter 8, the main conclusions of the study were summarized.

In chapter 9, based on the findings of this work, future works were proposed.

2

Literature review

A comprehensive review on the development of related topics was provided in this chapter. The fundamentals of solid-state sintering was introduced, followed by the review of various sintering modeling, and emphasis was given to the recently developed master sintering curve (MSC) theory. The application of yttria-stabilized zirconia (YSZ) in solid oxide fuel cell, and sintering and conductivity of the material were also discussed.

2.1 Solid-state sintering

Sintering is the process of converting a porous powder compact into a dense body by applying thermal energy. The strength of the sintered components is attained via inter-particle bonding accompanied by elimination of the pores, whereby the driving force is the reduction of interfacial energy. According to the firing conditions, sintering can be categorized as: solid-state sintering, liquid-phase sintering, pressure-assisted sintering and field-assisted sintering.

2.1.1 Sintering mechanisms

Sintering mechanisms define the specific paths along which atoms diffuse under high temperature. The matter is transported from regions of higher chemical potential

2.1 Solid-state sintering

and deposited at regions of lower chemical potential. Fig. 2.1 shows a schematic diagram of three spherical particles in contact, whereby six distinct mechanisms are clearly indicated. All these mechanisms lead to the growth of necks, however, they are basically two competing groups in respect of densification. The viscous flow, grain boundary diffusion and lattice diffusion from boundaries cause the particle centers to approach closer, i.e. the shrinkage of the body, and are thus referred as *densifying mechanisms*. Whereas, on the other hand, surface diffusion, lattice diffusion from the surface and vapor transport which only causes coarsening of the particles, are classified as *non-densifying mechanisms*. The non-densifying mechanisms play equally important role during sintering, because they consume particles' active surfaces, which leads to a reduced sintering potential and densification rate [19, 24].

Figure 2.1: Materials transport paths during sintering [19] (With permission).

2.1 Solid-state sintering

Figure 2.2: Illustration of the microstructural evolution that occurs during a complete densification process. (a) Initial stage, (b) Intermediate stage, and (c) final stage [24] (With permission).

2.1.2 Sintering stages

For the simplicity of numerical modeling, it is common to divide the continuous sintering process as three overlapping stages: *early*, *intermediate* and *final stage* [19]. The geometrical evolution during each sintering stage is schematically shown in Fig. 2.2. The spherical and identical particles are assumed in this idealized model. Early stage of sintering is characterized by the rapid neck formation between neighboring particles. The extent of shrinkage is small, typically limited to $\leq 5\%$ of the relative density. In the intermediate stage, the high curvatures of the initial stage disappears, and considerable densification, usually up to $\sim 90\%$ of the relative density is achieved at the end of intermediate stage. The microstructure consists of a three-dimensional network of solid grains, surrounded by continuous channel-like pores sitting on the edge of the grains (Fig. 2.2). During the final stage, the pores become isolated at the grain corners and continually shrink, which is accompanied by rapid grain growth.

2.2 Modeling of sintering

2.2 Modeling of sintering

2.2.1 Analytical models

2.2.1.1 Early stage

The models used to describe the early stage of sintering is derived from the idealized two-sphere construction (Fig. 2.3). Due to the difference in curvature, there is a stress gradient between the neck and grain boundary/particle surface, which provides the driving force for matter to flow to the neck. In terms of movement of atoms, the flux, J_a , can be expressed as [18, 19]:

$$J_a = \frac{D}{\Omega_a kT} \nabla \mu \quad (2.1)$$

where $\nabla \mu$ is the chemical potential gradient, D is the diffusion coefficient, Ω_a is the atomic volume, k is Boltzmann's constant and T is absolute temperature. The total volume of matter transported into the neck is:

$$V = \int J_a A \Omega_a dt \quad (2.2)$$

where A is the available area over which diffusion occurs, and it can be expressed as: $A = 2\pi x \delta_{gb}$ for grain boundary diffusion, and $A = 2\pi x^2$ for lattice diffusion. x is the radius of neck and δ_{gb} is the thickness of grain boundary.

In Fig. 2.3, densifying mechanisms are assumed to be dominant. The two particles of radius a penetrate each other by a distance of h , and the neck has developed with a concave surface of radius r . Regardless of the sintering mechanisms, the general equation for neck growth takes the form of [25]:

$$\frac{x^m}{a^n} = Bt \quad (2.3)$$

where m and n are numerical constants depending on the active sintering mechanism, and the geometrical and material parameters are contained in the function B . The values of m and n , and expression of B can be found in many handbooks [18, 26].

2.2 Modeling of sintering

Figure 2.3: Geometrical parameters for the idealized two-sphere model [19] (With permission).

2.2 Modeling of sintering

However, the direct measurement of neck size is always difficult in practical cases. In fact, the linear shrinkage of the sintered compact is usually measured instead. If a sintering system is primarily dominated by densifying mechanisms, Eq. 2.3 can be re-written to give the macro linear shrinkage based on geometrical relation:

$$\frac{\delta L}{L_0} = -\frac{h}{2a} \approx -\frac{r}{2a} = -\left(\frac{x}{2a}\right)^2 \quad (2.4)$$

where δL and L_0 are the change in length and original length, respectively. Based on the equations for mass transportation and the geometrical relation, it is easy to obtain the complete expression for grain boundary diffusion (Eq. 2.5) and volume diffusion (Eq. 2.6) [24, 25].

$$\frac{\Delta L}{L_0} = -\left(\frac{3D_{gb}\delta_{gb}\gamma\Omega_a}{2kTa^4}\right)^{1/3} t^{1/3} \quad (2.5)$$

$$\frac{\Delta L}{L_0} = -\left(\frac{D_l\gamma\Omega_a}{kTa^3}\right)^{1/2} t^{1/2} \quad (2.6)$$

2.2.1.2 Intermediate and final stage

Following Coble [27, 28], intermediate stage of sintering begins when the interparticle contact area exceeds ≈ 0.2 of the cross-section area of the particle. At this stage, grain growth is possible due to the increasing smoothness of neck surface. As illustrated in Fig. 2.4, the grain shape is represented by a space-filling body, *tetrakaidecahedra*, which is formed by removing a pyramid from each of the six apexes in an octahedron.

An assumption about the model is that cylindrical pores situated along the edge are uniform in geometry, which implies that only densifying mechanisms operate. The kinetic equation is derived by focusing on the the reduction of total porosity:

$$P_c = \frac{V_p}{V_t} = \frac{3\pi}{2\sqrt{2}} \left(\frac{r^2}{l_p^2}\right) \quad (2.7)$$

where V_p and V_t are the total volume of pores and *tetrakaidecahedra* body, respectively, r is the radius and l_p is the length of the pore. During both intermediate and final-stage sintering, the pores are filled by matters transported from the grain boundaries,

2.2 Modeling of sintering

Figure 2.4: Idealized geometrical model for intermediate stage [19] (With permission).

although the shape of pores evolves from a cylinder to a sphere. Therefore, a general equation has been developed for both stages, which relates the densification rate with the kinetic process [27]:

$$\frac{1}{\rho} \frac{d\rho}{dt} = A \left(\frac{DG}{G^m kT} \right) \left(\frac{\alpha\gamma}{r} \right) \quad (2.8)$$

where ρ is the relative density, t is the time, G is the grain size, and A is a constant obtained from the geometrical parameters. The diffusion coefficient D , constants m and α have specific values that depend on the particular mechanism, which are given in Table 2.1 [19].

Table 2.1: Values for constants of intermediate and final-stage model: D, m, α .

Sintering mechanism	Intermediate stage	Final stage
	$D = D_{gb}\delta_{gb}$	$D = D_{gb}\delta_{gb}$
Grain boundary diffusion	$m = 3$	$m = 3$
	$\alpha = 1$	$\alpha = 2$
	$D = D_l$	$D = D_l$
Lattice diffusion	$m = 2$	$m = 2$
	$\alpha = 1$	$\alpha = 2$

2.2 Modeling of sintering

2.2.2 Combined-stage model

The earlier works have primarily focused on establishment of single-stage sintering models based on simplified geometry, however, their practical applications in ceramic manufacturing has been a great challenge. Firstly, the sintered component is difficult to assume ideal geometry in real situation, and secondly, the treatment of entire sintering process is always found to be tedious. Therefore, there were many attempts to extend these models to the entire process without consideration of particle characteristics.

Sintering maps by Ashby [29] was the first attempt that integrates the separate sintering stages into a single diagram, yet the construction of sintering maps is difficult. Wang and Raj proposed a single equation in their study of activation energies [30], in which sintering rate was demonstrated to be a function of temperature, grain size and density-related quantities:

$$\frac{d\rho}{dT} = \frac{C\gamma V^{3/2}}{R} \left(\frac{e^{-Q/RT}}{T} \right) \frac{f(\rho)}{G^n} \quad (2.9)$$

where C is a constant, V is the molar volume, R is the gas constant, Q is the sintering activation energy, $f(\rho)$ is a function only of density, n is a constant that depends on the sintering mechanism ($n = 3$ for lattice diffusion and $n = 4$ for grain boundary diffusion), and other parameters have the same meaning as stated previously. Unfortunately, the derivation of the model was not presented. The model has been extensively applied to obtain activation energy by performing either isothermal sintering or sintering under constant rate of heating (CRH).

Hansen et al. [31] recognized the similarity in material transportation between three single stages, and they derived a single equation that describes the densification through the whole sintering process, which was referred as “combined-stage model”. The microstructure was characterized by two parameters: geometry and scale, where the scale parameter contained linear conversion factors between geometry and actual microstructure. The derived equation is a expression of linear-shrinkage rate assuming

2.2 Modeling of sintering

isotropic sintering,

$$-\frac{dL}{Ldt} = \frac{\gamma\Omega_a}{k_B T} \left(\frac{\delta D_{gb}\Gamma_{gb}}{G^4} + \frac{D_l\Gamma_l}{G^3} \right) \quad (2.10)$$

where $\frac{dL}{Ldt}$ is the linear shrinkage rate, D_{gb} and D_l are grain boundary diffusion and lattice diffusion coefficient, respectively. Γ_{gb} and Γ_l are quantities that contains all scaling parameters. The combined-stage model is comprehensive, however, one major problem is that it is extremely difficult to determine the geometric evolution of the powder compact. Instead, as an extension of the model, the master sintering curve (MSC) approach has been developed.

2.2.3 Master sintering curve

2.2.3.1 Master densification curve

The master sintering curve was developed by Su and Johnson [20] based on the combined-stage sintering model. By assuming only one dominant sintering mechanism exists, they rearrange Eq. 2.10 into a simplified form:

$$\frac{d\rho}{3\rho dt} = \frac{\gamma\Omega_a D_0(\Gamma(\rho))}{k_B T(G(\rho))^n} \exp\left(-\frac{Q}{RT}\right) \quad (2.11)$$

where G and Γ is are assumed to be the function of density only; and D_0 is pre-exponential factor that depends on whether it is lattice or grain boundary diffusion. The basic idea of MSC is to separate the parameters in the sintering rate equations into (a) microstructure-related terms, and (b) time- and temperature-related terms, which was achieved by a further rearrangement of Eq. 2.11:

$$\frac{k_B}{\gamma\Omega_a D_0} \frac{(G(\rho))^n}{3\rho(\Gamma(\rho))} d\rho = \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \quad (2.12)$$

and then, an integrating operation was made on both sides: the left-hand side (lhs) was integrated over density range from ρ_0 (green density) to ρ , while the right-hand side (rhs) was integrated over time range. A single term, $\Phi(\rho)$, which contains the microstructural and material parameters, was obtained from lhs as

$$\Phi(\rho) = \frac{k_B}{\gamma\Omega_a D_0} \int_{\rho_0}^{\rho} \frac{(G(\rho))^n}{3\rho(\Gamma(\rho))} d\rho \quad (2.13)$$

2.2 Modeling of sintering

The time and temperature parameters that characterize a particular heating process are incorporated in the term Θ , which is also referred as “thermal history”

$$\Theta[t, T(t)] = \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \quad (2.14)$$

Thus, Eq. 2.12 was converted into

$$\Phi(\rho) = \Theta[t, T(t)] \quad (2.15)$$

The relationship between the density ρ and $\Theta[t, T(t)]$ is defined as MSC. The MSC approach makes it possible to predict density evolution under any given thermal history, whereas the calculation of $\Theta[t, T(t)]$ requires a pre-knowledge of the activation energy, Q . However, MSC also applies to systems with unknown activation energies. If we take the advantage of equality in Eq. 2.15, the least experimental efforts is needed for estimation of Q based on a “trial and error” method.

The constant-rate of heating experiments are usually performed, which provides the density dependance on thermal history. The ρ - Θ trajectory under each heating rate is fitted using a sigmoidal function (Eq. 2.16) [32],

$$\rho = \rho_0 + \frac{100 - \rho_0}{1 + \exp\left(-\frac{\log \Theta - a}{b}\right)} \quad (2.16)$$

A first estimation of the activation energy will be made, which if it has been the correct value, all of the data points would converge on a single sigmoidal curve. If they fail to converge, a new value of Q is chosen and the above steps are iterated, until the best convergence is found. The extent of convergence is judged by the “least mean residual square (MRS)” criteria, the estimated Q that yields the minimum MRS would be accepted as the correct activation energy. The master sintering curve model have been successfully applied to the sintering of various materials, such as Al_2O_3 [33], Y-TZP [34], cubic zirconia [35], ZnO [36] and tungsten alloys [37].

2.2.3.2 Master grain growth curve

The master sintering curves for grain growth was not mentioned in Su and Johnson’s original work, whereas several recent work have developed the master grain growth

2.3 Yttria-stabilized zirconia (YSZ)

curve based on the similar approach [34, 38]. Grain growth can be analyzed by a well-known kinetic equation,

$$\frac{dG}{dt} = \frac{K_0}{G^{n-1}} \exp\left(\frac{-Q_G}{RT}\right) \quad (2.17)$$

where G_0 is the specific starting grain size, t is time, K_0 is the pre-exponential factor, n is the mechanism-controlled constant, and Q is the activation energy for grain growth. Following the derivation of MSC for densification, Eq. 2.17 is integrated and rearranged as

$$G^n - G_0^n = n \int_0^t K_0 \exp\left(-\frac{Q_G}{RT}\right) dt \quad (2.18)$$

Similarly, the parameter characterizing a particular sintering process is expressed as

$$\Theta_G = \int_0^t \exp\left(-\frac{Q_G}{RT}\right) dt \quad (2.19)$$

and the grain size-related parameters and constants are assembled together and is given by

$$\Phi(G) = \frac{G^n - G_0^n}{nK_0} \quad (2.20)$$

The parameters K_0 and Q_G are also determined by fitting of the experimental data, and the most appropriate activation energy will produce the least mean residual square.

2.3 Yttria-stabilized zirconia (YSZ)

2.3.1 Structure

The crystal structure of pure zirconia is monoclinic under room temperature. With the increase of temperature, ZrO_2 undergoes the phase transformation from monoclinic to tetragonal phase at 1170°C , and tetragonal to cubic fluorite structure at 2370°C [7]. From the technological point of view, the tetragonal and cubic structures are more useful, as they have good chemical stability, fracture toughness and ionic conductivity, and hence find a wide range of applications such as thermal barriers,

2.3 Yttria-stabilized zirconia (YSZ)

grinding media, cutting cools and electrochemical devices [6, 39]. The tetragonal and/or cubic forms can be stabilized at ambient temperature through the introduction of divalent or trivalent cations, such as Ca^{2+} , Mg^{2+} , Y^{3+} . Meanwhile, oxygen vacancies are created for charge compensation, which can be described as:

The phase composition of YSZ depends on the dopants content, and more than 8-9 mol% Y_2O_3 is required to fully stabilize the cubic form of zirconia [40, 41]. The cubic YSZ has a fluorite structure, as illustrated in Fig. 2.5, in which two Zr cations are substituted by two Y cations to generate one oxygen vacancy. Due to the larger ionic size and lower valence of Y^{3+} (1.019Å) with respect to Zr^{4+} (0.84Å), there are both elastic and electrostatic interaction in the unit cell. As a result, the cubic YSZ doesn't maintain an exact fluorite structure, instead, both the cations and anions will deviate from their ideal position. Among all types of defect-defect interaction, the cation-vacancy interaction plays the most important role, since it will directly influence the migration of oxygen vacancies [42]. In earlier studies, there was controversies over whether $\text{V}^{\bullet\bullet}_{\text{O}}$ locates at the nearest neighboring (NN) site or next nearest neighboring (NNN) site relative to Y cations. In recent years, however, both experimental and theoretical evidence tend to support that oxygen vacancy favors to be the NN site to Zr and NNN site to Y [43, 44]. The clarification of defect chemistry was necessary for simulating the dynamics of ionic conduction.

2.3.2 Application in SOFC

2.3.2.1 Solid oxide fuel cell

Solid oxide fuel cell (SOFC) is an energy conversion device that comprises all-solid-state components, in which, electricity is generated from electrochemical reaction by directly utilizing hydrogen or hydrocarbon fuels [7, 45–50]. Due to the high operation temperature (500-1000°C) and clean fuel sources, SOFC possesses the main advan-

2.3 Yttria-stabilized zirconia (YSZ)

Figure 2.5: Fluorite structure of cubic YSZ.

tages of high efficiency and environmental friendliness. The potential applications of SOFCs system have been explored as both auxiliary power unit for vehicles as well as stationary power generator [46, 50, 51].

A single SOFC essentially contains three basic components: an anode, a cathode and the electrolyte. Fig. 2.6 shows the schematic representation. The porous electrodes provide paths for fast gas transportation as well as adequate catalytic sites, whereas the dense-enough electrolyte ensures efficient ions transport and no gas mixing. The vast majority of electrolytes are currently based on oxygen-ion conductors. Under operation, oxygen/air supplied at the cathode is reduced to oxygen ions (O^{2-}) by the incoming electrons from external circuit. The produced O^{2-} migrate across the electrolyte and reach to the anode, where fuels are met and oxidized. Additionally, electrons are liberated at the anode, which flow through the external circuit to the cathode.

Ni/YSZ cermet is currently the most common anode material for SOFC [52–55]. The porous anode is usually fabricated from mixtures of YSZ and NiO, which was subsequently sintered and reduced under H_2 atmosphere. Nickel has good catalytic

2.3 Yttria-stabilized zirconia (YSZ)

Figure 2.6: Schematic representation of SOFC.

property for oxidation of hydrogen, and can also achieve fast electron transfer. YSZ constitutes a frame for the Ni phase particles, and with the induced pores, large areas of triple-phase boundaries can be provided.

The state-of-art cathode materials are based on perovskite-type ABO_3 oxides, where the explored compositions mainly include: $A=La, Sr$ and $B=Mn, Fe, Co$ [10, 53, 56, 57]. Ionic conduction occurs via oxygen vacancies, which can be achieved by rational choice of low-valence substitutional elements at either A or B site. On the other hand, the reducible transitional metals provide semiconducting structure at high temperature, leading to electronic conductivity. In order to improve the overall performance, both A and B site doping is preferred in most of the perovskite materials.

2.3.2.2 Electrolyte for SOFC

The recognized solid oxygen-ion conductors mainly include fluorite-type stabilized-zirconia and doped ceria, doped bismuth, perovskite strontium/magnesium-doped lanthanum gallate (LSGM) and apatite-type silicates/germanates [47, 58, 59].

2.3 Yttria-stabilized zirconia (YSZ)

8-10 mol% yttria-stabilized zirconia is to date the most widely used electrolyte material. The major advantages of YSZ include: pure ionic conductivity, remarkable chemical stability under both reducing and oxidizing conditions, good fracture toughness and abundant availability [60–62]. The main drawback of the material comes from its insufficient conductivity at intermediate temperature. As an alternative stabilizer, Sc_2O_3 -stabilized ZrO_2 has been proved to exhibit much higher conductivity, however, the instability of phases have limited the widespread application [61, 63].

