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Constitutive Modeling of Densification of Nano-materials

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Abstract

Ultrafine grained ceramic components, which are normally obtained by sintering nano-sized powder, possess excellent mechanical properties. Homogeneous submicron and nano-scaled microstructure have been formed to greatly improve the strength and ductility of ceramic components. However, it is very difficult to fully densify the nano-sized ceramic powder compact by sintering while maintaining its nanostructure. Defects, such as pores, micro cracks and stress concentrations, easily occur during densification. To produce high quality submicron and nano structural ceramic components, advanced processing techniques are required. A full understanding of material intrinsic sintering behavior is thus necessary.

In the present work, constitutive models which describe the sintering of ultrafine grained ceramic powder have been developed. Unlike most modeling studies which discuss densification and grain growth separately, the present models couple densification and grain growth process in its prediction. The models are applied to study the densification mechanism of near nano-sized and nano-sized powder on both free sintering and sinter-forging process. Experimental data have been carefully collected on both near nano-sized alumina powder and nano-sized yttria stabilized tetragonal zirconia polycrystalline powder (3Y-TZP). Based on experimental results, activation energies have been calculated and several kinetic constants for current materials have been studied. The dominant densification and grain growth mechanisms at different sintering stages are also investigated. It is found that interface reaction controlled diffusion mechanism is appropriate to describe the densification process of both studied materials. It is also found that Du and Cocks grain growth model works well on the free sintering of both materials. However, it is not appropriate for sinter-forging process. Therefore, a stress incorporated grain growth function is developed, and the function is integrated into present interface reaction model to study the sinter-forging of 3Y-TZP material. Lastly, a more appropriate sintering stress expression for nano 3Y-TZP material is also proposed based on the experiment data.

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Chapter 1. Introduction

1.1 Background

Nano-technology has been one of the most attractive research topics in the last decade. The ultra-fine grained ceramic components, which can be also regarded as nano-structural ceramics, are getting more and more fascinating especially for mechanical and functional applications. These nano-structural ceramic components are generally produced by sintering of nano-sized powders. Theoretically, nano-sized powder compacts will be sintered to high density with relatively low temperature because of the high specific area and surface energy they possess. However, many challenges still exist in practice of this area. Among them, the lack of suitable constitutive laws to describe the sintering of ultra-fine grained materials is one of the essential issues. Detailed process control requires a full understanding of the material constitutive law governing the sintering process. Therefore, to develop a constitutive model to study the sintering of nano-sized materials becomes very timely.

The constitutive law of sintering is a series of mechanical equations which describe the relationship between stress and strain in microstructural evolution of powder compact when it is sintered. Normally, densification and grain growth will occur during sintering, and the microstructure of compacts will change greatly. This results in dramatically variation in stress field and strains. To develop a constitutive model for sintering study can provide both theoretical understanding and precisely quantity analysis, and thus provides a clear and direct way to study the complex sintering phenomenon.

In general, the sintering process can be divided into two distinct stages based on the microstructures. The first stage, or Stage 1 of sintering, represents the early stage where the pores form an interconnected network. The second stage, or Stage 2, refers to the later stage of sintering when the pores pinch off forming an array of isolated pores. In densification of powder compacts, several mechanisms are involved, where the exact operating mechanism depends on the sintering conditions such as temperature, pressure and material parameters such as grain size, packing condition

and purity of raw powder. For high temperature sintering of fine-grained materials, it is well accepted that diffusional mechanisms dominates the sintering process. Therefore, we focus firstly on the examination the constitutive relationship of diffusional mechanisms in the densification of nano-materials.

1.2 Objectives

In the present work, the most important goal is to determine the dominant mechanisms for both densification and grain growth processes for nano-material sintering. The constitutive densification models and grain growth models are employed, examined and developed to suit the present sintering study of nano-scaled ceramic powder. Based on the mechanism study results, the appropriate models will be adopted to investigate the sintering process of nano-sized ceramic materials for both stage 1 and 2 sintering. Several kinetic constants will be discussed during the modeling.

1.3 Scope

The present report is made up of eight chapters. In Chapter 2, an introduction for sintering related knowledge is given. This part introduces the sintering concept, sintering stages, sintering mechanisms and essential sintering parameters. In the latter part of this chapter, properties and processing technique of nano-materials are also reviewed. In Chapter 3, the constitutive model is introduced and discussed. At first, the concept of constitutive law is explained. Then, this chapter gives the detailed descriptions and expressions of constitutive modeling of two diffusional mechanisms, namely, grain-boundary diffusion and interface reaction. The grain growth model is also discussed. Some specific expressions for sintering parameters are also presented. In Chapter 4, the specific expressions of constitutive models proposed by other researchers for the two diffusional mechanisms are evaluated, and then combined with grain growth models to establish a constitutive model for free sintering of nano-material. Then experiments are designed based on a commercial near nano-sized (150 nm) alumina powders. With experimental data, the dominant mechanism is determined using the present constitutive model. Several kinetic parameters, such as activation energies, and rate constants, are calculated. In Chapter 5, the constitutive

model was applied to study the free sintering of a nano-sized (around 50 nm) 3Y-TZP powder. In Chapter 6, the same 3Y-TZP powder is sintered by sinter-forging and the constitutive model is developed with an additional variable, applied stress. With experiment data obtained from free sintering and sinter-forging, this chapter analyze the densification mechanism and grain growth mechanism by another view. In Chapter 7, an expression for sintering stress is developed to overcome the discrepancy between previous sintering stress expression and current modeling result. Chapter 8 gives the future work of the constitutive modeling study on nano-material sintering.

Chapter 2. Literature Review

2.1 Sintering

Sintering is the most widely used technique to fabricate ceramic components in modern industry. Normally, it is a heat treatment at 0.7~0.8 of the melting temperature of the materials, through which densification of powder compacts can be achieved and porosity can be eliminated. For bulk ceramic components, a structure with nearly full density is preferred because this always results in good mechanical properties. For example, when a ceramic material is 100% dense after sintering, the hardness and strength can approach its theoretical value; however, if the material is porous, such mechanical properties will be much lower. But in some cases, a porous structure is also favoured to achieve some functional properties, especially in biomedical applications.

2.1.1 Sintering phenomenon

Densification and grain growth are two major phenomena during sintering of bulk ceramic materials. Sometimes, phase transformation and recrystallization may also occur.

In densification, the density of a specimen, which equals to its mass per unit volume, increases with dwelling time and densification will cease when the specimen reaches the theoretical density (TD); volume shrinkage is obvious and porosity will be reduced and eliminated. Generally, a coarse-grained powder compact will densify more slowly than a fine-grained compact. However, it is also related to the way the particles are arranged in the starting powder compact. It may be possible that a poorly structured fine-grained powder compact reaches a lower limiting density than that of a better-packed coarse-grained powder compact.

Grain growth takes place simultaneously with densification during sintering. The average grain size of the specimen will increase continuously without changing the grain size distribution, and will increase with an accelerating rate when densification

ceases. As a result, some grains shrink and disappear to maintain the mass conservation. Thus, the total grain boundary energy decreases related to the loss of total grain boundary area. This energy loss is the driving force of grain growth. When the sintered body reaches its full density, the grain growth will slow down because the most grain boundaries form flat interface and the driving force for boundary migration is reduced.

It is shown that densification and grain growth are closely related to each other. This is mainly because both densification and grain growth are tightly bonded with the microstructure of powder compacts and affect the microstructure at same time. In many sintering studies, the rate of densification is suggested to depend on the current grain size and, at the same time, grain growth rate is also a function of the density. Du and Cocks [1] have proposed that when grain growth is slow, densification can proceed at a high rate in fine-grained materials, but when grain growth becomes significant and grain size increases rapidly, the rate of densification is reduced. Obviously, there is a relation between densification and grain growth during sintering.

In a broad sense, densification and grain growth phenomena can be explained as the result of mass transportation during sintering. The atoms from inner grains will transport onto the free surface, which is inner pore interface. This transportation results in an increase of neck area of two contacting grains and a decrease in distance between two grain centres, shown in Fig 2.1. When densification proceeds, two grains become closer, and the contact area becomes bigger. The adjacent particles may merge into one grain, resulting in grain growth. At the same time, porosity of the powder compact decreases because atoms deposit on free surface, and the total area of free surface decreases. In the scope of energy equilibrium, the macroscopic driving force of mass transportation is excessive free surface energy. At the beginning of sintering, there are so many free surfaces and the starting porous powder compact is far away from the energy equilibrium. After sintering, the inner pores are closed and the solid-gas interfaces (free surface) are replaced by the solid-solid interfaces. Thus, the total energy level of powder compact decreases and the density and strength of the powder compact increase following densification.

Fig 2.1: Neck between two contacting particles and atom diffusion in sintering process, given by two-ball model.

Deformation, such as shear deformation will occur when the sintered body is heterogeneous or there is an external pressure applied. Different extents of sintering among different regions of the powder compact will give rise to strain gradients and the associated shear stress may inhibit sintering. Shear deformation can also relax the residue shear stress. Therefore, deformation is an important process for sintering.

Sometimes secondary recrystallization occurs when a small fraction of the grains grow to a large size by consuming the uniform-grain-size matrix. Once a single grain grows to such a big grain that has many more surfaces than the neighbouring grains, the curvature of each face increases, and it grows much rapidly than the normal grain. Secondary recrystallization is particularly likely to occur when the impurities or pores hamper continuous grain growth. Secondary recrystallization affects both sintering and the resultant properties. For example, excessive grain growth, which is controlled by secondary recrystallization, is harmful to mechanical properties although it may improve some electrical and magnetic properties.