Higher conductivities has also been achieved in doped ceria [58, 64–66] and doped bismuth [67, 68]. Nevertheless, the reduction of Ce^{4+} and Bi^{3+} to Ce^{3+} and Bi^{2+} under lower oxygen partial pressure (P_{O_2}) would give rise to unfavorable electronic conduction.

Doped LaGaO_3 with SrO and MgO (LSCM) was demonstrated to possess higher conductivity under intermediate temperature [67, 69, 70]. Further improvement on the conductivity of LSCM has been focused on optimization of the doping amount and adding transitional metal oxides, such as Fe_2O_3 and Co_2O_3 . The problems pertaining to LSCM as electrolyte are: difficulty in synthesis of pure phase and unfavorable reaction with Ni-containing anode [69].

In the multi-layered SOFC system, the electrolyte is sandwiched between the anode and cathode. This places stringent requirements on the selection of electrolyte. In addition to the high conductivity, the electrolyte is also required to have:

- long-term chemical stability
- chemical compatibility with neighboring anode/cathode
- proper thermal expansion coefficient (TEC)
- long-term mechanical strength
- ease of fabrication and low cost

In consideration of all the features, it is well accepted that YSZ is still the most promising electrolyte material for SOFC at present.

2.3 Yttria-stabilized zirconia (YSZ)

2.3.2.3 Fabrication

The construction of SOFC are largely based on two basic designs, i.e. tubular and planar structure [7, 46], which are illustrated in Fig. 2.7. Compared with the tubular design, the planar design offers much simpler fabrication and also higher power density [71], and hence is preferred by manufacturing.

Figure 2.7: The common structures of SOFC: (a) tubular design (b) planar design [7].

The planar type SOFCs can be further grouped into electrolyte-supported, anode/cathode supported and, more recently, metal-supported configuration [72]. Among these types of design, the anode-supported and metal-supported configurations are much preferred by manufacturers. The anode-supported SOFC utilizes a thick anode layer (e.g. NiO/YSZ cermet) as both supporting and functional component, and electrolyte film is made to be thin enough (typically around 10-50 μm) to reduce the ohmic loss. In contrast, the metal-supported design has its functional layers laminated onto a porous metal support (e.g. stainless steel), and the ceramics layers are only concerned for electrochemical functions. This design provides many benefits such as low cost, excellent mechanical ruggedness, and rapid thermal cycling.

It becomes clear that either electrodes or metal supported SOFC with thin-film electrolyte is necessary for higher power output, thus various techniques have been applied to fabricate the electrolyte layer with limited thickness, which includes chem-

2.3 Yttria-stabilized zirconia (YSZ)

ical vapor deposition (CVD), electrochemical vapor deposition (EVD), plasma flame spraying, sol-gel processing, tape casting and screen printing [9, 73, 74]. Compared with other methods, tape casting and screen printing are regarded as cost-effective and more suitable process for mass production [11], which has been widely adopted for fabrication of both electrode and electrolyte layers. The wet-processed layers can be laminated together and then sintered at the same time, i.e. via co-sintering technique, to obtain the final product.

Co-sintering is recognized as the most attractive technique mainly because of its cost-effectiveness and mass-productivity. In spite of the merits, one major concern with the process is the selection of co-sintering temperature. The YSZ electrolyte requires a temperature of $T_s \geq 1350^\circ\text{C}$ to be densified, while the ceria oxide needs a even higher temperature [8, 75, 76]. However, at such a high temperature, interfacial reaction occurs between LSM cathode and zirconia electrolyte, giving rise to low-conductive phases [51]. Moreover, Ni phase in Ni/YSZ anode would grow, accompanied by the reduction of porosity and triple-phase reactive site. To avoid these problems, lower temperature of sintering (better below 1250°C) is desirable [75, 77]. In fact, lower temperature heat treatment would also make it easier to control the flatness of the laminated layers. In order to achieve gas-tight electrolyte at lower temperature, there are two approaches mainly used, i.e. adoption of nano-particles and utilizing sintering additives. Details on this topic will be provided in later section, where the sinterability of YSZ electrolyte is thoroughly reviewed.

2.3.3 Sintering of YSZ

2.3.3.1 Synthesis and sintering

The sinterability of both tetragonal and cubic YSZ have been extensively investigated, which involve a wide range of topics, such as synthesis and sintering of nano-particles, sintering of commercial powders and study of sintering mechanisms [78–82]. Over the past years, synthesis of nano-powders attracted great research effort, because they

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are easy to densify at relatively lower temperature due to large surface areas. There are a number of synthesis routes applied, such as, sol-gel method [83], coprecipitation [78], hydrothermal processing [84] and polymeric routes [79]. The major concern for production of nano-powders is the formation of hard-agglomerates. The intra-agglomerate regions sinter at a higher rate and may detach from its surroundings, leading to micro-crack in the compacts. For either YSZ or Y-TZP nano-powders, if morphology is well controlled without hard-agglomerates, the densification temperature can be reduced to as low as 1000-1200°C [85].

The sinterability of commercially available YSZ powders are also widely studied, in particular, sintering mechanisms are explored by applying various sintering models [86, 87]. Matsui et al. systematically investigated the sintering behavior of YSZ and Y-TZP using the commercial powders from Tosoh Ltd (Tokyo, Japan) [80, 81]. The particles with larger surface area and higher yttria concentration was shown to have faster shrinkage rate, and they also claimed that the initial stage of sintering was dominated by grain boundary diffusion. Gibson et al. [86] compared the sinterability of three kinds of commercial Y-TZP powders with different particle size and morphology, which reported that powders prepared via spray-drying route are more readily to densify. The activation energy for densification is found to 605-645 KJ/mol by their group.

2.3.3.2 Sintering additives

There is a long history of using sintering additives in the production of ceramic bodies. Small amount of additives are purposely introduced to the host materials in order to reduce the sintering temperature, improve the densification process, or to control the microstructure evolution during heat treatment. Zirconia is one of the most common oxide, and undoubtedly there has been a great number of attempts in searching for suitable additives for this ceramic material.

The examined additives that is able to improve sintering of yttria-zirconia com-

2.3 Yttria-stabilized zirconia (YSZ)

pounds include Al_2O_3 [88–90], CuO [91] for Y-TZP, and Al_2O_3 [12–15, 92–95], Fe_2O_3 [12, 62], ZnO [96], Bi_2O_3 [62], NiO [97–99], SiO_2 [23] and MnO_2 [87] for cubic YSZ. As an example, an early study that compared the effectiveness of some sintering additives is shown in Fig. 2.8. It can be seen that final density of YSZ was improved by 10% upon 1.0 mol% Al_2O_3 and 1.0 mol% TiO_2 doping. Hirano et al. reported a reduction of 300°C in the sintering temperature of 10ScSZ by 1 mol% Bi_2O_3 addition [100]. Also, Matsui et al. observed that densification rate of 7.8YSZ was significantly enhanced by 0.25 wt.% Al_2O_3 addition at $T < 1290^\circ\text{C}$ [94]. However, there is an optimal concentration for most of the sintering additives, above which the effect for sintering of zirconia would turn into negative [12].

Figure 2.8: Density change of cubic YSZ by some additives sintered at 1480°C[62]
(With permission).

As sintering additives, the sintering aids are required not only capable to enhance sinterability, but also would not adversely affect functionalities of the host material. Among various additives for YSZ, Al_2O_3 offers several unique advantages. The benefi-

2.3 Yttria-stabilized zirconia (YSZ)

cial role in reducing sintering temperature of YSZ has been commonly realized [13, 15]. Besides, Al_2O_3 could improve the mechanical strength and fracture toughness of zirconia. For example, Esper et al. increased the mechanical strength of YSZ by 50% by the addition of 20 wt.% Al_2O_3 [101]. Meanwhile, Al_2O_3 is able to increase the conductivity, especially the grain boundary conduction, of YSZ by scavenging of SiO_2 impurities along the grain boundary [102, 103]. Hence, a small amount of Al_2O_3 is always purposely added into YSZ electrolyte to achieve a better performance. There has been extensive studies on sintering of YSZ with Al_2O_3 addition, the main agreements and conclusions are summarized as follow.

1. The solubility of Al_2O_3 in ZrO_2 is very low, which is only 0.5-0.8 mol.% at 1700°C [104], 0.5-1.0 wt.% at 1500°C in 8YSZ [14], and 0.1 mol% at 1300°C in Y-TZP [88]. The dissolved Al_2O_3 strongly segregates to the grain boundaries.
2. Beyond the solubility limit, Al_2O_3 predominantly precipitates along grain boundaries, either in the form of glassy phase [92] or crystallite second phase [105], depending on the impurity of the starting ZrO_2 .
3. Doping Al_2O_3 to yttria-zirconia can significantly enhance sintering by reducing sintering temperature and promotes densitication within a certain content. Higher doping level will decrease the final density due to microcracks [15].
4. Mechanical strength and fracture toughness of zirconia can be enhanced by Al_2O_3 dopants, which is attributed to the refinement of matrix of grains [13, 101].

On the other hand, there are still sufficient work or controversies over several topics. For example, the mechanisms for enhanced sintering is not well clarified. The reported mechanisms covers a wide range of possibilities, including liquid phase sintering [62] or particle rearrangement [13], grain growth inhibition [12] and solid state mechanism [90]. In addition, the sintering models used in the previous studies are mostly based on staged-sintering models, while application of more sophisticated models may provide new sights into the topic.

2.3 Yttria-stabilized zirconia (YSZ)

2.3.4 Conductivity of YSZ

2.3.4.1 Conductivity of $(Y_2O_3)_x(ZrO_2)_{1-x}$

In the family of doped zirconia, yttria-stabilized zirconia has the advantage of good conductivity and excellent phase stability, and has been widely used as oxygen gas sensors and electrolyte for SOFC. The conductivity of $(Y_2O_3)_x(ZrO_2)_{1-x}$ is closely related to the content of Y_2O_3 , which increases to the maximum at $x=0.08-0.09$, and then decreases for higher content of Y_2O_3 (Fig.2.9) [58, 106]. The decrease at higher dopant contents is attributed to the formation of defects association: $[Y'_{Zr} - V_O'']$ and $[Y'_{Zr} - V_O'' - Y'_{Zr}]^x$, which leads to a reduction in mobility of free oxygen vacancy and thus conductivity.

Figure 2.9: Temperature dependance of conductivity for $(Y_2O_3)_x(ZrO_2)_{1-x}$ ($x=0.05-0.12$) [106] (With permission).

During operation, aging of YSZ can lead to decreases in conductivity. The degradation of conductivity of YSZ originates from several reasons [107–109]: (1) precipitation of long-range ordered phases, such as $Y_2Zr_2O_7$, (2) formation and precipitation of tetragonal phase in the cubic grains, (3) segregation of dopant-rich layer near grain

2.3 Yttria-stabilized zirconia (YSZ)

boundaries, (4) short range of ordering of oxygen vacancies. Taking account into the aging effect, Hattori et al. suggested that 9.5 mol% YSZ would be a better candidate because it showed no conductivity degradation even after annealing for 1000h [109].

2.3.4.2 Conductivity of YSZ with impurity/additives

Ionic conductivity is the critical parameter of an electrolyte, which determines, to a large extent, the operating temperature and power output of a SOFC. In literature, a number of approaches have been employed to enhance the conductivity of YSZ, including either modifying the composition and microstructure, or tailoring of the processing condition [14, 22]. In polycrystalline zirconia electrolyte, the total conductivity is contributed by both bulk and grain boundary conduction. Generally, the resistivity of grain boundary can be over 2-3 orders magnitude higher than that of the grain interior due to a combination of impurity and space-charge layer effect [110].

The bulk conductivity of YSZ can be enhanced by partially substituting the Y_2O_3 dopant with rare earth dopant whose ionic radius is closer to the host Zr^{4+} , such as Sc_2O_3 ($r_{\text{Sc}^{3+}} = 0.87\text{\AA}$) and Yb_2O_3 ($r_{\text{Yb}^{3+}} = 0.985\text{\AA}$), while the total concentration of dopants is kept at 8-9 mol%. For example, the conductivity of 9YSZ is 0.166 S/cm at 1000°C. After Y_2O_3 was partially replaced by which was increased to Sc_2O_3 , the conductivity of $(\text{Sc}_2\text{O}_3)_x(\text{Y}_2\text{O}_3)_{0.09-x}(\text{ZrO}_2)_{0.91}$ was increased to 0.180 and 0.246 S/cm at $x = 0.03$ and $x = 0.06$, respectively [102].

In the heterogeneously doped YSZ, the grain interior conductivity is closely related to the solubility of dopant cations into the lattice. Transitional metals such as Ni, Fe, Co, Mn, Cr are the common constituents in anode, cathode or interconnect components of SOFC. The diffusion of these elements into electrolyte layers has been frequently observed during co-sintering process, and therefore, the influence of transitional metal oxides (TMOs) was investigated by a number of researchers [17, 111]. Zhang et al. found that upon 1.0 mol.% loading of TMOs such as NiO, Fe_2O_3 , MnO_2 and CoO, grain-interior (GI) conductivity of 8YSZ was decreased by 27-33%

2.3 Yttria-stabilized zirconia (YSZ)

[97]. Lewis investigated the effect of cobalt addition, and reported a decrease in both GI and grain-boundary (GB) conduction in the doped 8YSZ [112]. Also, Molin et al. confirmed that addition of either Fe_2O_3 or Cr_2O_3 oxide decreases total electrical conductivity of 8YSZ, however, chromium mainly influences GB conductivity, while iron influences electrical conductivity of both grain and grain boundary [111]. These studies indicate that incorporation of undersized cations are unfavorable in terms of ionic conductivity. Generally, it was considered that the dissolution of TMOs stimulate the formation of defect associations and hinder the mobility of oxygen vacancies. However, Zhang suggested the potential microstructural change, such as lattice distortion and the formation of microdomains, might also be responsible for the decreased conductivity [97].

Compared with bulk conduction, the interpretation of grain boundary conduction is more complicated. The grain boundary effect can be caused by either impurity segregation (particularly SiO_2) and/or space charge layers. Guo systematically investigated the grain boundary conduction of zirconia, and clarified that the space-charge layer predominantly contributes to GB effect in the highly pure material. In the space-charge layer model, the grain boundary is consisted of a grain boundary core and two adjacent space charge layers. The enrichment of Y^{3+} at the grain boundaries lead to a positive space charge potential, where it is depleted of oxygen vacancies and thus a higher resistivity.

It should be noted, however, the presence of SiO_2 impurity is ubiquitous, which may either exist in the starting materials or could be induced during processing or sintering. It has been widely reported silica greatly decrease the grain boundary conduction of zirconia and ceria [21, 113]. Badwal found that the addition of only 0.2 wt.% silica was sufficient to decrease the grain-boundary conductivity of YSZ by a factor greater than 15 [21]. Therefore, it is necessary to eliminate the impurity effect, from which the grain boundary conduction can be significantly benefited.

The addition of a small amount of Al_2O_3 is found to be effective for neutralizing

2.3 Yttria-stabilized zirconia (YSZ)

the detrimental effect of SiO_2 impurity in YSZ [14, 102, 113]. Butler and Drennan [92] have analyzed the microstructure of stabilized zirconia with Al_2O_3 additions. They suggested that Al_2O_3 acted as a scavenger for SiO_2 , removing the silicious phase from grain boundary localities. Lee et al. on the other hand [113] investigated the conductivity of ball-milled YSZ sample containing ≥ 120 ppm SiO_2 . The resistance per unit area was decreased from $2.01 \Omega \cdot \text{cm}^2$ to $0.24 \Omega \cdot \text{cm}^2$ upon 1 mol.% Al_2O_3 addition. The improvement of GB conduction Al_2O_3 is owing to Al_2O_3 can effectively scavenge silicious film through chemical reaction [92]. It is worth to mention, however, the amount of Al_2O_3 additive should be carefully manipulated, as below the solubility limit, Al_2O_3 would increase the Schottky barrier height of the space-charge layer and considerably decrease the GB conduction. [103, 110].

3

Experimental procedure

3.1 Introduction

The chapter presents details of the experimental procedure, covering approaches of experimental design, sample preparation and characterization, data collection and analysis.

3.2 Sample preparation

3.2.1 Starting materials

Commercially available 8 mol% YSZ (TZ-8Y, Tosoh Co. Tokyo, Japan) was used as starting material. The as-received powder is of spray-dried and free-flowing granules, which can be easily crushed into small particles. The morphology of as-received powder and that after crushing is shown in Fig. 3.1 (a) and (b) respectively. The average crystal size is 25 nm, and particle size distribution is illustrated in Fig. 3.2, with a median size (D_{50}) of 0.6 μm . The level of impurities are (wt%): $\text{Al}_2\text{O}_3 \leq 0.005$, $\text{SiO}_2 \leq 0.007$, $\text{HfO}_2 \leq 2.5$, $\text{Fe}_2\text{O}_3 \leq 0.007$, $\text{Na}_2\text{O} \leq 0.017$.

Aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99.99%, Sigma-Aldrich, Singapore) and nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.9%, Sigma-Aldrich, Singapore) were used as the source

3.2 Sample preparation

Figure 3.1: SEM micrograph of TZ-8Y powder (Tosoh, Japan), (a) as-received and (b) after crushing.

Figure 3.2: Particle size distribution of TZ-8Y (Tosoh, Japan). Blue color: differential size distribution; Dark grey color: cumulative undersize distribution.

3.2 Sample preparation

for Al_2O_3 and NiO dopant, respectively. Tetraethyl orthosilicate (TEOS, 99.999% trace metals basis, sigma-aldrich, Singapore) was used to introduce SiO_2 additive. At elevated temperatures ($>600^\circ\text{C}$), TEOS decomposes into SiO_2 through the following equation:

3.2.2 Green pellets preparation

The dopants were loaded into 8YSZ by wet chemical method. The desired quantities of dopant solution were ultrasonically mixed with 8YSZ powder to form a slurry, which were then dried and calcined at 600°C for decomposing dopant precursors into oxides. To ensure a homogeneous distribution of additives, the mixed powder was horizontally ball-milled for 24h in a polyethylene (PE) bottle with ethanol, where Y-TZP balls were used as media. After drying the powder mixture, a small amount of 15 wt%-PVA solution was added as binder. Green pellets were prepared by compacting the powders with a cylindrical stainless-steel die ($\phi 10$ mm) under 50 MPa, followed by cold-isostatic-pressing (CIP) for 5 min under 200 MPa. The binder was burnt out by holding the sample at 600°C for 0.5h, and then the mass, diameter, and thickness of the compacts were measured. The dimension of as-prepared green pellets is $\phi 9.5 \times (1.5 - 4)$ mm² to suit for different usage.

Theoretical density (ρ_T) is roughly estimated by the mixing law,

$$\rho_T = \frac{1}{\frac{W_{YSZ}}{\rho_{YSZ}} + \sum_{i=1}^n \left(\frac{W_i}{\rho_i} \right)} \quad (3.2)$$

where W_{YSZ} and ρ_{YSZ} are the weight percentage and theoretical density (5.98 g/cm^3) of YSZ, and W_i and ρ_i are the weight percentage and theoretical density of the i th dopant, respectively. Green density of the specimens is estimated to be in the range of 48.5-51.0% of the theoretical density.

3.3 Sintering of pellets

3.3 Sintering of pellets

3.3.1 Dilatometric shrinkage

The instantaneous shrinkage of the pellets were monitored by using a horizontal push-rod dilatometry (DIL 402C, Netzsch, Germany). A slight load of 20 cN was exerted on the sample so as to minimize the external effect. The heating rates used for constant rate of heating (CRH) experiments are between 2-20°C/min. After reaching the desired temperature, samples are cooled immediately to room temperature under the rate of 15°C/min. Some of the runs were repeated to examine the accuracy of the measurement, and the error was found to be within $\pm 0.1 \mu\text{m}$ ($\pm 0.02\%$). Besides, isothermal sintering was also performed on some selected sample, and the dimension change during both heating and soaking were recorded.