2.1.2 Sintering stages

Based on the experimental observations of Coble [2], following Ashby [3], Du and Cocks [1] identified four sintering stages during sintering, which is 1a, 1b, 2 and 3. The major characteristics of each of these stages are presented as follows: Stage 1a represents the early stages of sintering of loose packed particles with low initial relative densities (RD, which equals to measured density divided by theoretical density) when the pores form an interconnected network through out the material. As

the body sinters there is no change in the mean grain size. Stage 1b takes over from stage 1a at a low relative density of 0.6. The pore structure is the same as during stage 1a, but densification is now accompanied by grain growth. Stage 2 occurs during the later stage of sintering when the pores pinch off and form an array of isolated pores. In this stage the grains continue to grow as densification proceeds. The transition from stage 1b to 2 generally occurs at a relative density about 0.9 (this value may be different for different materials). Stage 3 intervenes when the migrating grain boundaries break away from the pores leaving them isolated inside grains. Densification virtually ceases at this point, but grain growth continues, often at an accelerated rate. To simplify, stage 1a and 1b are often combined together as stage 1.

2.1.3 Sintering mechanisms

As mentioned earlier, sintering is a process of mass transportation. To describe the way in which matter is transported, several mechanisms have been identified for solid-state sintering. They are: grain boundary diffusion (includes interface reaction), volume diffusion, evaporation-condensation, surface diffusion, dislocation creep, power-law creep and plastic yielding. These mechanisms can be classified into two groups: densification and non-densification mechanism, shown in Table 2.1.

Table 2.1: Densification and non-densification mechanisms.

	Sintering mechanism	Source of matter transportation	Sink of matter transportation
Densification mechanism	Grain boundary diffusion;	Grain boundary	Neck of contacting particles
	Interface reaction;	Grain boundary	Same
	Power law creep;	Volume of particle	Same
	Plastic yielding;	Volume of particle	Same
	Volume diffusion;	Grain boundary	Same
Non-densification mechanism	Surface diffusion;	Surface	Same
	Evaporation and condensation;	Surface	Same

Fig 2.2: Diffusion path for different sintering mechanisms on necks.

The substantial difference between mechanisms is different diffusion path or manner for atoms transportation, as shown in Fig 2.2. For example, grain boundary diffusion and interface reaction describes atoms mainly diffuse through grain boundaries from inner grain to free surface; however, for volume diffusion, atoms diffuse from lattice defects to free surface through grains. From the various paths that atoms can take, it is obvious that a continuous network of grains can only shrink when the matter is removed from the grains and deposited on the pore surface.

In grain boundary diffusion, grain boundaries are assumed to be perfect sinks of vacancy and sources of atoms and atoms diffuse along the grain boundaries to neighbouring pores and fill them. Thus, the grains move together to fill the space left by the migrated atoms which makes the centre of contacting particles closer. Densification occurs when pores shrink as the particle centres approach one other. Grain boundary diffusion mechanism is usually considered dominant in sintering of fine-grained ceramic materials.

The grain boundary diffusion model derived from the above mechanism claims that grain boundaries act as perfect sources and sinks for atoms during diffusion which leads to a linear relationship between strain rate response and stress. However, based on the experiment observations made by Arzt *et al.* [4], a nonlinear dependence of

strain rate and stress was found. A different creep rate and activation energy from continuum predictions, a nonlinear stress dependence of the creep rate, an unexpected dependence of creep rate and grain size, and a threshold stress below which no detectable creep occurs have been also found. The explanation for at least some of these discrepancies lies in the details that how a grain boundary acts as a sink or a source for transporting atoms. Some models suggested that a definite grain boundary structure could be disrupted if atoms were removed from or added onto it. It thus leads to the theory that the grain boundary surface is no longer the perfect sink or source for atoms; nevertheless, a divergence of diffusive flux of atoms can occur only at grain boundary defects, such as dislocation or interstice atom, which move in a non-conservative way on surface plane. In such situations, nonlinear relationships can arise from an interface reaction, where energy is expended mostly in the process of adding or removing atoms from grain boundaries. When this occurs, the whole densification process can be limited by this interface reaction because the interface reaction rate is much slower than diffusion rate, so localized interface reaction is more dominate rather than grain boundary diffusion in long-range. In the scope of nano-material sintering, the grain size is much smaller than normal material and the presence of excessive grain boundaries will lead to an extremely short diffusion path, which normally results in that interface reactions may become the controlling mechanism. Ma [5] has verified that the sintering mechanism of pure alumina material is interface reaction when grain size is less than 3 micron meter. The concept of interface reaction controlled grain boundary diffusion is not particularly new. Aspects of this idea have been developed by Ashby [6] and Burton [7]. Experimental studies by McCoy and Wills [8], Chen and Xue [9] and Besson and Abouaf [10] have also shown the importance of interface reactions during the sintering of fine-grained ceramic materials.

Volume diffusion, which is also called lattice diffusion, describes that atoms diffuse from lattice defects to the pores surfaces. Defects can introduce lattice vacancies, which facilitate diffusion through lattice. Dislocation creep can be also considered as a kind of volume diffusion, in which the defect is dislocation. Volume diffusion is much more important when the second component is added in the material system. Many observations have been made in this field, for example, Marshall *et al.* [11] reported that the addition of TiO_2 to ZnO increased the number of oxygen vacancies

and decreased the sintering temperature at which shrinkage could be observed in a powder compact of zinc oxide. It is deserved to take notice that although such an addition can introduce lattice vacancies and facilitate diffusion rate through the lattice, it seems unlikely to affect much on the structure of highly disordered grain boundaries.

When a pressure is applied to a powder compact, it is transmitted through the body of the powder compact, and acts as a set of forces applied to the particles contact regions. At first, the densification at these areas is elastic when the pressure is low. With increasing force when the pressure rises, these contact regions grow bigger with plastic yielding. Once the neck between two particles can support the forces without further yielding, a time dependent deformation process will determine the rate of densification. This phenomenon is also considered as power-law creep in the contact zones.

Surface diffusion is a general transporting mechanism that can produce smooth surfaces, particle joining and pores rounding. It is not a densification mechanism as mention in former section, because it does not lead to any decrease in the distance between particle centres. Although it does not increase the density of the powder compact, it can increase strength by enlarging the contact zones and reducing the notch effect of sharp pores.

Evaporation-condensation is another non-densification mechanism in which matter transports in gas phase by evaporation from the areas with large curvature and condense on those areas with smaller curvature. As a result, evaporation-condensation is neither a diffusion mechanism nor a densification mechanism. It is shown by Hwang and German [12] that its contribution in sintering is not significant because the evaporation temperature is usually near the melting point of materials, which is much higher than typically sintering temperatures.

2.1.4 Essential sintering parameters

Sintering potential

Sintering potential, which is also called sintering stress, is one of the fundamental parameters in the constitutive relationship of sintering. It is easy to notice that a powder compact will shrink obviously during sintering without any externally applied loading. Macroscopically, this volumetric shrinkage looks like to be created by an externally applied hydrostatic stress, which has the same effect on the deformation caused by densification, densification rate and other creeping rate when acting on grain boundaries and pores. Hence, to easily study this stress effect on creeping rates, the sintering potential is defined as an equivalent externally applied mechanical stress. This conception was first introduced by Raj and Bordia [13]. In their study, sintering potential was suggested to be induced by the surface tension. It is also noted that sintering potential arises from the change of the curvature of the pore surface, the internal surface and grain-boundary energy when densification occurs. As mentioned earlier, pores will be eliminated and the pore surface, which becomes interface, tends to become smoothened after densification, thus the surface energy will decrease dramatically after densification. The loss of surface energy is the driving potential for sintering, which indicates that sintering potential does not originate from any mechanical forces. Svoboda *et al.* [14] defined the sintering potential as the magnitude of a hydrostatic stress which can balance the internal surface tension so that the porous structure does not shrink. In fact, the sintering potential is not a real stress but an apparent stress that would give the same strain rate as if an actual stress is applied on sintered particles.

Activation energy

During sintering, heat treatment is necessary because densification itself requires energy to start. It can be explained that atoms need certain amount of thermal energy so that they can leave their equilibrium position and move to the surface of pores. This mass transportation cannot proceed unless atoms have enough energy to overcome the potential barrier and 'jump out' of their equilibrium position. Only a small fraction of the atoms have sufficient energy to move, so that a certain

magnitude of energy must be introduced for atoms to overcome the energy barrier in order to achieve macro-scaled densification. This part of energy is called activation energy. Activation energy is an intrinsic material characteristic, which means it is independent to process and condition, because of which it can be used to as a feature to estimate the dominant sintering mechanism.

Bulk viscosity and shear viscosity

In many constitutive models, the strain rate can be expressed as a product of viscosity and stress. Due to the stress space has principle stress and deviatoric stress, the viscosity also has bulk viscosity and shear viscosity correspondingly. The multiply of principle stress and bulk viscosity part provides volumetric (densification) component of total strain rate, and that of deviatoric stress and shear viscosity provides deviatoric (deformation) component. In this approach, the bulk viscosity and shear viscosity can be regarded as functions of density and grains size, which is interpreted as dimensionless functions. The dimensionless function is an essential variable to sintering study, which will be discussed in the later study.

2.2 Properties and processing of nano-grained ceramics

2.2.1 Motivation

In the past several years, a flourish of activity on research directed toward synthesizing and consolidating materials with nano-scaled dimensions has taken place. Although most of these works have been concerned with small clusters and compositionally modulated thin film for electro-optic devices, considerable interest has focused on synthesizing bulk nano-scaled structures in three dimensions. Motivation for this research is derived from several different considerations:

1. Nano-grained materials have a unique structure in that a large fraction of the atoms, about 5%-30%, are located on grain or interphase boundaries where their short-range order is far different than in the inner crystal. Consequently, the properties of these materials are expected to be different.

2. Nano-grained materials are interesting because of their small grain size, as many properties depend strongly on grain size. The mechanical properties, such as hardness and yield strength, are improved greatly for nano-grained materials.
3. Nano-sized particles are very helpful to synthesizing new composite structures on a nanometer length scale. During nano-sized powder synthesis process, different phases can be formed separately and then consolidated by mechanical means, thus many of the thermodynamic and kinetic constraints are relaxed, providing great flexibility in designing new materials.