Before the sample measurement, baselines were created using sapphire as a standard. The same heating profiles were applied, so that instrument length variation could be calibrated. Thermal expansion of the sample was corrected using the respective thermal expansion coefficient (TEC), which was determined from the cooling part of the shrinkage curve. Although there is small variation in the doping composition, TECs of all specimens were found to be close to that of undoped 8YSZ, i.e. around $9.9 \times 10^{-6}/\text{K}$. Nearly isotropic shrinkage was confirmed by measuring dimension changes in both radial and axial direction after heat treatment. Accordingly, the instantaneous linear shrinkage was converted into density by the equation

$$\rho_r = \frac{1}{(1 + \Delta L/L_0)^3} \rho_0 \quad (3.3)$$

where ρ_0 is the relative density of green pellets, and $\Delta L/L_0$ is the percentage of instantaneous shrinkage.

3.3.2 Conventional sintering

Samples for conductivity measurement and microstructure observation were prepared by sintering in a conventional electrical furnace under ambient atmosphere. The

3.4 Impedance analysis

furnace was preserved exclusively for this study so as to minimize external contaminations. Batch of samples were heated to the target temperatures (1000-1600°C) at 5°C/min, and soaking for various time between 0 to 8h before cooling down to room temperature.

3.4 Impedance analysis

The sintered pellets were polished on both sides, where silver paste and silver wire were attached to make electrodes. The organic additives in the silver paste was burned out at 800°C, after which electrodes with very limited contacting resistance were consolidated. The specimen were put into a tubular furnace, while a platinum thermal couple was placed neighboring to it for temperature calibration. At each ramp of temperature, samples were stabilized for 15 min before data collection.

Electrical properties were characterized with an two-probe AC impedance analyzer (Solartron 1260, UK). The measurement was conducted in the frequency range of 1 to 10^7 HZ at temperatures of 300-800°C in the air atmosphere. The supplied software package was used for processing the collected data.

In polycrystalline electrolyte, both grain interior and grain boundary conduction contribute to the measured impedance spectra. A typical impedance plot for a polycrystal sample is represented by three semicircles as illustrated in Fig. 3.3 (a), and the idealized equivalent circuit is shown in Fig. 3.3 (b). With decreasing frequency from the left to the right, the three successive semicircles correspond to response of grain interior, grain boundary, electrode-electrolyte polarization, respectively. The value of both resistance and capacitance can be fitted with the equivalent circuit.

The grain interior conductivity, σ_{gi} , and the total (or apparent) grain boundary conductivity, σ_{gb} , can be expressed as $\sigma_{gi} = \frac{L}{R_{gi}A}$ and $\sigma_{gb} = \frac{L}{R_{gb}A}$, where R_{gi} and R_{gb} are the grain interior and grain boundary resistance, respectively, L is the sample thickness and A is the cross-sectional area. Then, the total electrical conductivity, σ

3.5 Materials characterization

Figure 3.3: An idealized illustration of (a) typical impedance plot and (b) equivalent circuits.

can be calculated by,

$$1/\sigma = 1/\sigma_{gi} + 1/\sigma_{gb} \quad (3.4)$$

3.5 Materials characterization

3.5.1 Density measurement

For sintered samples with the relative density below 80%, the density is calculated from weighing the mass and measuring of the dimension of the sample,

$$\rho = \frac{4m}{\pi R^2 \cdot l} \quad (3.5)$$

where m is the mass, R is the radius, and l is the thickness of the sample. If the relative density is above 80%, then the Archimedes method is applied. The Archimedes method takes the procedure of: first, the weight of the dry pellet was measured in air (m_{dry}); second, the pellet was soaked in boiled water for 2h and held until cooling, and the wet pellet was taken out and measured as m_{wet} ; finally, the wet sample

3.5 Materials characterization

was placed in water bath and weighed as m_{water} . With the three weight obtained in different condition, the density is calculated by

$$\rho = \frac{m_{dry}}{(m_{wet} - m_{water})/\rho_{water}} \quad (3.6)$$

3.5.2 X-ray diffraction (XRD)

Phase identification was conducted with a X-Ray diffractometer (XRD, Bruker, D8 ADVANCE) using Cu_K α radiation ($\lambda = 1.5418\text{\AA}$) with step size of 0.002 and scan speed of 1°/min between 20°–90°. After acquiring the XRD spectrum, Rietveld analysis was applied to refine the structures, from which lattice parameters are calculated.

3.5.3 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) (JSM-6360, JOEL, Japan) and an field-emission SEM (JSM-6340F, JOEL, Japan) were used to observe the microstructure of samples. The samples were ground by a series of sand papers from grade 180 to 1200, and polished by clothes with diamond paste (0.1 μm). The surface of the polished sample was ultrasonically cleaned, and then thermally etched to get the mirror-like surface. The etching temperature is 50°C lower than its respective sintering temperature and the etching time is 30min. However, for samples with high porosity, fracture surface was directly observed. Grain sizes are estimated by the linear intercept method over at least 200 grains. The actual grain size is determined by multiplying a factor of 1.56 to the apparent size [114].

3.5.4 Transition electron microscopy (TEM)

Field emission transmission electron microscopy (FETEM, JEM-2100F) was used to observe the grain boundary structure. Specimens for TEM observation were prepared by mechanically grinding to a thickness of $\sim 50\mu\text{m}$, followed by ion-milling for electron transparency. The local energy-dispersive spectroscopy (EDS) nano-analysis was performed to identify the elementary distribution.

4

Master curves for sintering of undoped YSZ

4.1 Introduction

8 mol% YSZ (8YSZ) ceramic has been well reported to possess excellent chemical stability and good ionic conductivity, and has since found itself useful in a wide range of applications, such as gas sensors and electrolyte for SOFCs. To consolidate the ceramic powder compact for applications in functional devices, sintering is always the final step of processing. The performance is closely dependent on the microstructure of the material, which in turn is determined by the sintering process. It would be of great significance to obtain a sintered body with desired microstructure, and this can be achieved by engineering the sintering profiles.

As a simple yet powerful sintering model, master sintering curves (MSC) emerges in recent years, and have been successfully applied for the prediction of microstructural evolution and investigation of sintering mechanisms. The use of an effective model can greatly enhance the efficiency in establishing a process, and hence a reduction in manufacturing cost. In this chapter, the application of MSC on sintering of undoped YSZ was studied. The present work established master curves for both densification and grain growth of YSZ, and provided insight for the sintering mechanisms. The

4.2 Experiments

findings have also acted as a reference for the studying of additive effect in the latter chapters.

4.2 Experiments

In the dilatometric sintering experiments, both constant-rate of heating (CRH) and isothermal sintering were performed. For CRH, the specimen were heated to 1500°C under different rate, namely, 2, 5, 7.5, 10, 15 and 20°C/min; and then cooled down immediately to room temperature. Isothermal sintering was conducted by heating the sample to 1100-1300°C at 20°C/min, and soaked at the holding temperature for 2-6h.

Density-grain size trajectory was determined from sintered samples with relative densities of $\rho = 55 - 95\%$. In addition, static grain growth study was carried out. The samples were held at 1300-1500°C with soaking time from 0 to 8h to obtain different grain sizes.

4.3 Dilatometry

4.3.1 CRH sintering

The plot of linear shrinkage as a function of temperature under different heating rates is shown in Fig. 4.1. The temperature (T_{onset}) at which shrinkage starts to occur was determined by the extrapolation method [115], and was summarized in Table 4.1.

Apparently, the onset of shrinkage has been shifted to a higher temperature with the increase of heating rate. For instance, T_{onset} was determined to increase from 1055°C and 1093°C when the heating rate increased from 2°C/min to 20°C/min. Similar behavior has also been observed in other reported CRH experiments, e.g. sintering of nano Al_2O_3 [116] and nano 3Y-TZP [34]. In addition, it was observed that significant shrinkage took place above 1100°C, and exhibited a systematical depen-

4.3 Dilatometry

dance on heating rates; i.e. the lower the heating rate, the higher the shrinkage. This tendency is resulted from the fact that at a lower heating rate, a prolonged time was permitted for the occurrence of mass transport.

Figure 4.1: Linear shrinkage of 8YSZ under different rates of heating.

The linear shrinkage can be represented by density evolution as shown in Eq. 4.1,

$$\rho_r = \frac{1}{(1 + \Delta L/L_0)^3} \rho_0 \quad (4.1)$$

and using that, the relative density as a function of temperature is shown in Fig. 4.2 (a). The densification rate, $1/\rho d\rho/dT$, can be then computed from the derivative of densification strain over temperature, and is plotted in Fig. 4.2 (b). Table 4.1 summarizes several thermal related parameters that characterizes the CRH sintering process, e.g. the final density (ρ_f), maximum densification rate ($\dot{\rho}_{max}$), and the temperature (T_{max}) at which the maximum densification occurs. The sintering rate is found to have little influence to the final density, and all the samples could attain a final relative density of $\geq 98.0\%$. On the other hand, with the increase of heating rate, the densification strain curve (Fig. 4.2 (b)) shifts to higher temperature, while the

4.3 Dilatometry

value of $\dot{\rho}_{max}$ is found to decrease. The observation well explains the slower density evolution under higher heating rates.

Figure 4.2: (a) Density and (b) densification rate as a function of temperature at various heating rates.

4.3.2 Isothermal sintering

The densification behavior of 8YSZ was also monitored by performing isothermal sintering between 1150 to 1300°C. To minimize the thermal influence during the heating-up process, a higher heating rate of 20°C/min was employed. After correcting the thermal expansion of raw data, the linear shrinkage was converted into density evolution, as displayed in Fig. 4.3. The sintered density increases with the increase of time and temperature, and sintering rate is noted to be very fast at higher tem-

4.4 Density and microstructure

Table 4.1: Sintering characteristics determined from dilatometry experiments with different heating rates.

Heating rate (°C/min)	T_{onset} (°C)	T_{max} (°C)	Final Density (%)	Maximum denification rate ($\dot{\rho}_{max}$, $10^{-3}/^{\circ}\text{C}$)
2	1055	1309	99.0	4.25
5	1065	1345	98.6	4.22
7.5	1072	1353	98.4	4.11
10	1079	1366	98.6	3.69
15	1082	1384	98.3	3.48
20	1093	1403	98.0	3.41

peratures. For instance, at 1300°C isothermal condition, 8YSZ could be sintered to a relative density of 90% in less than 30mins from a near green-state ($\rho = 50\%$). After soaking at each specific temperature for 6h, the final densities achieved are 58.6%, 70.0%, 94.8% and 96.2% of the theoretical density, for $T_s=1150^{\circ}\text{C}$, 1200°C , 1250°C and 1300°C , respectively.

4.4 Density and microstructure

4.4.1 “Density-grain size” trajectory

Prior to the construction of MSC, it is necessary to examine the relationship between grain size and the sintered density, as the modeling of MSC assumes that grain size should be only a function of density. In order to obtain related data, conventional pressureless sintering was carried out in an electrical furnace in ambient atmosphere. The sintering profile involved heating the specimen to the target temperature (1150-1400°C) at 5°C/min, and the soaking time was from 0 to 240 min. Table 4.2 summarized the detailed information regarding relative densities, grain sizes of specimen subjected to various heat treatment conditions.

4.4 Density and microstructure

Table 4.2: Relative density (ρ , %) and grain size (G , μm) of specimen sintered at different temperature with various soaking time

Temperature (°C)		Soaking time (min)			
		0	30	60	120
1150	ρ	-	-	54.1	55.7
	(G)	-	-	(0.16±0.02)	(0.17±0.03)
1200	ρ	55.1	56.7	60.7	63.3
	(G)	(0.16±0.03)	(0.18±0.04)	(0.21±0.03)	(0.25±0.04)
1250	ρ	61.2	73.7	79.8	87.3
	(G)	(0.21±0.05)	(0.35±0.04)	(0.43±0.06)	(0.59±0.06)
1300	ρ	71.1	88.5	93.3	94.1
	(G)	(0.33±0.06)	(0.60±0.03)	(0.65±0.08)	(0.72±0.13)
1400	ρ	95.8	97.0	97.9	98.5
	(G)	(1.27±0.13)	-	(2.43±0.18)	(3.24±0.30)

(-) not measured

4.4 Density and microstructure

Figure 4.3: Density evolution during isothermal sintering at (a) 1150°C, (b) 1200°C, (c) 1250°C and (d) 1300°C. The dash-dot line illustrates the sintering profile used, where the heating rate is 20°C/min.

Fig. 4.4 shows the selected SEM micrographs of the sintered 8YSZ. The homogeneous microstructure was formed because both the grain/particle size and pore spacing are observed to be very uniform. Based on Table 4.2, the density-grain size trajectory, also referred as “sintering path”, is shown in Fig. 4.5. It is interesting to note that all the experimental points belong to a single continuous path, which means that grain growth is a function of only density in the present case. The behavior of single “sintering path” has also been reported in the sintering of Al_2O_3 [117].

It is also found that grain growth is quite limited at early and intermediate stage of sintering ($\rho \leq 94\%$). This is because the dispersed open pores pin the grain boundary and hinder grain boundary migration [34]. In contrast, significant grain growth begins when the relative density is over 94%, indicating the proceeding of sintering into the final stage, where pore-pinning effect is substantially decreased due to the collapse of open pores. It has been suggested not to include data taken at high densities, where exaggerated grain growth could result in the poor converging of the data on the single

4.4 Density and microstructure

“sintering path” [20]. Hence, the master densification curve is constructed over the range of $\rho \leq 94\%$.

Figure 4.4: SEM micrographs of sintered 8YSZ: (a) 1150°C-120min, RD=55.7%; (b) 1200°C-120min, RD=63.3%; (c) 1250°C-30min, RD=73.7% and (d) 1300°C-30min, RD=88.5% .

4.4.2 Static grain growth

Static grain growth study at various temperatures was carried out to study the grain growth kinetics of 8YSZ. Fig. 4.6 summarizes the average grain size of 8YSZ after isothermal sintering at 1350-1450°C for various length of time. The representative SEM micrographs from polished and thermally etched surface are shown in Fig. 4.7.

4.4 Density and microstructure

Figure 4.5: The relationship between grain size and relative density.

Figure 4.6: Grain size of sintered 8YSZ at 1350-1450°C with various soaking time.

4.4 Density and microstructure

Figure 4.7: SEM micrographs of 8YSZ under different isothermal sintering condition. (a) 1350°C-1 h; (b) 1350°C-4 h; (c) 1400°C-1 h; (d) 1400°C-1 h; (e) 1450°C-2 h and (f) 1450°C-4 h.

4.5 Construction of master curves

In the investigated range, the grain size is measured to be between 1.55 to 7.54 μm . The sintered samples were noted to have very dense microstructure, which contains only quite limited number of small pores. Compared to the early and intermediate stage ($\rho \leq 94\%$, Fig. 4.4), the pinning effect of pores on the migration of grain boundaries is much smaller, and hence the grain growth is much faster during the final stage. In addition, several studies have reported that the segregation of Y^{3+} along grain boundaries was significantly lower than in the case of tetragonal 3Y-TZP [118, 119], which implies that solute-drag mechanism is less dominating in cubic zirconia. The light enrichment of Y^{3+} at grain boundaries in cubic zirconia is hence reckoned to be the cause for its faster grain growth rate as compared to tetragonal zirconia [6].

4.5 Construction of master curves

4.5.1 Master densification curve (MDC)

The original work of MSC focus on the densification process only [20]. Later, several work applied similar principle onto the grain growth behavior, and successfully constructed master grain growth curve [34, 38]. In this study, the master curves for both densification and grain growth were studied. To make a distinction, MDC stands for master curves of densification, and MGGC represents the mastering grain growth curve hereafter.

MDC relates the evolution of density, ρ , with the accumulated thermal history, $\Theta[t, T(t)]$. As reviewed in Chapter 2, the thermal history parameter is described as the work of sintering:

$$\Theta[t, T(t)] = \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \quad (4.2)$$

If sintering is performed under isothermal condition, Eq. 4.2 can be simplified as,

$$\Theta[t, T(t)] = \frac{t}{T} \exp\left(-\frac{Q}{RT}\right) \quad (4.3)$$

4.5 Construction of master curves

where t is the time of sintering at temperature T , and if the CRH sintering is applied, then Eq. 4.2 takes the form of,

$$\Theta[t, T(t)] = \frac{1}{C} \int_{T_0}^T \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dT \quad (4.4)$$

where C is the rate of heating. The activation energy is a critical parameter for for construction of MDC, which is able to obtain by performing preliminary CRH experiments. After acquiring the required data, a trial method based on a sigmoidal function (see Eq. 2.16) [32] was applied for estimation of a most appropriate value of Q .

A first estimation of $Q=450$ KJ/mol is made, and the $\rho - \Theta$ curves for sintering under each heating rate are shown in Fig. 4.8. Apparently, the curves are not converging, so another estimation of Q is attempted and the calculation is repeated. Following the iteration, for each activation energy attempted, the sigmoidal-curve fitting yields a mean residual square (MRS), and the vary of MRS with Q is shown in Fig 4.9. However, it is difficult to establish a good fitting. Although the minimal of MRS was found to be at $Q=600$ KJ/mol, the computed $\rho - \Theta$ curves by the value do not converge very well over the entire range.

As suggested by Su and Johnson [20], the deviation from the expected curve can be resulted from several factors, such as the existence of surface diffusion and vapor transport. It is also worthy to note the assumption that a single mechanism dominates throughout the entire process. The unsatisfactory construction of MDC in the present case suggests that the assumption may not be appropriate for the entire process of sintering, in other words, a change of the dominate sintering mechanism may have occurred. Indeed, Bernard-Granger et al. studied the activation energy for the sintering of 3Y-TZP powder [82], and found that the activation energy decreases with relative density, which is especially evident at the earlier densification stage.

To represent the densification process in a more accurate manner, here we propose a two-stage MDC approach: the entire densification process are divided into two consecutive stages, over which MDCs are constructed separately. The boundary between

4.5 Construction of master curves

Figure 4.8: Master densification curve for 8YSZ with an activation energy of 450 KJ/mol; the failure of convergence means that an inappropriate value of Q has been used.

Figure 4.9: The variation of mean residual squares with sintering activation energy. The minimum of of MRS was obtained at $Q=600$ KJ/mol.

4.5 Construction of master curves

Figure 4.10: MDC for 8YSZ with the minimal MRS at $Q=600$ KJ/mol.

two stages is set at 60% of the relative density, which corresponds to the end of early stage of sintering. The constructed $\rho - \Theta$ diagram for the first stage ($\rho < 60\%$), along with the dependance of MRS on the activation energy were shown in Fig. 4.11. The best fitted MDC was achieved at $Q=715$ KJ/mol. Similarly, MDC was constructed for the second stage with sintered relative density from 60 to 94%, and the sintering activation energy was found to be 580 KJ/mol (Fig. 4.12). Through the two-stage MDC approach, the minimum of MRS obtained were 0.049 and 0.251 for the first and second stage, respectively, whereas it was 0.463 if MDC was constructed over the entire stage.

Meanwhile, the constants are determined via the curve-fitting process, and this completes the expression of MDC for sintering of 8YSZ. The density evolution during first and second stage of sintering are represented by Eq. 4.5 and 4.6, respectively.

$$\rho = 50.4 + \frac{49.6}{1 + \exp\left(-\frac{\log \Theta + 25.47}{0.94}\right)} \quad (50.4\% \leq \rho \leq 60\%) \quad (4.5)$$

$$\rho = 58.0 + \frac{42.0}{1 + \exp\left(-\frac{\log \Theta + 21.06}{0.40}\right)} \quad (60\% \leq \rho \leq 94\%) \quad (4.6)$$

4.5 Construction of master curves

Figure 4.11: Constructed MDC for the first stage of sintering ($\rho = 50.5 - 60\%$ relative density): (a) variation of mean residual squares with activation energy, (b) the best fitted $\rho - \Theta$ diagram was achieved at $Q=715 \text{ KJ/mol}$.