2.2.2 Properties of nano-grained ceramics

Ceramics with grain size in the nanometer scale have received much attention in the last decade, as they possess promising functional and structural properties. The high specific surface area and the large amount of defects in nanocrystalline materials could lead to better catalytic or sensoric properties [15]. The small grain size and the large amount of grain boundaries could also provide excellent mechanical and thermo-mechanical properties, e.g. high hardness and super-plasticity. A reduction in the grain size to the nanometer level could provide 4~5 times increase in the strength and hardness over the coarse-grained ceramics. The increase in hardness and strength with a decrease in grain size can be explained by the Hall-Patch relationship as

$$H = H_0 + C \cdot d^{-1/2} \quad (2.1)$$

$$\sigma = \sigma_0 + C \cdot d^{-1/2} \quad (2.2)$$

where H is hardness with decreasing grain size d according to Hall-Patch relation, σ is the 0.2% yield strength and σ_0 is the lattice friction stress to move individual dislocations. Surprisingly, nano-grained bulk materials can possess high hardness and high yield strength concurrently, which are excluded from each other in coarse-grained materials. However, a contradictory reduction in hardness with decreasing grain size was reported for Cu and Pd and Ni-P samples by Lu *et al.* [16]. This phenomenon was widely investigated and now it is generally accepted that there exists a critical grain size in nanocrystalline materials above which the Hall-Patch relationship is valid and below which the relationship fails.

Since nano-grained ceramic materials have a very large fraction of atoms on grain boundaries, the numerous interfaces provide a high density of short range diffusion paths. Hence, they are expected to exhibit an extra diffusivity in comparison with coarse-grained ceramic materials with the same chemical composition [17]. This enhanced diffusivity has a significant effect on some mechanical properties, such as super plasticity and the ability to dope efficiently nano materials with impurities at relatively low temperature. Another important consequence of increased diffusivity is higher sinterability, which means full sintering of nano-sized ceramics powders can occur at lower temperatures compared with conventional powders. For example, starting with 10-30 nm Y-TZP powder, Gao *et al.* [18] obtained a 99% dense component after 5 hours sintering at 1050°C, which was nearly 400°C lower than that required to sinter the coarse-grained Y-TZP to the same density.

During the sintering of nano-sized ceramic powders, densification is very often accompanied with an accelerated grain growth, which always occurs when the density exceeds about 90% theoretical density. This is because the capillary forces for grain growth via surface diffusion and bulk diffusion become comparable in magnitude when the particle size reduces to nano-scale. Based on experimental observation and study on conversion from nano- to micron-sized structure using aluminium oxide and Sialon ceramics, Shen *et al.* [19] found a critical temperature T_g . Above T_g rapid grain growth takes place, while below T_g nano-sized powder can be fully densified with very limited grain growth. Although in their study, several T_g for different materials was found, the instinct relationship between temperature and grain growth has not been developed.

A critical issue of nanophase ceramics is their difficulty in processing. Large surface area gives rise to large inter-particulate forces compared to bulk force, hence results in unusual powder properties such as extreme low tap densities. As a result, the production of green bodies with high density needs special effort, such as elaborate wet chemical methods. High green density is thus necessary in order to control grain growth during sintering. On the other hand, lower green densities in the green compact can be remedied by application of pressure during the densification process. Another major problem in the processing of nanophase oxide powders is the existence of agglomerates, which is result of Van der Waal forces, which induces the formation

of relatively large interagglomerate pores during sintering, shown in Fig 2.3. While small inter-particle pores are easily closed and eliminated during sintering, large interagglomerate pores need high sintering temperatures or long sintering time to be eliminated. Pores exceeding a critical size will grow during sintering. There are basically two kinds of agglomerate: soft and hard agglomerates. The difference between them lies in the bonding force between the particles in the agglomerate. Soft agglomerates can be broken away during processing while hard ones cannot. So hard agglomerates must be reduced or eliminated as much as possible during the powder synthesis and processing steps.

Fig 2.3: Agglomerations in nano-sized powder.

One possible way to overcome this problem is the use of sinter-forging technique. In this process the large pores can be closed by the plastic deformation of the ceramic and as a result finer-grained sintered body can be obtained. Grain sizes of 60 nm and a density of 97% TD have been achieved [15], which is much lower than that for free sintered material at same density. Although sinter-forging technique is effective in closing the large interagglomerate pores, it is not an economic method. Thus, the large interagglomerate pores must be reduced as much as possible in green compacts during powder processing in common industries.