4.5 Construction of master curves

Figure 4.12: MDC for the second stage of sintering ($\rho = 60 - 94\%$ relative density): (a) variation of mean residual squares with activation energy, (b) the best fitted $\rho - \Theta$ diagram was achieved at $Q=580$ KJ/mol.

4.5 Construction of master curves

4.5.2 Master grain growth curve (MGGC)

Through the control of sintering profiles, the ability to determine the final microstructure, especially the average grain size, is of equal importance to densification. Therefore, the master curve approach was extended to study grain growth kinetics of 8YSZ. The construction of MGGC takes the same procedures as that of MDC. It has been shown that a modified equation for grain growth kinetic has the form of (section 2.2.3.2):

$$G^n - G_0^n = n \int_0^t K_0 \exp\left(-\frac{Q_G}{RT}\right) dt \quad (4.7)$$

Starting with $\Theta_G = \int_0^t \exp\left(-\frac{Q_G}{RT}\right) dt$, Eq. 4.7 can be written as

$$G^n - G_0^n = nK_0\Theta \quad (4.8)$$

where G_0 is the specific initial grain size. Therefore, the relationship between grain size, G , and the work of sintering, Θ_G , can be expressed as

$$G = \sqrt[n]{G_0^n + nK_0\Theta} \quad (4.9)$$

The activation energy for grain growth is determined via a curve fitting method with Eq. 4.9. Although sintering was conducted under isothermal condition, the heating-up step was also considered in the calculation of Θ_G .

The master curve analysis of static grain growth data from Fig. 4.6 yields the value of mechanism controlled parameter $n = 2.3$ and the activation energy $Q = 330$ KJ/mol. The constructed MGGC using $Q = 330$ KJ/mol is shown in Fig. 4.13.

4.5.3 Validation of master curves

The practical significance of master curves lies in the ability to predict and control densification and grain growth behavior. Before applying the master curves to industrial practice, its validity needs to be verified. In order to examine the effectiveness of constructed MDC, the density evolution during isothermal sintering (Fig. 4.3) at 1200 and 1250°C was used. The thermal history parameter, Θ , was calculated by

4.5 Construction of master curves

Figure 4.13: Master grain growth curve for 8YSZ, and the determined activation energy is 330 KJ/mol.

taking the activation energy of 715 KJ/mol and 580 KJ/mol for the first and second stage of sintering, respectively. Fig. 4.14 shows the calculated “ $\rho - \Theta$ ” curve from the experimental data. It can be seen that there is good agreement between the model prediction and the experimental results.

Here, it is worthy to mention that a break occurs with the increase of thermal history (horizontal axis) at $\rho = 60\%$. The sudden jump of the Θ value is resulted from that the employed activation energy decreases abruptly from the first to second stage of sintering, whereas in reality, Q would have changed gradually with the smooth progress of the sintering stage. Despite of this, the constructed MDC is noticed to be able to represent the entire sintering process with reasonably good result. In addition, Fig. 4.14 illustrates clearly that the constructed MDC can be used with confidence for isothermal sintering profiles. In general, it can be concluded that the master densification curve based on the two-stage approach could provide a more precise prediction on the densification behavior.

Sintering cycles for static grain growth were also performed to evaluate the validity

4.6 Discussion of sintering mechanisms

Figure 4.14: The prediction of density evolution during isothermal sintering by the constructed master densification curve.

of MGGC. The final grain sizes of 8YSZ were $3.93 \pm 0.32 \mu\text{m}$, $4.50 \pm 0.41 \mu\text{m}$ and $5.66 \pm 0.46 \mu\text{m}$ when sintered at 1500°C for 30, 60 and 120 min, respectively. Fig. 4.15 shows the comparison between the model prediction and the experimental results. Reasonable agreement was observed. The result shows the MGGC model is capable for predicating grain growth behavior. Since the original kinetic equation is derived from the final stage of sintering, the constructed MGGC is also considered for application to the final stage of sintering, where the influence of open pores is excluded.

4.6 Discussion of sintering mechanisms

4.6.1 densification mechanisms

Pressureless sintering is generally a diffusion-controlled process, where the diffusion of the slowest atoms/ions moving along the fastest diffusion path determines the rate of sintering. The activation energy is a characteristic parameter reflecting the depen-

4.6 Discussion of sintering mechanisms

Figure 4.15: Prediction of grain growth by the constructed MGGC.

dence of sintering kinetics on temperature, and it is commonly used for identification of the fundamental mass transport mechanism. Table 4.3 summarizes the diffusion mechanisms and activation energies of cubic zirconia, which is obtained through various experimental approaches, such as tracer diffusion and diffusional creep [6, 120]. For example, Kilo et al. measured the ^{96}Zr diffusion in a series of cubic YSZ single crystals [120, 121], have determined that the activation energy is 440–463 kJ/mol. With the same method, they also reported that the activation energy for grain boundary diffusion in ScSZ polycrystals to be 376 KJ/mol [122].

Due to the different measuring methods, and the difficulty in controlling tracer impurities in the tested specimen, the literature data of activation energy seems to be scattering, yet it is recognized that reported value for lattice diffusion locates within the range of 460–616 kJ/mol, while it is estimated to be mostly between 309 and 373 kJ/mol for GBD.

In the practical case of solid-state sintering, however, several mechanisms (lattice diffusion, grain-boundary diffusion, etc.) often operate simultaneously. Therefore, the resultant activation energy may not be exactly corresponding to one specific sintering

4.6 Discussion of sintering mechanisms

Table 4.3: Diffusion mechanisms and activation energies for cubic zirconia

Sample	Method	Rate-controlling species	Temperature range (°C)	Activation energy (KJ/mol)	Diffusion mechanism	Reference
7.8 mol% YSZ	sintering	–	1130-1240	702	GBD	[118]
9.4 mol% YSZ single crystal	Dislocation loop annealing	Zr point defect	1100-1300	511	LD	
12 mol% ScSZ	Tracer diffusion	Zr ⁴⁺	1200-1600	481	LD	[122]
				376	GBD	
8-32 mol% YSZ single crystals	Tracer diffusion	Zr ⁴⁺ via vacancies	1125-1460	440-463	LD	[120]
8 mol% YSZ	Diffusional creep	Zr ⁴⁺	1200-1600	460	LD	[6]
				309	GBD	
9.4 mol% YSZ single crystal	Diffusional creep	–	1450-1550	616	LD	[123]
25 mol% YSZ	Diffusional creep	Cations	1400-1600	550	LD	[124]

4.6 Discussion of sintering mechanisms

mechanism, but more likely a weighted average of multiple sintering mechanisms. As the contribution of each diffusion mechanism changes, the apparent activation energy would change correspondingly. In the present work, it was demonstrated that, if a single dominating mechanism is assumed by using one constant activation energy, the fitting of MDC over the entire sintering stage is unsatisfactory. On the other hand, the proposed two-stage MDC approach provides a better representation of the densification behavior. It is also reckoned that the two-stage MDC model can predict the densification evolution under any arbitrary sintering profile.

In the present work, the investigated densification range was from 50% to 94% of the theoretical density. In the construction of MDC, the whole process was divided to two consecutive stages, with $\rho = 60\%$ as the boundary. The activation energy was revealed by the sigmoidal fitting method. During the first stage of sintering, the activation energy is determined to be 715 kJ/mol. Similar results was also reported by Matsui et al [118]. Although they attributed the sintering mechanism to grain-boundary diffusion, it is noted that most of the reported activation energy for grain-boundary diffusion range from 309 to 373 kJ/mol. The value obtained is also higher than those of lattice diffusion reported in [6, 123]. It is, however, noted that this abnormally higher activation energy has been observed by Hollenberg et al. in the initial-stage sintering of Ti-doped Al_2O_3 [125]. They explained that this phenomenon was originated from a “defect formation” process. As pointed by Kilo et al., the defect type could most probably be the cation vacancies [120]. At the reduced temperature, the concentration of intrinsic defects is lower, the activation energy for sintering essentially contains not only the term of defect motion (ΔH^m), but also a term (ΔH^f) related to defect formation [125]:

$$\Delta H = \Delta H^m + \Delta H^f \quad (4.10)$$

Therefore, the apparent activation energies was noted to be larger. Additional evidence was provided by Bernard-Granger, who reported that the activation energy of 3Y-TZP was as high as 935 kJ/mol, and the value decreased with the sintering

4.7 Concluding remarks

process [82]. The defect formation process is also believed to be responsible for the abnormally high activation energy at the lower density range.

On the other hand, it is noted that diffusion along sample surface has been neglected in the MDC model. Despite surface diffusion do not facilitate densification, it consumes the sintering potential and hence results in an increased activation energy for densification [126]. It is therefore concluded that both mechanisms have probably contributed to the high activation energy at the first stage of sintering. During the second stage, the activation energy obtained is 580 KJ/mol, which is comparable to the values reported for volume diffusion [123, 124]. Hence, the dominant sintering mechanism at this stage is most appropriately assigned to lattice diffusion.

4.6.2 Grain growth mechanisms

The master grain growth curve has been constructed for static grain growth behavior of YSZ, from which the activation energy for grain growth (Q_g) is determined to be 330 KJ/mol. Lee and Chen [127] reported the activation energy for the grain growth of 8YSZ was only 289 kJ/mol at 1300-1700°C using $n=2$ (Eq. 2.18). Tekeli et al., applied the parabolic rate law with a grain growth exponent of 2, have determined the value of Q_g to be 298 kJ/mol [95]. Our result is noted to be higher than both studies, as a fitted value of $n=2.3$ was used. Despite of a small difference, it is reckoned that the grain growth kinetic of 8YSZ follows the parabolic law, which means that the mechanism for grain growth is grain boundary-controlled.

4.7 Concluding remarks

The densification and static grain growth behavior of 8 mol% YSZ was modeled by master sintering curves. The master densification curve (MDC) established based on the proposed two-stage approach has shown to provide a better representation of the entire densification process. The constructed MDCs has also shown to be able to

4.7 Concluding remarks

precisely predict density evolution of 8YSZ under a given time-temperature profile. The activation energy for 8YSZ is determined to be 715 KJ/mol and 580 KJ/mol during the first ($\rho = 50 - 60\%$) and second stage ($\rho = 60 - 94\%$) of densification, respectively. With reference to the literature findings, the higher activation energy for the first stage probably was attributed to the defect formation process and surface diffusion, while lattice diffusion is most appropriately assigned as the dominant mechanisms in the second stage of sintering.

The master grain growth curve (MGGC) was also established, and was verified with additional sintering cycles. The activation energy for grain growth is determined to be 330 KJ/mol, and the grain growth exponent was found to be $n=2.3$, which suggests that grain growth kinetics of 8YSZ follows the parabolic rate law.

5

Master curves for sintering of doped 8YSZ

5.1 Introduction

Thus far, 8 mol% YSZ is probably the most promising electrolyte material for SOFC. Advantages of 8YSZ over other types of electrolyte material have been well reported, however, the application of 8YSZ electrolyte is still restricted by its relatively high sintering temperature and poor toughness [76, 85], where both factors are unfavorable for the cost-effective co-sintering technique during fabrication of SOFC.

Generally, 8YSZ electrolyte requires a temperature of $T \geq 1350$ °C to attain a dense microstructure, whereas the electrodes prefer a lower co-sintering temperature ($T \leq 1250$ °C) to (1) maintain porosity, (2) prevent coarsening of NiO particles, and (3) avoid harmful interface reaction [75, 76, 79, 128]. Thereby, extensive work has resorted to the use of sintering additives for reducing sintering temperature of YSZ. Among the numerous additives, Al_2O_3 has been recognized as an effective sintering aid for YSZ [92, 95]. For example, Matsui et al. observed that densification rate of 7.8YSZ was significantly enhanced by 0.25 wt.% Al_2O_3 addition at $T < 1290$ °C [94]. Meanwhile, it was demonstrated that mechanical strength could also be enhanced upon the addition of Al_2O_3 [15]. In addition, Al_2O_3 is able to improve the conduc-

5.1 Introduction

tivity of YSZ via scavenging of SiO_2 impurities along the grain boundary [102, 103]. Due to these advantages, a small amount of Al_2O_3 is always purposely added to 8YSZ when applied as electrolyte for SOFC.

On the other hand, NiO/YSZ composite is widely used as starting material for SOFC anode. So far, the interaction between YSZ and NiO has received considerable attention, especially the YSZ-NiO composites with high NiO contents (≥ 40 mol%) [129]. However, with the preference to carry out co-sintering technique, the effect of small amounts of NiO (present as an impurity) on the performance of 8YSZ electrolytes has become increasingly important, as the diffusion of Ni^{2+} ions from the anode side towards the electrolyte is an unavoidable phenomenon. It is noted that Ni ions could diffuse tens of micrometers into the contacting YSZ layer during co-sintering [16]. Joo et al. have also reported that the Ni content in 10 mol% Sc_2O_3 -stabilized zirconia (10ScSZ) was found to be ~ 1.7 mol% after the co-sintering of a NiO layer/ ~ 10 mm thick 10ScSZ film at 1600°C for 3h [17]. Although the co-sintering temperature they used is higher than the common practice, it is evident that the diffusion of small amount of NiO will inevitably affect not only the interface (anode/electrolyte) but also the entire electrolyte [130].

The previous chapter has demonstrated the effectiveness of master sintering curve in the modeling of densification and grain growth behavior of undoped 8YSZ. Here, the same approach is applied to 8YSZ with Al_2O_3 and NiO additives. Master curves are established for doped 8YSZ, which make it possible for predicting or controlling the microstructural evolution at a wide range of sintering profiles. Furthermore, the effectiveness of the additives as sintering promoters are examined by preparing samples including a wide range of additive content. The microstructure of doped 8YSZ was studied with SEM and TEM.

5.2 Experiments

Table 5.1: compositions and abbreviation for investigated specimen

Sample	Composition	Sample	Composition
8Y	$(\text{ZrO}_2)_{0.08}(\text{Y}_2\text{O}_3)_{0.92}$		
8Y005Al	8Y+0.05 wt.% Al_2O_3	8Y006Ni	8Y+0.06 wt.%NiO
8Y020Al	8Y+0.2 wt.% Al_2O_3	8Y011Ni	8Y+0.11 wt.%NiO
8Y050Al	8Y+0.5 wt.% Al_2O_3	8Y028Ni	8Y+0.28 wt.%NiO
8Y100Al	8Y+1.0 wt.% Al_2O_3	8Y056Ni	8Y+0.56 wt.%NiO
8Y200Al	8Y+2.0 wt.% Al_2O_3	8Y112Ni	8Y+1.12 wt.%NiO
8Y500Al	8Y+5.0 wt.% Al_2O_3	8Y276Ni	8Y+2.76 wt.%NiO

5.2 Experiments

The details of sample preparation has been documented in Chapter 3. Additives are introduced into 8YSZ by a wet chemical method, where the nitrate solution of Al^{3+} and Ni^{2+} were used as dopant source. The investigated compositions are undoped 8YSZ, 0.05-5 wt.% Al_2O_3 -doped 8YSZ, and 0.06-2.76 wt.% NiO-doped 8YSZ, and a detailed description of the sample compositions are listed in Table 5.1. The abbreviations will be used hereinafter to stand for a specific composition.

5.3 Phase and lattice parameter of doped-YSZ

Phase identification was performed on the sintered and surface-polished pellets with an X-ray diffractometer. After acquiring the XRD spectra, refinement of the structure was carried out based on the Rietveld method, from which the lattice parameter was calculated.

The XRD patterns of Al_2O_3 -doped 8YSZ, and the variation of lattice parameter with the content of Al_2O_3 are shown in Fig. 5.1(a) and 5.1(b), respectively. For the undoped 8YSZ, the diffraction peak at 29.8° and 50.2° is noted to exhibit slight broadening. The composition of 8YSZ locates exactly at the boundary of $c \rightarrow t$

5.3 Phase and lattice parameter of doped-YSZ

phase transformation, and tetragonal zirconia has very close cell parameter as that of the cubic phase [40, 131]. Therefore, the broadening is due to the existence of small portions of tetragonal phase. However, the peak becomes sharp upon Al_2O_3 addition, which indicates that Al_2O_3 can help stabilize the cubic phase of zirconia. In addition, the peaks characterizing the second phase Al_2O_3 begin to emerge when its concentration exceeds 1.0 wt%.

The ionic radii of Al^{3+} and Ni^{2+} are 0.63 and 0.83 Å, respectively, which are of both lower valence and smaller size than Zr^{4+} (0.84 Å). The dissolved dopant cations were shown to enter the substitutional position of host cations (Eq. 5.1), and thus lead to a contraction of the lattice parameter [93].

From Fig. 5.1(b), the solubility of Al_2O_3 in 8YSZ is determined to be around (slightly less than) 0.5 wt%, and the sintering temperature of 1400°C and 1500°C seems to yield little difference. Several previous studies have reported that the solubility of Al_2O_3 in zirconia is limited, which is only 0.1 mol% in Y-TZP when sintered at 1300 °C [88], and 0.5-1.0 wt.% in 8YSZ when sintered at 1500 °C [14]. Our result is close to those reported value.

Fig. 5.2 shows the XRD patterns of NiO-doped YSZ sintered at 1400°C for 2h. Similarly, NiO is also found helpful for stabilization of cubic phase of zirconia, and there is no chemical reaction between NiO and YSZ. The solubility of NiO in YSZ has been reported by a number of researchers, but the literature data are quite scattered from 1.0 wt.% to 5.4 wt.% [16, 129]. In our case, the solubility limit is determined from the variation of lattice parameter with NiO doping content, which is around 0.56 wt.%. This value is smaller than that reported by Kuzjukevics (0.85 wt.%) at the same temperature [98]. This should be ascribed to both the shorter sintering time and lower cooling rate used in the present study. On the other hand, it is interesting to note that no NiO second phase was detected, even in the sample with 2.76 wt.% NiO loading. The existence of undissolved NiO has been revealed by high resolution

5.3 Phase and lattice parameter of doped-YSZ

Figure 5.1: (a) XRD spectra of Al_2O_3 -doped YSZ sintering at 1400°C for 2h. (1) 8Y, (2) 8Y020Al, (3) 8Y050Al, (4) 8Y100Al, (5) 8Y200Al, (6) 8Y500Al. (b) Lattice parameter of doped YSZ as a function of Al_2O_3 contents

5.3 Phase and lattice parameter of doped-YSZ

Figure 5.2: (a) XRD spectra of NiO-doped YSZ sintering at 1400°C for 2h. (1) undoped 8YSZ, (2) 8Y006Ni, (3) 8Y011Ni, (4) 8Y028Ni, (5) 8Y056Ni, (6) 8Y112Ni, and (7) 8Y276Ni. (b) lattice parameter of YSZ as a function of NiO additive content

5.4 Effect of Al₂O₃ additives on sintering of YSZ

TEM, which will be discussed later.

5.4 Effect of Al₂O₃ additives on sintering of YSZ

5.4.1 Densification

Samples containing a wide range of Al₂O₃ content from 0.05-5 wt.% were prepared, and dilatometric measurement under a constant rate of 5 °C/min was carried out to study the sintering behavior. Fig. 5.3 shows the density evolution and densification rate as a function of temperature for both undoped and Al₂O₃-doped 8YSZ. Several important characteristic parameters related to the densification process are summarized in Table 5.2, where T_{onset} and T_{max} have the same meaning as explained in section 4.3.1, and $T_{95\%}$ is the temperature at which 95% of the theoretical density can be attained.

It can be seen from Fig. 5.3 that sintering behavior of 8YSZ was remarkably changed upon Al₂O₃ addition. In the doped-sample, it is observed that the start of densification begins at a reduced temperature, and the temperature of maximum densification rate also decreases. For example, with 1.0 wt.% Al₂O₃ additive, T_{onset} of 8YSZ shifts from 1065°C to 1009°C, and T_{max} decreases from 1345°C to 1243°C. In addition, the temperature required to sinter 8YSZ to 95% relative density was reduced by 89°C by 0.5 wt.% Al₂O₃ addition. The significant reduction in these characteristic temperatures well demonstrates that Al₂O₃ can be used as effective sintering aid for 8YSZ.

On the other hand, it is found that there is an optimal amount of Al₂O₃ addition, i.e. 1.0 wt.% Al₂O₃, that enhance the densification of 8YSZ most effectively. When the Al₂O₃ content is ≥ 2.0 wt.%, the enhancement in densification becomes less pronounced, particularly the maximum densification rate was noticed to decrease remarkably (Fig. 5.3(b)). It is also seen that the one prominent peak of densification rate, which is common for samples containing ≤ 1.0 wt.% Al₂O₃, was split into two

5.4 Effect of Al_2O_3 additives on sintering of YSZ

Figure 5.3: (a) Density evolution, and (b) densification rate as a function of temperature during dilatometric sintering of undoped and Al_2O_3 -doped 8YSZ

5.4 Effect of Al_2O_3 additives on sintering of YSZ

Table 5.2: Information of investigated samples: compositions and name abbreviation

Sample	T_{onset} ($^{\circ}\text{C}$)	T_{max} ($^{\circ}\text{C}$)	$T_{95\%}$ ($^{\circ}\text{C}$)	Final relative density (%)
8Y	1065	1345	1438	98.6
8Y005Al	1047	1307	1402	98.7
8Y020Al	1032	1278	1352	99.1
8Y050Al	1029	1248	1349	99.3
8Y100Al	1009	1243	1359	98.6
8Y200Al	1026	1257	1377	98.1
8Y500Al	1019	1259	1402	98.7

broader peaks with the increasing of Al_2O_3 content up to 2.0 wt%. The emergence of the second peak correspond probably to the sintering of Al_2O_3 , according to the dilatometric sintering of pure Al_2O_3 [132]. Our SEM micrographs also supports this proposal, as severe segregation of Al_2O_3 was observed. Therefore, it is concluded that the less pronounced densification in samples containing ≥ 2.0 wt% Al_2O_3 was due to the severe clustering of Al_2O_3 at the grain boundary, which limits the grain boundary diffusion of the host 8YSZ.

To look at the additive's effect on densification, isothermal sintering was performed at temperatures of 1150-1400 $^{\circ}\text{C}$ with a holding time of 2h. Fig. 5.4 shows the sintered density as a function of Al_2O_3 content. The density of 8YSZ initially increases with Al_2O_3 additive, and then decreases with further Al_2O_3 addition, and the optimal amount is found to be 0.5-1.0 wt.%, depending on the sintering temperature. When sintered at 1100 $^{\circ}\text{C}$, 1.0 wt.% Al_2O_3 addition results in the highest density, while at higher temperatures, 0.5 wt.% Al_2O_3 is found to be the most effective amount. Further addition of Al_2O_3 above the optimal content would lead to a slow densification of 8YSZ. For example, the sintered density of 8YSZ increases from 63.3 to 83.3% with 0.5 wt.% Al_2O_3 additive, and decreases to 71.1% in 5.0 wt.%-doped 8YSZ when sintered at 1200 $^{\circ}\text{C}$ for 2h. Nevertheless, the content of Al_2O_3 have little influence on

5.4 Effect of Al_2O_3 additives on sintering of YSZ

the final densification of 8YSZ, as all samples are noticed to be able to reach almost full densification, with density of $\geq 98.2\%$ when sintered at 1400°C for 2h.

Figure 5.4: Final density of Al_2O_3 -doped 8YSZ isothermally sintered at $1150\text{--}1400^\circ\text{C}$ for 2h

5.4.2 Microstructural development

The effect of Al_2O_3 addition on grain growth of 8YSZ was also clarified. Fig. 5.5 (a)-(g) shows the representative SEM micrographs of specimen containing 0-5.0 wt.% Al_2O_3 addition after isothermally sintered at 1400°C for 2h. When the content of Al_2O_3 is ≤ 0.2 wt.%, the microstructure exhibits clean grain boundaries and well distributed grains. Once the Al_2O_3 content exceeds the solubility limit, the segregation of Al_2O_3 second phase is expected to appear. This is the case we observed in samples containing ≥ 0.5 wt.% Al_2O_3 , where the dark areas corresponds to the clustering of second phase. The undissolved Al_2O_3 mainly locates at triple junctions or along grain boundaries, although a number of Al_2O_3 particles were also found within the matrix.

5.5 Effect of NiO additives on sintering of YSZ

Average grain sizes were determined by the linear-intercept method, and were presented in Fig. 5.6 as a function of Al_2O_3 content and temperature. It can be seen that grain growth of 8YSZ was significantly enhanced with the addition of Al_2O_3 up to 0.2-0.5 wt.%, or more specifically, the amount of Al_2O_3 that leads to the largest grain size decreases from 0.5 wt.% at 1300°C to 0.2 wt.% at $1350\text{-}1500^\circ\text{C}$. With further addition of Al_2O_3 above the range, grain growth of 8YSZ becomes retarded and fine microstructure was formed (Fig. 5.5 e-g).

The enhancement in grain growth can be ascribed to the “undersized effect”, as proposed by Chen and chen [133] in the study of grain growth of CeO_2 . Due to the smaller ionic radii of Al^{3+} ($0.53 \text{ \AA}$), the dissolved Al^{3+} would cause certain distortion of the lattice, and lead to a faster diffusion of the cations. However, above the solubility limit, the segregation layers of solute cations or even intergranular phase will appear, which restricts the migration of grain boundaries.

5.5 Effect of NiO additives on sintering of YSZ

5.5.1 Densification

It was demonstrated that a small amount of NiO would diffuse from the anode side into the electrolyte, and thus affect the sintering behavior of 8YSZ [130]. A series of compositions containing 0.06-2.76 wt.% NiO were prepared, and both the densification and grain growth behavior of NiO-doped 8YSZ were investigated to clarify the effect of NiO existed as impurities.

Fig. 5.7 presents the density and densification rate as a function of temperature. It was found that, with 0.06-2.76 wt.% NiO addition, the densification of 8YSZ was also significantly promoted. The temperature of maximum densification rate decreases in the order of 8Y (1345°C) > 8Y006Ni (1290°C) > 8Y011Ni (1264°C) > 8Y028Ni (1255°C). However, as NiO content increases to 0.28-1.12 wt.%, there is

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Figure 5.5: SEM micrographs of undoped and Al₂O₃-doped 8YSZ sintered at 1400°C for 2h

5.5 Effect of NiO additives on sintering of YSZ

Figure 5.6: Grain size of 8YSZ containing 0-5 wt.% Al₂O₃ additives sintered at 1300-1500 °C for 2h

hardly any difference in the densification behavior of 8YSZ. This indicates that 0.28 wt.% (8Y028Ni) is the minimum amount to promote effective densification of 8YSZ. On the other hand, higher levels of NiO up to 2.76 wt.% is noticed to display negative effect, as the densification rate curve shifts to the higher temperature. Similar phenomenon was also observed in the sintering of Al₂O₃-doped 8YSZ earlier.

To look at the addition's effect on densification, isothermal sintering was performed at temperatures of 1150-1500 °C with a soaking time of 2h. Fig. 5.8 shows the final density of samples as a function of NiO content. The result of undoped-8YSZ was also included for comparison. The change of density during isothermal sintering agrees well with the CRH sintering. There is the obvious increase in the final density, for example, when sintered at 1200°C the relative density of 8YSZ increases from 63.3% to 87.4% with 0.28 wt.% NiO addition. Nevertheless, in contrary to the case of Al₂O₃ addition, NiO-doped 8YSZ was found unable to achieve full densification when the sintering temperature rises to 1500°C. The sample of 8Y276Ni achieved a relative

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Figure 5.7: (a) Density and (b) densification rate of 8YSZ containing 0-2.76 wt.% NiO as a function of temperature, heating rate is 5°C/min

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density of 95.7% when soaking at 1500°C for 2h, in comparison to that of almost full density for undoped samples.

Figure 5.8: Final density of samples isothermally sintered at 1150-1500°C for 2h

Our previous XRD result has determined that the solubility of NiO in 8YSZ is only 0.28-0.56 wt%, however, the undissolved NiO was not detected by XRD in higher percentage doped samples. Since the diffusion of NiO has been frequently observed in the multi-layered SOFC system [16], it is speculated that undissolved NiO may have either evaporated or diffused away from the host 8YSZ. The alumina backing tile used for supporting samples was examined after sintering at 1400°C and 1500°C for 2h, and the photograph is shown in Fig. 5.9. It is observed that there are patterns beneath the samples that have printed on the substrate, which indicates the diffusion of NiO. On the other hand, thermal gravimetric analysis (TGA) result also shows that there is around 1.0% of weight loss in the sample of 8Y276Ni after sintering at 1450°C (Fig. 5.9). Hence, the reduced density of samples is attributed to the loss of NiO dopant when sintered at high temperature. This has been further supported by the presence of pores seen in SEM observation, and will be presented in the next section.

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Figure 5.9: Diffusion pattern of NiO-doped 8YSZ after sintering at (a) 1400°C for 2h and (b) 1500°C for 2h

Figure 5.10: Thermal gravimetric analysis of 2.76 wt.% NiO-doped 8YSZ

5.5 Effect of NiO additives on sintering of YSZ

5.5.2 Microstructure

5.5.2.1 Grain growth

The effect of NiO on grain growth of 8YSZ was studied by measuring the average grain size of samples after isothermal sintering between 1300°C to 1500°C for 2h. Fig. 5.11 shows the average grain size as a function of NiO content. The grain growth of 8YSZ was initially promoted with the addition of NiO up to 0.56 wt.%, and then inhibited with further addition of NiO.

Figure 5.11: Grain size of 8YSZ containing 0-2.76 wt.% NiO after sintering at 1300-1500°C for 2h.

The representative SEM micrographs are shown in Fig. 5.12. Compared with Al_2O_3 -doped 8YSZ, there are more pores present both within the grain matrix and along the grain boundaries, especially in the sample containing the largest amount of NiO (8Y276Ni). As discussed earlier, the porous structure is mainly resulted from the diffusion of NiO at high temperature.

Due to the loss of NiO discussed earlier, there is no segregation of NiO could be

5.5 Effect of NiO additives on sintering of YSZ

Figure 5.12: SEM micrographs of NiO-doped 8YSZ sintered at 1500°C for 2h. (a) 8Y006Ni, (b) 8Y011Ni, (c) 8Y028Ni, (d) 8Y056Ni, (e) 8Y112Ni and (f) 8Y276Ni.

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clearly identified, even in the heavily doped sample of 8Y276Ni. Additional evidence comes from the previous dilatometric sintering experiment. It can be recalled from Fig. 5.3, there exists a second peak in the densification rate curve of Al_2O_3 -doped 8YSZ, which has been ascribed to the sintering of Al_2O_3 . On the other hand, the densification rate curves of all NiO-doped samples (5.7) show only a single peak corresponding to the densification of pure 8YSZ, which means that the remaining NiO dopant do not coarsen readily.

5.5.2.2 Distribution of undissolved NiO

Although both XRD and SEM observation could not detect the undissolved NiO, it is of interest to examine whether there is remaining NiO secondary phase in 8YSZ. This was studied with a field emission transmission electron microscopy (FE-TEM) in the following section.

Fig. 5.13 shows the microstructure of 2.76 wt.% NiO-doped sample by FE-TEM. It reveals clearly the existence of secondary phase. Local EDS nano-analysis under scanning-transmission-electron-microscopy (STEM) mode was performed with a probe size of 1 nm, and the clustering of NiO micro-sized crystals (in the range of around 200nm) can be easily identified from Fig. 5.13(b). Besides, NiO crystals are found to locate both within the grain interior and along the grain boundaries. Fig. 5.13 (c) shows the distribution of Zr element, where the Zr-devoid areas were confirmed, as indicated by the circles. Combining with the location of NiO crystals, it is also able to verify the presence of residual pores, which have been indicated by arrows in Fig. 5.13 (a). This is in agreement with our previous SEM observation.

The microstructure of samples were also examined by high resolution TEM (HRTEM). 5.14(a) shows the HRTEM micrograph 0.06 wt.%NiO-doped 8YSZ sintered at 1500°C for 2h. The sample was noted to have both very clean grain-interior and grain boundary. As the content of NiO exceeds its solubility limit, the grain boundaries becomes more disordered, which is considered to have been resulted from the enhanced segre-

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Figure 5.13: .

(a) Microstructure of 2.76 wt.% NiO-doped YSZ sintering at 1500°C for 2h; arrows indicate the location of pores, (b) local EDS mapping of Ni using Ni_K peaks, and (c) local EDS mapping of Zr; circled areas represent Zr-devoid regions [99].

gation of NiO at the interface. Besides, the existence of nano-sized crystals of NiO was able to be detected; the typical existence is circled in Fig. 5.14 (b). The characterization confirms the existence of the undissolved NiO secondary phase in 8YSZ. Both nano and micro-sized NiO crystals are found either within grain interior or along grain boundary.

5.6 Construction of master curves for doped YSZ

5.6.1 CRH sintering

Following the procedures in the earlier chapter on the construction of MDC for undoped 8YSZ, CRH sintering was carried out with a dilatometer to obtain the relationship between the relative density, ρ , and the work of sintering, Θ . The sample containing 0.5 wt.% Al_2O_3 was referred as example for the following discussion. Fig. 5.15 presents the density evolution as a function of temperature under 4 different constant heating rates (2, 5, 10, 15°C/min). The effect of heating rates is the same as was observed during sintering of undoped 8YSZ: the onset of densification shifts to a higher temperature with increasing heating rate. In addition, the higher the heating

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Figure 5.14: HRTEM image of (a) 0.06 wt.% NiO-doped YSZ and (b) 2.76 wt.% NiO-doped YSZ ; the circled area indicates nano-sized crystals of secondary NiO.

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rate, the lower is the sintered density at a given temperature. As explained earlier, the slower densification under higher heating rate is resulted from the shortened thermal history.

Figure 5.15: Density as a function of temperature under constant heating-rates of 2, 5, 10, 15°C/min.

5.6.2 Density-grain size trajectory

In MSC theory, microstructural evolution is represented as a function of density only. Hence, the dependence of grain size on sintered density requires to be established. Fig. 5.16 presents the relationship between ρ and G for both undoped and doped 8YSZ, to give a comparison of the microstructural development for both cases. In addition, the representing microstructural evolution of 8Y050Al was also shown in Fig. 5.17.

It can be seen that the grain growth is quite sluggish before the final stage of sintering. For example, the grain size of 8Y050Al increases to only 0.49 μm with the green compact sintered to 90% relative density, which indicate that porous structure would significantly inhibit grain growth. On the other hand, it is interesting to notice

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Figure 5.16: Grain size versus relative density for undoped 8YSZ, 0.5 wt.%Al₂O₃-doped, and 0.28 wt.% NiO-doped 8YSZ.

Figure 5.17: SEM micrographs of sintered 8Y050Al: (a) 1150°C-30 min, $\rho = 69.9\%$, $G = 0.20 \mu\text{m}$; (b) 1200°C-60 min, $\rho = 79.6\%$, $G = 0.29 \mu\text{m}$ and (c) 1250°C-30 min, $\rho = 90.4\%$, $G = 0.48 \mu\text{m}$.

5.6 Construction of master curves for doped YSZ

that sintering additives actually slow down grain growth rate during the early and intermediate stage, although they would promote grain growth at higher density. This is possibly one of the reasons for the enhanced densification rate in the doped sample, as small particle size offers larger sintering potential. Finally, despite grain size-density trajectories of the samples show slightly different tracks, the respective sintering path of each composition are found to follow the single curve. This hence shows the applicability of the master curves to doped 8YSZ.

5.6.3 Master densification curve

5.6.3.1 Construction of MDC

The $\rho - \Theta$ curve obtained from different heating rate was fitted with the sigmoidal function. Fig. 5.18 shows the best fitted MDC over the 50.5%-92% relative density range studied, and the inset figure presents the variation of MRS with the value of activation energy. The most appropriate activation energy was found to be 480 KJ/mol. Nevertheless, as we noticed in undoped 8YSZ, the curves were not fitting sufficiently well. It is again attributed to the assumption of single mechanism dominating over the entire process.

Following that reported in undoped 8YSZ, the two-stage MDC approach was used and MDCs are constructed over $\rho = 50.5 - 60\%$ and $\rho = 60 - 92\%$ separately. Fig. 5.19 and Fig. 5.20 shows the constructed MDC by using the most appropriate activation energy of $Q=680$ kJ/mol $Q=430$ kJ/mol, respectively, and the minimum of MRS (inset figures) obtained are 0.00379 and 0.0782, respectively. Obviously, the constructed MSC based on the two-stage approach provide a better representation of the sintering behavior than fitting a single Q value for the whole sintering process.

The master curve model was also applied to the sintering of NiO-doped 8YSZ. Similarly, it was found a better modeling of the densification process was achieved by the two-stage master sintering curve approach. Due to the similarity to that of undoped and Al_2O_3 -doped 8YSZ, the modeling procedures for NiO-doped 8YSZ is

5.6 Construction of master curves for doped YSZ

Figure 5.18: The constructed MDC for 0.5 wt.% Al_2O_3 -doped 8YSZ over $\rho=50$ -94%; the minimum of MRS is obtained by $Q=480$ KJ/mol, however, the convergence is not good.

Figure 5.19: The constructed MDC for 8Y050Al during first stage of sintering ($\rho=50$ -60%); the best fitted MDC is minimum of MRS is given at $Q=680$ KJ/mol.

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Figure 5.20: The constructed MDC for 8Y050Al during first stage of sintering ($\rho=60$ -92%); the best fitted MDC is minimum of MRS is given at $Q=430$ KJ/mol.

not presented. However, all the constants and activation energy values have been summarized in Table 5.3 and 5.4 for Al_2O_3 -doped and NiO-doped 8YSZ, respectively. As previous, these values are obtained via the sigmoidal-function fitting method [32],

$$\rho = \rho_0 + \frac{100 - \rho_0}{1 + \exp\left(-\frac{\log \Theta - a}{b}\right)} \quad (5.2)$$

It can be seen for all samples, there is a big difference in Q between first and second stage of sintering, which implies that different mechanism operates in the respective stage, and therefore the two-stage MDC approach is believed to provide a more accurate representation of the initial process.

5.6.3.2 Validation of MDC

The effectiveness of MDC for doped 8YSZ was verified in this section. Fig. 5.21 presents the density as a function of time, where the sintering profile involves heating the sample to 1200 °C at 20°C/min, and followed by soaking at 1200 °C for 360 min. At the end of heating step, the sintered density achieved is 58.7%, while it increases to 95.3% after isothermal sintering.

5.6 Construction of master curves for doped YSZ

Table 5.3: Activation energies and the constant parameters for MDCs of Al₂O₃-doped YSZ

Al ₂ O ₃ content (wt.%)	$\rho = 50.5 - 60\%$			$\rho = 60 - 92\%$		
	Q (KJ/mol)	a	b	Q (KJ/mol)	a	b
0.05	707	25.48	0.93	510	19.01	0.45
0.2	680	25.19	0.83	480	18.75	0.36
0.5	680	25.65	0.78	430	16.83	0.43
1.0	630	24.00	0.86	390	15.45	0.43
2.0	630	23.64	0.87	460	17.67	0.46

Table 5.4: Activation energies and the constant parameters for MDCs of NiO-doped YSZ

NiO content (wt.%)	$\rho = 50.5 - 60\%$			$\rho = 60 - 92\%$		
	Q (KJ/mol)	a	b	Q (KJ/mol)	a	b
0.11	675	25.47	0.75	500	19.13	0.44
0.28	620	23.56	0.81	410	16.22	0.43

5.6 Construction of master curves for doped YSZ

Figure 5.21: The increase of relative density with time for 8Y050Al (solid line); the sample is heated at 20°C/min to 1200°C and soaked for 6h (dash line).