2.2.3 Synthesis of nano-sized ceramic powders

The synthesis of nano-structured materials from atomic or molecular sources depends on the control of a variety of “nanometer scale” attributes desired in the final products. To produce nano-scaled ceramic powders most of the techniques need a high density of nucleation sites in a gaseous or liquid medium. The formed small clusters have to

be removed rapidly from the supersaturated region, so that significant growth of individual particles can be avoided [20]. There are basically two major routes to produce nanoceramic powders: namely, physical method and chemical method. Physical method includes inert gas condensation and deformation. The inert gas method is to evaporate the precursor materials in the medium of inert gas and make atoms condense on the cold collector surface. The deformation method is to grind the coarse-grained powder using high-energy ball milling. During the milling, mechanical collision and shear deformation occur between particles, and the grain size will be reduced to nanometre scale finally. Compared with physical production, the primary advantage of chemical synthesis route is that it offers good chemical homogeneity, as mixing is performed at the molecular level. Commonly, nano-sized particles can be prepared by, MOCVD (Metal Organic Chemical Vapour Deposition), CVC (Chemical Vapour Condensation), CF-CVC (Combustion Flame-Chemical Vapour Condensation) or sol-gel method. Among these methods, MOCVD and CVC methods are promising for structural materials, due to possibility of mass-production of highly pure nano-sized particles with good uniformity in size. In the CVC and MOCVD processes, a chemical precursor is converted into the gaseous state and it then undergoes decomposition or chemical reaction at either low or atmospheric pressure to generate the nanostructural particles. These products are subjected to transport in a carrier gas and collected on a cold substrate, from where they are scraped and collected. The general procedure of sol-gel method involves reactions in aqueous or nonaqueous solutions containing the soluble or suspended salts under low temperature. Once the solution becomes supersaturated with the product, the precipitate is formed by either homogeneous or heterogeneous nucleation. The growth of the nuclei after formation usually proceeds by diffusion, in which case concentration gradient and reaction temperature are very important in determining the growth rate of the particles, for example, to form mono-dispersed particles. Synthesizing of nano-sized powder by sol-gel or thermo-precipitation way has become popular to avoid hard agglomerates [21].

2.2.4 Processing of nano-sized ceramic powders

As mentioned in previous section, due to the presence of agglomeration and low packing density, the densification of nano-sized ceramic powder is not easy and very

sensitive to powder processing procedures, which is normally referred to powder forming technique. In order to fully densify nano-sized ceramic powder, powder compact with high green density (density before sintering) and homogeneous microstructure must be prepared before sintering.

There are several methods to prepare green powder compacts, namely, die pressing, CIP (Cold Isostatic Pressing), pressure filtration, slip casting and gel casting. Among these techniques, die pressing is the most commonly used method due to its less constraint and convenience. CIP is similar to die pressing, except that the pressure transmitting media is liquid and the pressure applied is isotropic. However, die pressing and CIP method are not very effective in preparing compacts of nano-sized powder because of the presence of large inter-particle forces increase the resistance force for pressing. Also an inhomogeneous microstructure will easily occur, which will encumber the following densification. Other forming techniques, which are called the 'wet' shaping methods, such as slip casting, gel casting, pressure filtration and extrusion, have been widely adopted to obtain homogenous and dense powder compacts. These techniques have been proven to be superior compared with CIP and uniaxial pressing, with which the components with high density can be obtained at low cost and sintering temperature. As it is shown in Fig 2.4 [22], sintering temperature required for wet methods is much lower than those processed by 'dry' methods, *i.e.* CIP and uniaxial pressing. This will help to obtain finer grains and fewer defects in the sintered compacts. To provide homogenous microstructure is another important advantage of wet shaping methods, which is necessary in nanometer powder processing. This is because inhomogeneous packing of powders could lead to agglomeration, a vital defect for densification. All wet methods need a good casting body, or slurry, to make good sintering compacts. Slurry, which means a dispersion of ceramic powder in an aqueous solution, has a high solid content. In general, the slurry must satisfy the following conditions to produce dense and homogenous green bodies. They are: (1) low viscosity, (2) high solid content, (3) good dispersion and (4) complete degas [22]. Low viscosity is required to maintain a relative high casting rate, which means the gypsum mold has high absorb water rate. Furthermore, low viscosity is necessary to avoid casting layer, which is caused by 'sticky' slurries. Particle distribution is another important variable for nano-sized powder compact. Narrowly distributed particle size is favoured because it will lead to a narrower distribution of

grain size after sintering without abnormally grain growth. Thus, in a colloid aqueous system, uniformly dispersed solution is most important, which provide a narrow particle size distribution, pore size distribution and weak agglomeration.

Fig 2.3: Sintering temperature required for different processing methods [23].

In general, further electric-chemical and rheological analysis of the colloid aqueous system is needed to ensure a homogeneous final powder compact. If a dispersant is added into slurry, the dispersant molecules tend to adsorb on the surface of ceramic particles. The particle together with its adsorbed layer consist an effective particle, which represents the actual particle size in an aqueous system, shown in Fig 2.5 [24]. High solid content is preferred to produce slurries with small effective particle size. The smaller the effective particle size, the closer the compaction, the finer the grain size after sintering. The *Zeta*-potential, which describes the ability for a particle absorbing the neighbouring solution or particles with electric charges in slurry, must be studied. The study on pH value of the slurry is also needed because it is closely related to *Zeta*-potential. According to the Robert's report [25], the *Zeta*-potential of several ceramics slurry were measured with electroacoustic method. The relationship between the *Zeta*-potential and pH value was then discovered for alumina slurry. It is shown in Fig 2.6 [25], the *Zeta*-potential reaches it maximum when pH value is between 3.5~4.0 and at lowest point when pH value is 11~12. It was also reported by Yuji *et al.* [26], that adding organic deflocculates could help to obtain slurries with good characteristics. The sugar alcohol, oligosaccharide alcohol, was adding together with PMMA into alumina slurry. This organic material increased the particle absorbing ability of PMMA thus enhanced the *Zeta*-potential of the slurry. It was

shown that the oligosaccharide alcohol improved the efficiency of PMMA in alumina slurry.