The $\rho - \Theta$ curve was calculated for the specific sintering profile by using the activation energy of 680 KJ/mol for $\rho \leq 60\%$, and 430 KJ/mol for $\rho \geq 60\%$ respectively. Fig. 5.22 compares the experimental results and the prediction of MDC model. Except for the densification range between $\rho = 65\%$ to 72% , very good agreement has been achieved. The relatively unsmooth fitting in the 65% - 72% range is attributed to the transition of the mechanism. In practical case, the sintering mechanism in operation transits smoothly; however we have applied a sharp change of the activation energy in our modeling. Nevertheless, the constructed MDC for doped-8YSZ is still noted to give the essential stages a good representation of the process, also under different heating profiles.

5.6.4 Master grain growth curve

For the sample of 0.5 wt.% Al_2O_3 -doped 8YSZ, the average grain size after isothermal sintering at 1350-1450°C with various soaking time (1-8 h) was presented in Fig. 5.23.

5.6 Construction of master curves for doped YSZ

Figure 5.22: The experimental results and MDC model prediction on the density evolution of 8Y050Al

The final grain size is noted to be between 1.89 to 7.45 μm . The data are subsequently used for construction of master grain growth curve.

The activation energy for grain growth is fitted with Eq. 5.3 (see section 2.2.4 and 4.5.2 for more details).

$$G = \sqrt[n]{G_0^n + nK_0\Theta} \quad (5.3)$$

Fig. 5.24 shows the constructed MGGC for 8Y050Al with a best fitted activation energy $Q_G = 470 \text{ KJ/mol}$, and the mechanism controlled exponent is obtained as $n = 4.5$.

Generally, the value of n is accepted as $n = 2$ for normal grain growth, and $n = 3$ indicates a solute drag mechanism [134]. However, there are also a number of studies that have reported of $n \geq 4$ [135, 136]. Thus far, there is no consistent explanation given for the higher value of n obtained. In our case, it has shown that the largest grain size is achieved in 8YSZ containing 0.2 wt.% Al_2O_3 at temperature above 1350°C. With further Al_2O_3 addition, the grain growth essentially becomes sluggish. Therefore, the fitted kinetic exponent of $n = 4.5$ can probably relate to a

5.6 Construction of master curves for doped YSZ

Figure 5.23: Average grain size of 8YSZ containing 0.5 wt.% Al_2O_3 after sintered at 1350-1450°C for various time.

Figure 5.24: Master grain growth curve for 8Y050Al with a best fitted $Q_G = 470$ KJ/mol.

5.7 Discussion

solute drag-controlled mechanism.

5.7 Discussion

5.7.1 Activation energy and sintering mechanism

The activation energy for densification of Al_2O_3 -doped and NiO-doped 8YSZ has been determined based on a two-stage MDC model. For all the compositions, there is a large decrease of the activation energy from the first to second stage of sintering, which indicates the presence of a change of the dominant sintering mechanism.

The activation energy for first-stage sintering ($\rho \leq 60\%$) is obtained to be 620- 707 KJ/mol. This value is higher than that of both GBD and LD, but agrees well with the “defect-formation” mechanism as we proposed for undoped 8YSZ. It is reckoned that the defect-formation process also operates in the sintering of additive-containing samples.

During the second stage of sintering, the activation energy is found to be between 390 KJ/mol and 580 KJ/mol. As summarized in Table. 4.3, the activation energy is between 460 and 616 KJ/mol for lattice diffusion, and 309-373 KJ/mol for grain boundary diffusion [120, 122]. It can be seen that lattice diffusion still dominates the process, whereas the contribution from grain boundary diffusion increases gradually as the additive increases. In particular, the activation energy for densification of 8Y containing 1.0 wt.% Al_2O_3 and 0.28 wt.% NiO is 390 KJ/mol and 410 KJ/mol, respectively, which is very close to that of grain boundary diffusion.

On the other hand, compared with undoped 8YSZ, the activation energy of doped 8YSZ is noted to have decreased, especially during the second stage of sintering. For example, it decreases from 580 KJ/mol to 390 KJ/mol upon 1.0 wt.% Al_2O_3 addition, and to 410 KJ/mol in 0.28 wt.% NiO-containing samples. The effect of additives on the sintering and activation energy will be discussed in the next section.

5.7 Discussion

5.7.2 Effect of sintering additives

The use of sintering additives has a long history in ceramic processing as an effective strategy for microstructure control. However, fundamental mechanisms are still discussed until today [3, 137]. Nevertheless, the recent development in computational science and advanced electron microscopy technique have begun to offer new perspectives for this phenomenon.

The interface, or grain boundary, always plays an important role, especially during the early and intermediate stage of sintering. The grain boundary structure for ceramics with sintering additives has been systematically studied by Dillon et al. [3, 138]. The heterogeneous dopants inclined to segregate along the grain boundary in the host material [139], and consequently influence the grain boundary characteristic. Dillon [138] has identified at least six distinct structural states (complexion) at grain boundaries, in respect of the dopant atom adsorption. They established the unequivocal correlation between the structural disorder and grain boundary mobility. The disordered films (from 0.6 to 10 nm thickness) originated from the segregation of additives, which is driven by a reduction in the free energy of the grain boundaries, could promote mass transport over one to two orders of magnitudes faster when compared with that of undoped case. In the present case, the segregation of Al^{3+} at the grain boundary of YSZ has been confirmed in literature [105, 118]. According to Dillon [138], the adsorption of Al_2O_3 produces extended “softened” grain boundaries due to the interaction of Al^{3+} with its environment, which facilitates the mass transport during early stage of sintering.

As sintering temperature increases, a small portion of additives would dissolve into the lattice of YSZ, the solubility of which has been determined in the study. The incorporation of external atoms/ions into the host would change the local chemical bonding state. Theoretical calculations carried out by Boniecki et al. [140] revealed that the dissolution of Al^{3+} could weaken the ionic bonding strength between cations and oxygen ion in zirconia, which means that a smaller energy would be required

5.8 Concluding remarks

for the diffusion of Zr^{4+} ($/\text{Y}^{3+}$). Indeed, the reduction of activation energy upon Al_2O_3 addition has been observed. On the other hand, there is a lack of theoretical verification regarding to the effect of NiO on zirconia lattice. It is speculated that the same mechanism might operate in the case of NiO-doped 8YSZ, while further investigation by first-principle molecular orbital calculation will be required to confirm this effect.

5.8 Concluding remarks

In this chapter, the densification and microstructure evolution of 0.05-5.0 wt.% Al_2O_3 -doped and 0.06-2.76% NiO-doped 8YSZ were investigated, and the sintering behavior was modeled by the master curve approach. The main findings are:

1. Both Al_2O_3 and NiO are helpful in stabilizing cubic phase zirconia. The solubility of Al_2O_3 and NiO is determined to be around 0.5 wt.% and 0.28 wt.% at 1400°C, respectively. As the content of additives exceed the solubility limit, excessive Al_2O_3 is mainly found to segregate along grain boundaries as second phase, while undissolved NiO is not detected by both XRD and SEM observation. This is caused by the loss of NiO dopant via diffusion or evaporation. TEM observation reveals that the remaining NiO has a highly dispersed distribution; both micro and nano-sized crystals are found either within grain interior or along grain boundary.
2. Both additives promote the densification of 8YSZ. The densification of 8YSZ is most effectively enhanced by addition of 1.0 wt.% Al_2O_3 , or 0.28 wt.% NiO. Under the heating rate of 5°C/min, the temperature of maximum densification rate is reduced from 1345°C for undoped 8YSZ to 1243°C in 8Y100Al, and 1255°C in 8Y028Ni, respectively. In the heavily doped sample with ≥ 2.0 wt.% Al_2O_3 , or 2.76 wt.% NiO, the densification curve is shifted to higher temperature, indicating a retarded densifying process. In particular, fully densification

5.8 Concluding remarks

is prevented in 8Y276Ni, which attains only 95.7% relative density at 1500°C heat treatment.

3. Grain growth of 8YSZ was initially promoted by addition of Al_2O_3 up to 0.2 wt.%, NiO up to 0.56 wt.%, while further addition lead to a decrease in grain size. Besides, there are more pores in 1.12-2.76 wt.% NiO-containing 8YSZ, compared to Al_2O_3 -doped samples. The porous structure of NiO-doped 8YSZ is attributed to the loss of NiO when sintered at high temperatures.
4. Master densification curves are constructed for doped samples. Similar to the case of undoped 8YSZ, the two-stage approach could provide a better representation of the entire sintering process, indicating the dominant sintering mechanism have changed from the first ($\rho \leq 60\%$) to second stage ($\rho \geq 60\%$) of sintering. The constructed MDC also verified the ability to predict density evolution with reasonable accuracy.
5. Compared with undoped 8YSZ, the activation energy is found to decrease upon Al_2O_3 and NiO addition, especially in the second stage of sintering. In the doped sample, the first-stage is also ascribed to be “interface-reaction” controlled, due to the abnormally high activation energy obtained. However, as the sintering proceeds to later stage, grain boundary diffusion began to contribute significantly, especially in the sample of 8Y100Al and 8Y028Ni. The reduction in activation energy is speculated as the effect of dissolved dopant cations weakening the ionic bonding strength between the host Zr^{4+} and oxygen ions.

6

Sintering behavior and mechanism of 8YSZ containing Al_2O_3 and SiO_2 co-additives

6.1 Introduction

Our previous study has elucidated the sintering behavior and mechanisms of 8YSZ containing a single dopant, either of the purposely induced Al_2O_3 , or a small amount of NiO that is diffused from the contacting anode layer. Besides, master curves for both densification and grain growth have been established, which are of significant importance for industrial applications.

However, the situation may become complicated due to the ubiquitous presence of SiO_2 impurity. There are a number of possible routes that could lead to SiO_2 contamination [141–143]. First, SiO_2 can be easily introduced from the starting material, especially in industrial manufacturing environment where technical grade raw materials are always used for economic purposes [130]. Second, the scalable fabrication increases the chance of SiO_2 contamination from the surrounding environment, particularly from the furnace refractories during high-temperature sintering. Third, SiO_2 is an important constituent for the glass sealant component of planar SOFC,

6.2 Experiments

for example, the best sealant to date is based on RO- Al_2O_3 - SiO_2 ($\text{R}=\text{Ca}, \text{Ba}$) system [142]. SiO_2 could be possibly introduced to the electrolyte during operation. On the other hand, SiO_2 is even added intentionally into YSZ to achieve desired mechanical properties, such as to impart superplasticity [144, 145]. As a result, it is of interest to take the role of SiO_2 into consideration.

It is commonly accepted that SiO_2 is detrimental to the conductivity of YSZ, especially the grain boundary conduction by forming a resistive siliceous films along grain boundaries [21, 22]. However, the detrimental effect of SiO_2 is possible to be eliminated by the addition of Al_2O_3 , which has the scavenging effect of siliceous films [14]. On the other hand, it was reported that SiO_2 is beneficial to the densification of YSZ [23]. Since the role of Al_2O_3 in assisting densification of 8YSZ has been confirmed in the previous study, our hypothesis is that, the addition of both Al_2O_3 and SiO_2 would lead to a synergistic improvement on densification of 8YSZ. Meanwhile, it is expected that the conductivity of 8YSZ would, if not, be least impaired through the careful manipulation of additive content.

The effect of SiO_2 (0-0.3 wt.%) on sintering and conductivity of pure 8YSZ and 0-5.0 wt.% Al_2O_3 -containing 8YSZ was investigated. It is aimed to further improve the densification of 8YSZ via the coupling effect of Al_2O_3 and SiO_2 , and in the meanwhile to clarify the sintering mechanism in samples containing co-additives. The densification and grain growth behavior was reported in this part, while the conductivity measurement of the same batch of specimen will be presented in next chapter.

6.2 Experiments

Specimens were prepared with the same procedures as described in Chapter 3. Eight powder blends with varying amount of Al_2O_3 and SiO_2 were prepared, and Table 6.1 summarizes their respective composition and designation. The content of SiO_2 is fixed at 0.05 and 0.3 wt.%, corresponding to the impure and highly impure level, while the amount of Al_2O_3 addition is varying between 0-5.0 wt.%. We also investigated the

6.3 Dilatometry

Table 6.1: Information of investigated samples: compositions and designations

Designation	TZ8Y (wt.%)	Al ₂ O ₃ (wt.%)	SiO ₂
8Y	100	0	0
8Y-5A	99.5	0.5	0
8Y-05S	99.95	0	0.05
8Y-3S	99.7	0.5	0.3
8Y-5A-05S	99.45	0.5	0.05
8Y-5A-3S	99.2	0.5	0.3
8Y-10A-3S	98.7	1.0	0.3
8Y-20A-3S	97.7	2.0	0.3
8Y-20AKP-3S	97.7	2.0 wt.%AKP	0.3
8Y-50A-3S	94.7	5.0	0.3

effect of doping methods by preparing one additional powder blend, where the additives were introduced via powder-mixing of 2.0 wt.% AKP30 ($d_{mean}=0.3\ \mu\text{m}$), 0.3 wt.% TEOS and 8YSZ. The sintering behavior of samples with same additive compositions but different doping approach. Hence, chemical route and powder mixing method can be compared and discussed.

6.3 Dilatometry

Fig. 6.1 depicts the evolution of relative density, which is converted from the recorded linear shrinkage, as a function of temperature under 5 °C/min. The derivatives of density over temperature, $1/\rho \cdot d\rho/dT$, was calculated to give the densification rate (Fig. 6.2).

It can be seen that densification of 8YSZ was moderately enhanced by the single additive of SiO₂, but less pronounced than by Al₂O₃ addition, probably because SiO₂ is less effective in activating a reactive interface layer in zirconia than Al₂O₃ [146]. It

6.3 Dilatometry

Figure 6.1: Density evolution as a function of temperature for 8YSZ containing Al_2O_3 and SiO_2 .

was reported that SiO_2 could effectively promote the densification behavior of Y-TZP [88, 147] and calcium-stabilized zirconia [148]. Tekeli et al. also found that up to 1.0 wt.% SiO_2 addition was able to reduce the sintering temperature of 8YSZ [23]. However, our result seems to show that SiO_2 alone is not a good sintering additive for cubic zirconia, as the sintered density is essentially noticed to decrease during final stage of sintering, compared to undoped YSZ. Similar results to our case were reported by Zhang et al [87], who explained that the difference with that of Tekeli's [23] is mainly due to the different doping levels of SiO_2 .

On the other hand, it was observed that the most effective densification was achieved in 8YSZ containing 0.5-1.0 wt.% Al_2O_3 and 0.3 wt.% SiO_2 additions. Thermal parameters of dilatometric sintering under $5^\circ\text{C}/\text{min}$ was summarized in Table 6.2. There is dramatic decrease observed in the characteristic temperatures upon addition of co-additives. In the specimen of 8Y-5A-3S, the onset of sintering was decreased to 1005°C , and a further reduction to 988°C is achievable in the sample of 8Y-10A-3S. The temperature of maximum densification rate (T_{max}) is shifted to 1309°C , which is

6.3 Dilatometry

Figure 6.2: Densification rate as a function of temperature for 8YSZ containing Al_2O_3 and SiO_2 .

6.3 Dilatometry

Table 6.2: Thermal characteristics of 8YSZ containing Al_2O_3 and SiO_2 under constant rate of sintering ($5^\circ\text{C}/\text{min}$)

Sample	T_{onset} ($^\circ\text{C}$)	T_{max} ($^\circ\text{C}$)	$T_{95\%}$ ($^\circ\text{C}$)	Final relative density (%)
8Y	1065	1345	1438	98.6
8Y-5A	1029	1248	1349	99.3
8Y-05S	1033	1319	1411	98.4
8Y-3S	1031	1290	1409	98.0
8Y-5A-05S	1020	1210	1330	99.0
8Y-5A-3S	1005	1219	1309	99.2
8Y-10A-3S	988	-	1322	98.7
8Y-20A-3S	1009	-	1360	98.3
8Y-50A-3S	1027	-	1413	98.0

126°C lower than that of undoped YSZ. Additionally, 8Y-5A-3S only requires 1309°C to be sintered to 95% of theoretical density. All of the observations manifest the fact that co-addition of Al_2O_3 and SiO_2 can be more effective in promoting densification of YSZ.

However, as the content of Al_2O_3 is over 1.0 wt.%, the densification curves shift to higher temperature, similar to the sintering behavior of 8YSZ containing Al_2O_3 addition alone. This is probably due to the formation/clustering of second phase, which inhibited the diffusion of species along or across the grain boundary.

From Fig. 6.2, it is also interesting to note the appearance of multi-peaks in the densification rate curve. For example, there are three peaks emerging at 1118, 1160, 1216°C , respectively, in 8Y-10A-3S, and the observation becomes even more evident in the sample of 8Y-50A-3S. Multi-peaks can be always associated with the multi-staged sintering process [149], which implies the combination and transition of sintering mechanisms. The improved densification in SiO_2 -containing YSZ has been attributed to the mechanism of viscous flow [87], enhanced grain boundary diffusivity

6.4 Sintering kinetics

[144], and more often, to the promotion of liquid phase sintering [23, 150]. For a better understanding of the sintering process, especially in the samples containing both Al_2O_3 and SiO_2 , the sintering kinetics is re-evaluated with an attempt to clarify the sintering mechanisms.

Despite the successful application of master curves model for both undoped and $\text{Al}_2\text{O}_3/\text{NiO}$ -doped 8YSZ, it seems not appropriate to be applied in the present case, mainly due to the fact that the complicated sintering mechanism, particularly the potential existence of liquid-phase sintering, which could not meet the assumption of master curves. Although a multi-stage MSC approach might provide a possible solution [151], its efficiency and accuracy as a prediction tool would certainly be weakened. Therefore, instead of MSC approach, alternative sintering models are adopted,

6.4 Sintering kinetics

6.4.1 Early-stage sintering

Several theoretical models have been developed to analyze early stage of sintering. A general kinetic equation for nonisothermal sintering is proposed by Woolfrey [152], who found that there is a relationship between the linear shrinkage, $\Delta L/L_0$, and the heating rate, C :

$$\left(\frac{\Delta L}{L_0}\right)^{n+1} = \frac{K_1 RT^2 n}{CQ} \exp(-Q/RT) \quad (6.1)$$

where K_1 is a constant, and n is a mechanism-controlled exponent, where $n = 0$ for the case of viscous flow, $n = 1$ for volume diffusion and $n = 2$ for grain boundary diffusion mechanism. They suggested that n can be determined from Eq. 6.2 by performing CRH experiments, i.e.,

$$\ln\left(\frac{\Delta L}{L_0}\right)_T = -\frac{\ln C}{n+1} + \ln A \quad (6.2)$$

where A is a constant depending on the material parameters and the sintering mechanism. The plot of $\ln(\Delta L/L_0)_T$ at specific temperature versus $\ln C$ should give a

6.4 Sintering kinetics

straight line with slope of $-1/(n+1)$.

The early-stage sintering of 8YSZ containing 0.5 wt.% Al_2O_3 and 0.3 wt.% SiO_2 (8Y-05A-3S) was analyzed by the model. Fig. 6.3 shows the dependance of $\ln(\Delta L/L_0)_T$ on the natural logarithm of heating rate (2.5, 5, 10, 15 K/min). The studied temperature range is from 1050 to 1220°C, while the linear shrinkage is between 1 to 8.8% under different heating rate. It can be seen that good linearity has been achieved for all the plots, where the average linear regression coefficient, R , is up to 0.992. Meanwhile, the average value of n is determined to be 2.13 ± 0.15 , indicating that the sintering mechanism of 8Y-05A-3S during early-stage can be appropriately ascribed to grain boundary diffusion.