Fig 2.4: Effective particles made by dispersion of nano powder in slurry.

Fig 2.5: Zeta-potential values at different pH for alumina slurry [25].

In the development of consolidating nano-sized ceramic powder into fully dense material, normal pressureless sintering does not appear able to fully densify powder compacts while maintaining a nanocrystalline grain size. However, sinter-forging technique has been shown to be quite effective in achieving fully densification without significant grain growth. Sinter-forging is the simultaneous densification and deformation under a uniaxial stress. During sinter-forging at an elevated temperature, pores of porous ceramic powder compact will be pressed flatten, and the contact area between particles will be enlarged. Thus the rate of atoms diffusion is enhanced which

is helpful for densification. Based on the experiment observation, sinter-forging is not only effective in limiting grain growth but also in reducing the sintering temperature at which fully densification can be achieved.

Chapter 3. Constitutive Laws

In this chapter, a general introduction on constitutive law for sintering is given. The specific expressions of constitutive model are also discussed. Based on the sintering mechanism definition, constitutive densification models for grain boundary diffusion and interface reaction are derived.

3.1 Constitutive laws

In the scope of solid mechanics, to get a definite status of object requires solving three sets of equations: the equation of equilibrium, the equation of compatibility and a constitutive law. The constitutive law describes the relationship between stress and strain. Clearly, the first two equations are independent of a particular material, while the influence of the materials can be expressed by the constitutive law. In this section, the origin of constitutive law was given on the basis of solid mechanics. Then the development of constitutive law in densification study was introduced.

3.1.1 Strain and stress tensor

In a three dimension Cartesian coordinate, the stress and strain can be defined as stress tensor and strain tensor. The stress tensor has nine components as

$$\sigma = \begin{Bmatrix} \sigma_x & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & \sigma_y & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & \sigma_z \end{Bmatrix} \quad (3.1)$$

where $\sigma_x, \sigma_y, \sigma_z$ is principle stresses and others are shear stresses. Correspondingly, the strain tensor also has nine components, it can be expressed as

$$\varepsilon = \begin{Bmatrix} \varepsilon_x & \gamma_{xy} & \gamma_{xz} \\ \gamma_{yx} & \varepsilon_y & \gamma_{yz} \\ \gamma_{zx} & \gamma_{zy} & \varepsilon_z \end{Bmatrix} \quad (3.2)$$

where $\varepsilon_x, \varepsilon_y, \varepsilon_z$ is normal strains in principle direction, and others are shear strains.

3.1.2 Constitutive equations

Constitutive law is an equation that describes the relationship between strain (strain rate) and stress tensor of solid materials. Due to different deforming characteristic of solids, constitutive law normally has several approaches, which are elastic approach, plastic approach and viscous approach. In the elastic approach, the stress can be expressed as a product of elastic constant tensor and strain tensor as

$$\sigma_{ij} = E_{ijkl} \cdot \varepsilon_{kl} \quad (3.3)$$

However, the constitutive relationship of a plastic approach is far more complicated, in which the strain rate is a function of stress, grain size and density.

$$\dot{\varepsilon}_{ij}^p = \dot{\varepsilon}_{ij}^p(\sigma, \rho, L) \quad (3.4)$$

For ceramic materials, because the deformation of ceramic materials is both elastic and plastic, the constitutive relationship is always expressed in the viscous approach, in which total deformation rate consists of elastic strain rate $\dot{\varepsilon}_{ij}^e$ and plastic strain rate $\dot{\varepsilon}_{ij}^p$.

$$\dot{\varepsilon}_{ij} = \dot{\varepsilon}_{ij}^e + \dot{\varepsilon}_{ij}^p \quad (3.5)$$

In many sintering studies, such as Hsueh *et al.* [27], Cocks [28], it is generally observed that the inclusion of the elastic strain rate does not influence the analytical results significantly, especially for the case where the creep (plastic) deformation is large. Therefore, the elastic strain rate can be ignored when analyzing the densification of ceramic materials.

$$\dot{\varepsilon}_{ij} = \dot{\varepsilon}_{ij}^c(\sigma, \rho, L) \quad (3.6)$$