Figure 6.3: $\ln(\Delta L/L_0)$ versus $\ln C$ for calculation of mechanism-controlled exponent, n , for 8Y-10A-3S.

On the other hand, the sintering activation energy is determined based on the rate equation developed by Wang and Raj [30](see section 2.2.3.3),

$$\frac{1}{\rho} \frac{d\rho}{dt} = D_0 \frac{f(\rho)}{kTG^m} \exp\left(-\frac{Q}{RT}\right) \quad (6.3)$$

where $D_0 = (D_v)_0$ and $m = 3$ for lattice diffusion, and $D_0 = (\delta D_b)_0$ and $m = 4$ for grain

6.4 Sintering kinetics

boundary diffusion, respectively. It is possible to obtain the value of Q by plotting the densification rate function, $\ln T \frac{1}{\rho} \frac{d\rho}{dt}$, versus the reciprocal of temperature at a given relative density (ρ). If data from CRH sintering was used, the left-hand side would take of form of $\ln[T \cdot C(\frac{1}{\rho} \frac{d\rho}{dT})]$.

The procedure has been applied to the relative densities range of 52-65%, and the arrhenius plots was shown in Fig. 6.4. The average activation energy is obtained as 499 ± 10 KJ/mol. To our knowledge, there is no literature report on the activation energy of 8YSZ containing Al_2O_3 and SiO_2 co-additives.

Figure 6.4: Arrhenius-type plot of 8Y-5A-3S for estimation of activation energy.

Fig. 6.5 compares the sintering activation energy obtained by the above model. It can be seen the activation energy of 8YSZ was significantly decreased upon co-addition of Al_2O_3 and SiO_2 , especially at the very early stage of sintering. Our previous result suggests that “defect-formation” and surface diffusion dominates in the first stage of sintering of undoped 8YSZ, however, with the co-additive of Al_2O_3 and SiO_2 , the dominant mechanism was found to have changed to grain boundary diffusion. It was reported that, SiO_2 tends to segregate in the vicinity of the interface [119, 139] due to

6.4 Sintering kinetics

the solute misfit between Si^{4+} ($0.4\text{\AA}$) and Zr^{4+} ($0.84\text{\AA}$). In fact, the grain boundaries are the dopant-rich area where Y^{3+} and Al^{3+} were also observed to segregate over a width of 4-10 nm [105, 118, 119]. The complex interface reaction of the segregated dopants could probably produce a disordered grain boundary structure, and hence a higher grain boundary diffusivity and the accelerated densification rate.

Figure 6.5: Activation energies estimated from Wang's model for 8YSZ with/without additives.

6.4.2 Intermediate and final-stage sintering

Fig. 6.6 shows the sintered density of samples after isothermal-sintering at the target temperature for 2h. In agreement with the dilatometric sintering experiment under constant heating-rate, 8Y-5A-3S exhibits the highest density among the samples with varying amount of additives. The relative density of 8Y-5A-3S obtained can go up to 89.7% when sintered at 1150°C , whereas it is only 55.7% for undoped 8YSZ, and 72.7% for 8YSZ containing 0.5 wt.% Al_2O_3 alone. The good sinterability of the sample containing co-additive allows the fabrication of dense electrolyte under 1200°C .

6.4 Sintering kinetics

Figure 6.6: Sintered density of samples sintered at various temperature for 2h.

The formation of intergranular liquid-phase is typically observed in SiO_2 -containing YSZ when sintering at above 1350°C [23, 153, 154]. Relevant phase diagrams shows that the ternary eutectic of $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ forms at 1539°C [155], and $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ eutectic at $1320 - 1371^\circ\text{C}$ [156]. Whereas, the phase diagram of quaternary $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ is unknown yet. Our previous study has demonstrated that solid state sintering dominates in the composition of $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$. However, the addition of SiO_2 could dramatically decrease the eutectic temperature of the quaternary phase [144]. On the other hand, Luo [157] pointed out that a quasi-liquid interfacial layer can be formed at a temperature which is $100\text{-}400^\circ\text{C}$ lower than the bulk eutectic phase.

Fig. 6.7 shows the microstructure of 8Y-5A-3S sintered at 1350°C . The round edges of grain boundary (indicated by arrows), especially at the triple junction was clearly observed, which is one of the evident characteristics of liquid phase sintering. Hence, the intermediate and final stage of sintering is believed to be dominated by liquid-phase sintering mechanism.

6.5 Effect of doping method

Figure 6.7: SEM micrograph of 0.5 wt.% Al_2O_3 and 0.3 wt.% SiO_2 -doped 8YSZ sintered at 1350°C .

6.5 Effect of doping method

Fig. 6.8 compares the densification behavior of 8YSZ containing 2.0 wt.% Al_2O_3 and 0.3 wt.% SiO_2 , which are prepared from different doping method, i.e. chemical route and powder mixing method.

Apparently, the sample by chemical route shows a better sinterability than that formed by powder mixing. The sintered density of 8Y-20A-3S is higher by 10% than 8Y-20AKP-3S before preceding to the final stage of sintering. Also, the former achieves a higher final density of 98.7%, as compared to 96.3% for that of 8Y-20AKP-3S. In the chemical route, the Al_2O_3 dopant is more homogeneously distributed with fine particle size, consequently there are increased reaction sites between both additives. The enhanced interface reaction could facilitate the formation of intergranular film, and hence a higher rate of mass diffusion. The results indicate that, introducing of additives via chemical route is more effective in terms of densification.

6.6 Grain growth

The average grain sizes of specimen sintered at 1300 - 1500°C are summarized in Table 6.3. The grain size increases with sintering temperature, but shows no systematic

6.6 Grain growth

Figure 6.8: Comparison of the densification behavior between 8Y-20A-3S and 8Y20AKP-3S under constant rate of sintering (10°C/min).

6.6 Grain growth

Table 6.3: Average grain size of 8YSZ containing Al_2O_3 and SiO_2 sintered at 1300-1500°C for 2h

Sample	1300°C-2h	1400°C-2h	1500°C-2h
8Y	0.72 ± 0.13	2.94 ± 0.56	5.66 ± 0.46
8Y-5A	2.61 ± 0.46	4.18 ± 0.35	8.37 ± 1.03
8Y-05S	1.46 ± 0.29	4.31 ± 0.39	6.07 ± 0.73
8Y-3S	2.42 ± 0.31	4.75 ± 0.69	6.98 ± 0.62
8Y-5A-05S	2.64 ± 0.38	4.85 ± 0.65	7.93 ± 0.91
8Y-5A-3S	2.36 ± 0.25	4.13 ± 0.45	9.08 ± 0.70
8Y-10A-3S	2.23 ± 0.24	3.93 ± 0.42	10.20 ± 1.21
8Y-20A-3S	2.10 ± 0.33	3.39 ± 0.34	9.12 ± 0.53
8Y-20AKP-3S	2.18 ± 0.26	3.76 ± 0.51	8.43 ± 0.77
8Y-50A-3S	1.55 ± 0.27	2.81 ± 0.30	5.42 ± 0.68

dependence on the doping composition. At lower temperatures (1300-1400°C), the maximum grain growth is observed in 8Y-5A-05S. However, when the sintering temperature increases to 1500°C, the sample of 8Y-10A-3S exhibits the largest grain size, which is due to the sufficient formation of liquid phase at higher temperatures. In general, except in the sample containing highest amount of Al_2O_3 (5.0 wt.%) at 1400-1500°C, the grain growth of 8YSZ is promoted by all doping compositions, particularly in the sample containing certain amount of co-additives. The final grain size ranged from $0.72 \mu\text{m}$ of undoped 8YSZ to $10.20 \mu\text{m}$ for 8YSZ containing 1.0 wt.% Al_2O_3 and 0.3 wt.% SiO_2 .

Fig. 6.9 shows the microstructure of samples sintered at 1500°C from SEM observation. In the only SiO_2 -containing samples, well packed grains with no sign of liquid phase formation was observed. In addition, there is a number of residual pores existed in 0.3 wt.% SiO_2 -doped 8YSZ, which confirms the previous densification study that full densification is impeded in 8Y-3S. With the addition of Al_2O_3 , the edge of grain

6.6 Grain growth

Figure 6.9: SEM micrographs of (a) 8Y-05S, (b) 8Y-3S, (c) 8Y-5A-05S, (d) 8Y-5A-3S, (e) 8Y-10A-3S, (f) 8Y-20A-3S, (g) 8Y-20AKP-3S and (h) 8Y-50A-3S sintered at 1500°C for 2h.

6.7 Concluding remarks

boundaries becomes smooth and round, indicating a small portion of liquid phase was squeezed to the triple junction, which probably occurred during the cooling process. On the other hand, in the highly impure samples (with 0.3 wt.% SiO_2) containing heavier amount of Al_2O_3 , the grain boundary was fully wetted by the formation of intergranular films, evident from the continuous grain boundary phase. Moreover, if the content of Al_2O_3 is increased to 5.0 wt.%, second phase is identified to segregate along the grain boundaries, which contributes to the retarded grain growth in the sample. All the microstructural studies are closely correlated with the electrical properties. The results will be presented in the next chapter.

6.7 Concluding remarks

The densification and grain growth behavior of 8YSZ containing 0-5.0 wt.% Al_2O_3 and 0-0.3 wt.% SiO_2 were studied in this chapter. The results verified our hypothesis, that densification of 8YSZ can be further enhanced by synergistic effect of Al_2O_3 and SiO_2 as co-dopants. The temperature dependence to densification process is found to reduce. For instance, in 8YSZ containing 0.5 wt.% Al_2O_3 and 0.3 wt.% SiO_2 co-additives, the onset of sintering shifts to 1005°C, from 1065°C for undoped, and 1029°C for 0.5 wt.% Al_2O_3 -doped 8YSZ, respectively. The lowest temperature of maximum densification rate (T_{max}) is obtained in 8Y-5A-3S as 1309°C. Meanwhile, the modeling study of 8YSZ containing co-additives demonstrates that, grain boundary diffusion dominates in the early stage of sintering, while the intermediate and final stage are ascribed to liquid-phase sintering.

The grain growth shows no systematic dependence on the doping composition of co-additives. This could be due to the influence of temperature on grain boundary wetting properties. However, in general, the grain growth is enhanced upon introducing of co-additives, and the largest grain size was also obtained in samples containing certain amount of both Al_2O_3 and SiO_2 .

7

Conductivity of 8YSZ containing Al_2O_3 and SiO_2 co-additives

7.1 Introduction

Ionic conductivity of a solid electrolyte, to a large extent, determines the operation temperature and power output of a SOFC stack, and thus it is a critical parameter for evaluation of the electrolyte materials. In polycrystalline electrolytes, the total conductivity is noted to come from both bulk and grain boundary conduction. Typically, the GB conductivity is 2 or 3 orders of magnitude lower than that of the grain interior [158].

The GB effect has been mainly attributed to two factors. Firstly, the SiO_2 impurity can be extremely detrimental to the grain boundary conduction, yet the existence of which is nearly ubiquitous. Badwal [21] found that the presence of only 0.2 wt.% silica was sufficient to decrease the GB conductivity of YSZ by a factor greater than 15. A number of studies have clarified that SiO_2 tends to segregate at triple grain junctions, instead of forming continuous layers along two-grain boundaries [92, 110, 159]. However, the segregation of Si^{4+} is commonly observed by high resolution TEM to segregate along grain boundaries [159, 159]. The blocking effect can be contributed by a reduction of direct grain-grain contact as well as Si^{4+} segregation. On the other

7.2 Conductivity of undoped 8YSZ

hand, it is noted that even in the high purity material, the intrinsic space-charge layer (usually several nm in thickness) would cause a reduced GB conductivity as compared to that of the bulk [110]. In YSZ electrolyte, the space-charge layer is formed by enrichment of Y^{3+} in the vicinity of grain boundaries, which results in the positive potential, and oxygen vacancies are depleted in the area.

Due to the ubiquitous existence of SiO_2 as well as the difficulty in tailoring of the intrinsic space-charge layer, more research efforts has been given to mitigating SiO_2 effect. Among various additives, Al_2O_3 is found effective in neutralizing the resistive siliceous phase [14, 102, 113]. Lee et al. [113] investigated the conductivity of ball-milled YSZ sample containing ≥ 120 ppm SiO_2 . The resistance per unit area was noted to decrease from $2.01 \Omega \cdot cm^2$ to $0.24 \Omega \cdot cm^2$ upon 1 mol.% Al_2O_3 addition. The improvement of GB conduction via Al_2O_3 owes to the fact that Al_2O_3 can effectively scavenge silicious film through chemical reaction [92]. It is worth to mention, however, the amount of Al_2O_3 additive should be carefully manipulated, as below the solubility limit, Al_2O_3 would increase the Schottky barrier height of the space-charge layer and considerably decrease the GB conduction [14, 103, 110].

To date, most of the conductivity studies used 8YSZ material with only background SiO_2 impurity or less than several hundred ppm SiO_2 addition [102]. However, we are more concerned about how effective Al_2O_3 can operate in impure (0.05 wt.% SiO_2) or highly impure 8YSZ (0.3 wt.% SiO_2), since the co-additive of Al_2O_3 and 0.05-0.3 wt.% SiO_2 was found capable to enhance the densification of 8YSZ. The electrical properties of the same batch of specimen as that fabricated in Chapter 6 was used in the present investigation.

7.2 Conductivity of undoped 8YSZ

A.C impedance spectroscopy was widely used for the study of the electrical properties of solid electrolyte. Fig. 7.2 shows the complex impedance spectra collected at 360°C and 402°C for undoped 8YSZ sintered at 1500°C. The inset figure illustrates the

7.2 Conductivity of undoped 8YSZ

corresponding equivalent circuits. With the decrease of frequency, three successive semicircles can be generated, which are deconvoluted as responses from grain interior, grain boundary, electrode-electrolyte polarization, respectively. In practice, however, whether all arcs can be observed is dependent on the nature of the samples and testing conditions. In our case, the grain interior and grain boundary components can be clearly identified, whereby both the values of resistance, R_{gi} and R_{gb} , and capacitance, C_{gi} and C_{gb} , are fitted with the equivalent circuits.

Figure 7.1: Impedance spectra of undoped 8YSZ (1300°C-2h) measured at 360°C and 402°C.

The conductivity was obtained by the relation of $\sigma_{gi/gb} = \frac{L}{R_{gi/gb}A}$, using the measured resistance, the sample thickness, L , and the cross-sectional area A . The calculated σ_{gb} in the present form refers to apparent or total grain boundary conductivity. Historically, the "brick layer model" [62] has been widely used for estimation of the true GB conductivity, i.e. the so called "specific GB conductivity" (σ_{gb}^{sp}). In the model, the material is assumed to consist of an array of cubic shaped grains with edge-length d_g , separated by flat grain boundaries of thickness δ_{gb} . The current flow through grain

7.2 Conductivity of undoped 8YSZ

boundaries in parallel to the current direction is neglected since always $\sigma_{gb}^{sp} \ll \sigma_{gi}$. According to the model, specific GB conductivity is expressed by,

$$\sigma_{gb}^{sp} = \sigma_{gb}^{app} \frac{\delta_{gb}}{d_g} \quad (7.1)$$

However, it is always difficult to determine the effective grain boundary thickness. Many researchers have suggested to compute σ_{gb}^{sp} from the capacitance [110, 160],

$$C_{gi} = \varepsilon_{gi} \varepsilon_0 \frac{A}{n d_g} \quad (7.2)$$

$$C_{gb} = \varepsilon_{gb} \varepsilon_0 \frac{A}{n \delta_{gb}} \quad (7.3)$$

where n is the number of grains to be trespassed in the current direction. In YSZ, it was demonstrated that the dielectric constant can be reasonably approximated to that of the bulk [161], hence, the thickness of grain boundary would be,

$$\frac{\delta_{gb}}{d_g} = \frac{\varepsilon_{gi}}{\varepsilon_{gb}} \frac{C_{gi}}{C_{gb}} \approx \frac{C_{gi}}{C_{gb}} \quad (7.4)$$

and accordingly, the specific grain boundary conductivity can be approximate as

$$\sigma_{gb}^{sp} \approx \sigma_{gb}^{app} \frac{C_{gi}}{C_{gb}} \quad (7.5)$$

The GI and GB conductivity of 8YSZ sintered at 1500°C for 2h were shown in Fig. 7.2 as a function of temperature, which was analyzed by the Arrhenius equation,

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{E_a}{kT}\right) \quad (7.6)$$

In Eq. 7.6, σ_0 is the pre-exponential constant, E_a is the activation energy, and k is the Boltzmann constant. The value from literature was also included in Fig. 7.2 as reference [106]. There is good agreement observed between our results and that from literature. Activation energies for GI and GB conduction are determined to be 1.05 eV and 1.20 eV, respectively, which is also close to that reported [87, 102]. The specific grain boundary conductivity is found to be 3 orders of magnitude lower than that of the GI, mainly due to the space-charge layer effect in the high-purity YSZ.

7.3 SiO₂-doped YSZ

Figure 7.2: Grain interior (GI), grain boundary (GB), specific GB conductivity of undoped YSZ (1500°C-2h) as a function of temperature; literature value from [58] is also included for comparison.

7.3 SiO₂-doped YSZ

The impedance spectra of YSZ containing SiO₂ impurity are shown in Fig. 7.3. Upon SiO₂ addition, the grain interior resistivity (ρ_{gi}) of 8YSZ was hardly affected. The only exception was for the sample 8Y-05S heat-treated at 1300°C, where the resistivity of which is 13.4 kΩ·cm comparing to 11.6 kΩ·cm of the undoped 8YSZ, which is due to its lower relative density (90.8%). However, the grain boundary conduction was noted to be significantly deteriorated, which was found to decrease by 57-76% when 0.3 wt.% SiO₂ was added, depending on the sintering temperature.

The dependence of GB conduction on heat treatment temperature also show some interesting features. At lower sintering temperature (1300-1350°C), GB conductivity decreases with the content of SiO₂ impurity. As the sintering temperature reaches above 1400°C, however, the samples containing 0.05 and 0.3 wt.% addition have almost the same GB conductivity. While on the other hand, GI conductivity was found to

7.3 SiO₂-doped YSZ

Figure 7.3: Impedance spectra of 8YSZ containing 0.05 and 0.3 wt.% SiO₂ sintered at 1300-1500°C for 2h. The data was recorded at 400°C.

7.3 SiO₂-doped YSZ

decrease slightly with the increasing SiO₂ content (e.g. 11.0 kΩ·cm for 8Y-05S vs 11.5 kΩ·cm for 8Y-3S at 1500°C). The observation can be well explained by the dissolution of SiO₂ into zirconia lattice with the increase of temperature. Tekeli et al. has also pointed out that up to 0.3 wt.% SiO₂ could dissolve into YSZ [23].

The grain boundary conduction of 8Y-3S was further analyzed by plotting the Arrhenius equation (Fig. 7.4). With the increase of temperature, both specific and total GB conductivity are found to increase, while the latter seems to be more sensitive to the heat treatment. The specific GB conductivity is strongly correlated with factors such as impurity segregation, space charge layer, lattice mismatch, and so on. In our case, it is inferred that the change of SiO₂ segregation status should be dominant factor. This is because at higher sintering temperature, most SiO₂ impurities could dissolve into the lattice [162], leaving a relatively “clean” grain boundary, and the blocking effect was hence mitigated. On the other hand, the increase of apparent GB conductivity is mainly due to the reduction of grain boundaries area, although it is also benefited by the increase of specific GB.

Figure 7.4: Apparent and specific GB conductivity of 8Y with 0.3 wt.% SiO₂ at different heat treatments.

7.4 YSZ containing Al₂O₃ and SiO₂ co-additives

7.4 YSZ containing Al₂O₃ and SiO₂ co-additives

Fig. 7.5 and 7.6 presents the impedance spectra collected at 400°C for all the specimen sintered at 1300°C-1500°C. The addition of SiO₂ alone considerably decreases the grain boundary conductivity, and details of which has been discussed previously. The background silica impurity of 8YSZ used in this study is around 70 ppm, as quoted from the supplier. All the figures confirm that Al₂O₃ is effective in mitigating the harmful effect of silicious phase, as the highest grain boundary conductivity is observed in “pure” 8YSZ containing 0.5 wt.% Al₂O₃ alone. The scavenging of SiO₂ by Al₂O₃ is ascribed to the chemical reaction of

where the reacted phase is mostly squeezed to the triple grain junctions during liquid phase redistribution process [22, 153].

However, we are more interested in how effective Al₂O₃ can neutralize the silicious effect in the impure (0.05 wt.% SiO₂) and highly impure (0.3 wt.% SiO₂) samples. The discussion will start from the impure sample with 0.05 wt.% SiO₂ impurity. From Fig. 7.5 and 7.6, it can be seen that when 0.5 wt.% Al₂O₃ is introduced into impure YSZ, the sample exhibits quite comparable conduction behavior as that of 0.5 wt.% Al₂O₃-doped “pure” YSZ. More importantly, the grain boundary conductivity was only slightly affected at all heat treatment temperatures. For instance, at a measurement of 400°C, GB conductivity of 8Y-5A is 3.43×10^{-4} S/cm, while it is 2.85×10^{-4} S/cm for 8Y-5A-05S sintered at 1400°C. It seems that 0.5 wt.% Al₂O₃ is adequate to neutralize the silicious effect, hence no further addition Al₂O₃ is attempted in the impure sample.

On the other hand, in the highly impure 8YSZ with Al₂O₃ additions, the situation is more complicated. There are several interesting findings. Firstly, except for the heavily doped 8Y-50A-3S, the grain interior conduction of 0.3 wt.% SiO₂-containing 8YSZ was hardly affected. However, the grain boundary conductivity is noted to be

7.4 YSZ containing Al_2O_3 and SiO_2 co-additives

Figure 7.5: Impedance spectra collected at 400°C for specimen sintered at (a) 1300°C-2h and (b) 1400°C-2h.

7.4 YSZ containing Al_2O_3 and SiO_2 co-additives

Figure 7.6: Impedance spectra collected at 400°C for specimen sintered at 1500°C for 2h.

lower than samples containing ≤ 0.05 wt.% SiO_2 , regardless of the content of alumina addition, even up to 5.0 wt.%. Secondly, the GB conductivity increases with Al_2O_3 content up to 1.0-2.0 wt.%, and further addition can deteriorate the GB conduction. Thirdly, the influence of Al_2O_3 is dependent on the heat treatment temperature. When sintered at 1300°C, the samples with 0.5-5.0 wt.% of Al_2O_3 addition all could achieve higher GB conductivity than the undoped 8YSZ, while the lowest ρ_{gb} is obtained in 8Y-10A-3S, which is 8.03 kΩ-cm, a reduction of 63.2% as compared to that of undoped 8YSZ. However, with the increase of sintering temperature, the total grain boundary conductivity decreases significantly. It was found that the value of σ_{gb} (8Y-10A-3S)/ σ_{gb} (8Y) decreases from 2.72 to 0.078 as temperature raised from 1300°C to 1500°C, which indicates that high temperature heat treatment should be avoided.

To address the observed phenomenon, the coverage fraction of the resistive silicious phase is evaluated by a factor defined as: $\alpha = R_{gb}/(R_{gi} + R_{gb})$ [87], where R_{gi} and R_{gb} represents GI and GB resistances, respectively. Fig. 7.7 shows the variation of α with sintering temperature. As expected, 8YSZ with only 0.3 wt.% SiO_2 addition has the

7.4 YSZ containing Al₂O₃ and SiO₂ co-additives

highest GB coverage fraction. When Al₂O₃ is introduced to the sample, the value of α is decreased significantly, which is also lower than that of undoped 8YSZ, indicating a relatively “clean” grain boundary can be achieved through the scavenging effect of Al₂O₃. However, as the temperature increases, α is noticed to increase considerably in the highly impure sample, which means that siliceous phase would propagate along grain boundaries at $\geq 1400^\circ\text{C}$. The GB coverage fraction in both 8Y-10A-3S and 8Y-20A-3S already exceeds that of undoped 8YSZ at 1400°C . On the other hand, in the 0.05 wt.% SiO₂-containing 8Y-05A-5S, α -value is still comparable to 8YSZ, indicating the harmful siliceous effect can be eliminated.

Figure 7.7: Variation of GB coverage fraction ($R_{gb}/(R_{gi} + R_{gb})$) with temperature.

The total conductivity (σ_{tot}) of specimen is shown in Fig. 7.8 as a function of measured temperature. In agreement with the previous impedance study, 8Y-5A-05S exhibit the identical total conductivity to that of undoped 8Y at all heat treatments. For the samples sintered at 1300°C , 1.0 wt.% Al₂O₃-doped highly impure sample also shows a comparable σ_{tot} to that of undoped 8Y. In fact, the total conductivity of

7.4 YSZ containing Al_2O_3 and SiO_2 co-additives

8Y-10A-3S is even higher than 8YSZ when measured at below 450°C . However, when the sintering temperature increases to 1400°C and above, σ_{tot} readily decreases below that of undoped 8YSZ in the highly impure sample.

Figure 7.8: Total conductivity dependence on temperature for the samples sintered for 2 h at (a) 1300°C , (b) 1350°C , (c) 1400°C and (d) 1500°C .

The significance of the finding lies in that, the co-addition of Al_2O_3 and SiO_2 could not only be able to significantly enhance densification of 8YSZ, but also be able to result in a comparable conductivity to that of undoped YSZ, provided the additive content and heat treatment condition are well manipulated. In fact, the purpose throughout the study is to fabricate YSZ electrolyte at reduced temperature. From the observations in this chapter, it can be reasonably expected that co-additive of 0.5 wt.% Al_2O_3 + 0.05 wt.% SiO_2 , or 1.0 wt.% Al_2O_3 + 0.3 wt.% SiO_2 are both capable of having superior overall performance than that of undoped 8YSZ, in respect of densification and conductivity.

7.5 Concluding remarks

7.5 Concluding remarks

The electrical properties of specimen containing Al_2O_3 and SiO_2 additives is investigated. As expected, the addition of SiO_2 alone could significantly deteriorate the grain boundary conductivity. Upon 0.3 wt.% SiO_2 addition, the total σ_{gb} of 8YSZ is decreased by 57-76% at 1300-1500°C heat treatment. The specific GB conductivity of SiO_2 -containing sample was evaluated by the brick layer model, which was found to increase with the sintering temperature. The phenomenon is explained by the dissolution of SiO_2 at higher temperatures ($> 1400^\circ\text{C}$).

In the impure 8YSZ containing 0.05 wt.% SiO_2 , 0.5 wt.% Al_2O_3 addition is sufficient to neutralize the silicious effect. The total conductivity of 8Y-5A-05S is comparable to that of undoped 8Y under any heat treatment. As the impurity level of SiO_2 increases to 0.3 wt.%, the optimum content of Al_2O_3 is determined to be 1.0-2.0 wt.% for mitigating the harmful effect of SiO_2 , while the heavily doped 8Y-50A-3S is noted to have both reduced GI and GB conductivity.

In addition, the conductivity of highly impure 8YSZ containing Al_2O_3 additions is closely dependant on the sintering temperature. With the temperature increases from 1300°C to 1500°C, the ratio of σ_{gb} (8Y-10A-3S)/ σ_{gb} (8Y) is found to decrease from 2.72 to 0.078, which is due to the propagation of silicious phase as well as a reduction in total grain boundary area.

Combining with the previous densification study, it is concluded that the existence of SiO_2 impurity is not as detrimental as the prevailing thought. On the contrary, by carefully varying the concentration of Al_2O_3 and SiO_2 , both densification and conductivity of 8YSZ can be enhanced. The concentration of co-additives is optimized as 0.5 wt.% Al_2O_3 +0.05 wt.% SiO_2 , or 1.0 wt.% Al_2O_3 +0.3 wt.% SiO_2 . Compared with undoped 8YSZ, the advantages of sample with co-additives would be more evident at lower heat treatment temperature.

8

Conclusions

Sintering of ceramics is an important process in the processing of many functional devices for advanced applications. For example, to fabricate high-performance SOFC in an economical way, co-sintering is widely acknowledged as the most suitable technique. When 8YSZ is applied as the electrolyte for SOFC, however, there are several practical concerns, i.e. higher sintering temperature of YSZ, unavoidable interdiffusion of NiO and ubiquitous presence of SiO₂ impurity. Directed by these problems, the present study has been carried out with attempt to lower the sintering temperature of YSZ, eliminate the negative effect of impurities, and more importantly, to establish models that could accurately predict microstructural evolution during sintering. Meanwhile, the effect of additives on conductivity of 8YSZ has been studied. Both experimental observation and theoretical approach in the present study have shed light to the optimizing of co-sintering technique for SOFC.

8.1 Master curves for undoped YSZ

The master sintering curve theory is adopted, and applied to undoped YSZ to establish both master densification curve (MDC) and master grain growth curve (MGGC). It was found that a better representation of the sintering behavior was provided by a two-stage MDC approach, i.e., MDCs are constructed separately over two consecutive

8.2 Sintering and modeling of $\text{Al}_2\text{O}_3/\text{NiO}$ -doped YSZ

densification stages with $\rho = 60\%$ as boundary. The newly proposed MDCs was verified by additional sintering experiments, where the good agreement between the model and experimental results was observed. Meanwhile, the activation energies during the two-stage densification are determined to be 715 KJ/mol and 580 KJ/mol during first ($\rho = 50 - 60\%$) and second stage ($\rho = 60 - 94\%$), respectively. Based on the activation energies evaluated, it is proposed that “defect-formation process” and surface diffusion have contributed to the abnormally high energy during the first stage, while lattice diffusion is proposed as the most appropriate operating mechanism for the second stage of sintering.

The grain growth behavior was also modeled via the construction of MGGC. The activation energy for grain growth was determined to be 330 KJ/mol, with the grain growth exponent of $n=2.3$, which suggests that grain growth of undoped 8YSZ is controlled by grain boundary migration.

8.2 Sintering and modeling of $\text{Al}_2\text{O}_3/\text{NiO}$ -doped YSZ

A comprehensive study has been performed in the sintering of 0.05-5.0 wt.% Al_2O_3 -doped and 0.06-2.76 wt.% NiO-doped 8YSZ, while the phase and microstructure were examined by XRD, SEM and TEM. The main conclusions of this part are:

1. Both Al_2O_3 and NiO are helpful in the stabilizing of cubic phase of zirconia. The solubility limit of Al_2O_3 and NiO was determined to be around 0.5 wt.% and 0.28 wt.% at 1400°C, respectively. As the content of additives exceed the solubility limit, excessive Al_2O_3 was found to cluster along grain boundaries. While undissolved NiO is not detected by both XRD and SEM observation, it is reckoned that undissolved NiO content is very little, since NiO dopant can be easily diffused or evaporate. However, the existence of undissolved NiO in YSZ can be confirmed by TEM. Both nano and micro-sized NiO crystals were found either within grain interior or along grain boundary.

8.3 8YSZ containing Al_2O_3 and SiO_2 co-additives

2. Both additives promote the densification of 8YSZ. The densification of 8YSZ was most effectively enhanced by the addition of 1.0 wt.% Al_2O_3 , or 0.28 wt.% NiO. Under the heating rate of $5^\circ\text{C}/\text{min}$, the temperature of maximum densification rate was reduced from 1345°C for undoped 8YSZ to 1243°C in 8Y100Al, and 1255°C in 8Y028Ni, respectively. In the heavily doped sample with $\geq 2.0\text{wt.}\%$ Al_2O_3 , or 2.76 wt.% NiO, the densification was observed to have been retarded.
3. Grain growth of 8YSZ was initially promoted by addition of Al_2O_3 up to 0.2 wt.%, and for NiO, up to 0.56 wt.%, while further addition leads to a decrease in grain size. Besides, compared to that of Al_2O_3 -doped 8YSZ, there are more pores present in the samples of 8YSZ containing $\geq 1.12\text{wt.}\%$ NiO, which is due to the diffusion/evaporation of NiO when sintered at high temperatures.
4. Master densification curves are constructed for doped samples for the first time. Similar to the case of undoped 8YSZ, the two-stage approach has shown to provide a better representation of the entire sintering process, indicating the dominant sintering mechanism have changed from the first ($\rho = 50 - 60\%$) to second stage ($\rho = 60 - 92\%$) of sintering.
5. Compared with that of undoped 8YSZ, the activation energy is found to decrease upon Al_2O_3 and NiO addition, especially in the second stage of sintering. In the doped sample, the first-stage is also ascribed to be “defect-formation process” controlled. However, as the sintering proceeds to the later stage, grain boundary diffusion become significantly contributing to the process, especially in the sample of 8Y100Al and 8Y028Ni.

8.3 8YSZ containing Al_2O_3 and SiO_2 co-additives

Sintering and conductivity of so called “impure/highly impure” 8YSZ with 0.05-0.3 wt.% SiO_2 impurity were investigated. It has been reported and confirmed by our results that SiO_2 alone is extremely harmful to the conductivity of 8YSZ. However,

8.3 8YSZ containing Al₂O₃ and SiO₂ co-additives

our results have also demonstrated that the disadvantage of SiO₂ contamination can be neutralized via the co-addition of Al₂O₃ with the optimized content. The densification of 8YSZ can be further enhanced by the synergistic effect of Al₂O₃ and SiO₂, as compared to samples containing Al₂O₃ alone. The onset of sintering is shifted from 1065°C in undoped 8YSZ to 988°C upon 1.0 wt.% Al₂O₃ and 0.3 wt.% SiO₂ co-additives. The lowest temperature of maximum densification rate (T_{max}) was obtained in 8Y-5A-05S as 1210°C, while it is 1248°C and 1243°C for 8YSZ with only 0.5 wt.% and 1.0 wt.% Al₂O₃, respectively.

Meanwhile, it was found that MSCs is not appropriate to apply to 8YSZ containing co-additives. Instead, alternative models were used, and grain boundary diffusion is found to be the dominant mechanism in the early stage of sintering, while the intermediate and final stages are ascribed to liquid-phase sintering.

The electrical properties of specimens containing Al₂O₃ and SiO₂ additives were also investigated. As expected, the addition of SiO₂ alone could significantly deteriorate the grain boundary conductivity. However, in the impure 8YSZ containing 0.05 wt.% SiO₂, 0.5 wt.% Al₂O₃ addition is sufficient to neutralize the silicious effect. The total conductivity of 8Y-5A-05S is comparable to that of undoped 8YSZ after heat treatment. The conductivity of highly impure 8YSZ (0.3 wt.% SiO₂) containing Al₂O₃ additions is closely dependant on the sintering temperature. With the temperature increases from 1300°C to 1500°C, the ratio of σ_{gb} (8Y-10A-3S)/ σ_{gb} (8Y) is found to decrease from 2.72 to 0.078. This is due to the propagation of silicious phase as well as a reduction in total grain boundary area.

With respect to both densification and conductivity, the optimum concentration of co-additives was identified as 0.5 wt.% Al₂O₃+0.05 wt.% SiO₂, or 1.0 wt.% Al₂O₃+0.3 wt.% SiO₂ for the present system. The advantages of 8YSZ with such composition would be more evident at lower heat treatment temperature.

9

Future work

The present work has provided both experimental and analytical insight to the sintering of undoped and doped 8YSZ ceramics, and also proposed appropriate models for the process. The conductivity of doped 8YSZ with co-dopants was also studied. Following the work accomplished in this study, there are several related topics that could be of interest for further investigation.

1. The densification behavior of undoped and Al_2O_3 and NiO-doped 8YSZ has been modeled by the master densification curve approach. With the established model, the instantaneous density of 8YSZ electrolyte can be predicted with good accuracy under the given heating profiles. Therefore, the established model can be applied to the co-sintering of NiO/8YSZ anode and 8YSZ electrolyte for evaluation of the stress, which is induced from the different shrinkage behavior of the individual layer [163]. Generally, a minimized stress is preferred to obtain a co-sintered system with certain flatness. This can be achieved by effectively engineering the sintering profile with the help of master curves approach. On the other hand, to gain a more continuous model for the co-sintering system, it is meaningful to incorporate the effect of stress into the master curves. A similar approach has been recently attempted by applying the master sintering curve theory to the field-assisted spark plasma sintering of alumina [164].

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2. The effect of NiO on sintering of 8YSZ has been studied, because the diffusion of NiO from anode side towards electrolyte has been frequently observed during co-sintering [17]. Although it is clear that the inter-diffusion of NiO would occur, the diffusion kinetics of NiO in 8YSZ has not been studied. Nevertheless, the relevant knowledge is important, as the present study has demonstrated that a small amount of NiO can significantly influence the entire sintering process of 8YSZ. The diffusivity of NiO in 8YSZ is suggested to be determined by secondary ion mass spectrometry (SIMS) analysis, as adopted by Kilo et al. in a wide range of tracer diffusion studies [120, 121].

A second issue that needs to be clarified is how the dissolved Ni^{2+} will interact with its surrounding environment, and thus change the bonding status of the host zirconia. In the case of Al_2O_3 -doped 8YSZ, there are a number of studies that have clarified the effect of Al^{3+} on the atomic level by the first-principle molecular orbital calculation, and pointed out that the incorporation of Al^{3+} into the lattice could weaken the ionic bonding strength between the host Zr^{4+} and oxygen ions [140]. However, there is a lack of theoretical verification regarding to the effect of NiO on zirconia lattice. It is speculated that the same mechanism might operate in the case of NiO-doped 8YSZ, while further investigation is required to confirm this effect.

3. In order to improve the reliability of 8YSZ-based functional device, the mechanical properties of 8YSZ have attracted great research effort [13, 144]. For example, a superplastic electrolyte is of great significance, as it allows a more flexible co-sintering process, as well as the fabrication of complex shapes of SOFC. It has been reported that the three phase YSZ- Al_2O_3 - SiO_2 system demonstrates improved superplastic behavior as compared to either YSZ- Al_2O_3 or YSZ- SiO_2 composite, and the strain rate of 8YSZ with 1.0 wt.% Al_2O_3 and 5.0 wt.% SiO_2 was obtained to be as high as $2 \times 10^{-4} \text{ s}^{-1}$ at 1200°C [144]. The finding implies that co-addition of Al_2O_3 and SiO_2 not only promotes densification of 8YSZ,

but also could increase ductility of 8YSZ. It is probably that both behaviors are closely related to the grain boundary diffusivity. A more comprehensive assessment is thus worth to be carried out.

4. The conductivity of 8YSZ with Al_2O_3 and SiO_2 additions has been demonstrated to be able to offer comparable conductivity to that of undoped YSZ. In practical application, long-term stability is important for evaluation of a solid electrolyte. The conductivity degradation of undoped and Al_2O_3 -doped YSZ has been extensively investigated. The origin of degradation has been ascribed to the following reasons: (1) precipitation of long-range ordered phases, such as $\text{Y}_2\text{Zr}_2\text{O}_7$, (2) formation and precipitation of tetragonal phase in the cubic zirconia, (3) segregation of dopant-rich layer near grain boundaries, (4) short range of ordering of oxygen vacancies [108]. However, it is unclear yet whether the mechanisms would operate in the present co-dopant system. Therefore, the relevant study on long-term stability of 8YSZ with Al_2O_3 and SiO_2 co-additive can be of significance.

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Declaration

I herewith declare that I have produced this paper without the prohibited assistance of third parties and without making use of aids other than those specified; notions taken over directly or indirectly from other sources have been identified as such. This paper has not previously been presented in identical or similar form to any other Singapore or foreign examination board.

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