3.1.3 Development of constitutive model for sintering study

From the last decade, many research interests have been focused on developing constitutive model to study sintering. The model not only can be applied to describe and integrate the whole process of densification including grain growth, but also provides great industrial valuable prediction before a sintering process is designed. It is noted that, a number of constitutive laws have already been proposed for the sintering process of engineering materials. These models can be generally divided into two groups, namely, empirical models and micromechanical models. The empirical models, which assume basic forms of the constitutive law and follows by validation

with suitable experiments. The basic forms used might be guided by certain assumptions about the mechanisms of deformation and densification and no detailed modeling of the mechanism is undertaken. On the contrary, micromechanical constitutive laws originate from the way in which the microstructure evolves during the sintering process. Unlike empirical models, these models provide specific forms of relationship, which can be compared with and calibrated against experiment data. Thus far, different forms of micromechanical constitutive laws have been proposed for different mechanisms and different sintering stages. As far as the methodology of developing constitutive model is concerned, there are two different distinct philosophies: the microscopic approach and macroscopic approach. In the microscopic approach, the local behaviour of the particle neck is considered. The various mechanisms of densification are analysed in terms of a single particle and its surroundings. Densification-rate equations are then obtained. On the basis of the densification-rate equations, the density and final shape of components, as well as their variations with time, temperature and pressure, can be predicted. In the macroscopic approach, porous powder compacts are regarded as continuous bodies. By modifying the plasticity theory for solid materials, constitutive equations, which describe the macro-scale deformation behaviour of porous materials, can be established. Solving these equations for the processing conditions will provide information on the density distributions and final shape of the sintered components.

Norton [29] had described the first relationship between strain-rate and stress of a fully dense crystalline material under uniaxial load when materials creep. In 1945, Frenkel [30] firstly proposed a model for the sintering of viscous materials. Since then, many efforts to understand sintering mechanisms had been attempted. From 1983 to 1990, Ashby *et al.* [3] had developed micro-mechanical models for densification under simple applied stress states. He also divided the process of densification into two stages as mentioned in early section, and the classical work by Ashby and co-workers has since formed the basis of the micromechanical constitutive modelling for sintering. Frost *et al.* [31] also obtained a constitutive model by combining the models of Nabarro-Herring for volume diffusion and that of Coble for grain-boundary diffusion in 1982. The general constitutive relationships for deformation and densification for both stage 1 and 2 sintering, in which grain-boundary diffusion is dominant mechanism, had been obtained by Swinkels *et al.* [32], Helle *et al.* [33] and

McMeeking and Kuhn [34]. Based on the sintering mechanism, Swinkels and Ashby provided the rate equations for the grain-boundary diffusion mechanism and the corresponding sintering diagrams were also constructed [32]. These diagrams can be applied to predict some sintering process. To develop the HIP diagram, Helle *et al.* [33] simplified and clarified the equations and procedures for constructing HIP diagram. This simplification and modification allows for the computation of diagrams in a fast, straightforward way and lead to good agreement between theoretical prediction and experimental data for copper, steel and alumina. Later, McMeeking and Kuhn [34] had modelled the creep behaviour of powder due to mass diffusion on the interparticles contact area. In their work, a constitutive law, which is for the grain-boundary diffusion of powder aggregate bonded together by isolated contact region, was developed. Nevertheless, the model predicted that the bulk and shear viscosities are zero at random close packing and increase with relative density of the powder compact. The densification rate is predicted to be infinite at random close packing and will decrease as the relative density rises. It is also noted that in fine-grained materials, diffusion can be limited by interface reactions when grain boundaries no longer act as perfect sources and sinks for vacancies. This opinion was supported by a number of studies. Performing a lot of experiment of sintering alumina ceramic, Canon, Rhodes and Heuer [35] had suggested that in fine-grained ceramic materials with low pressure applied, the grain boundaries can neither operate as complete sources and sinks for vacancies nor slide easily, and diffusional deformation becomes mainly interface-controlled.

In constitutive modeling of sintering, grain size and density are two important state variables. On Shewon *et al.* [36] studies of grain growth, they analysed the dragging effect of an array of spherical pores on a migrating grain boundary in 1964. Hillert [37] modelled the process of grain growth in fully dense materials. These analyses were combined by Brook [38] and Yan *et al.* [39] to provide a set of equations for grain-growth during Stage 2 of sintering, and to define the condition under which the pores break away from the grain-boundaries. Brook indicated that grain growth is based on migration of pores, migration of solid solution impurities, or coalescence of a second phase, and the interactions between pores and grain-boundaries are functions of pore size and grain size. Yan *et al.* [39] had also suggested that, at any porosity level, a minimum intrinsic and solute drag force on the grain boundary is required to prevent

pore separation and that this drag force is affected by the grain size distribution. The analyses of Shewon [36], Hillert [37], Brook [38] and Yan *et al.* [39] can be considered as the basic work for study on grain growth. In 1998, Zhao and Harmer [40] developed a model to examine the interaction between grain growth and densification during Stage 2, taking into account the effect of the variation of pore size in the compact. The model predicted that increasing the number of pores per grain unit could increase the densification rate, the grain growth rate, and the relative density densification rate to grain growth rate ratio. Narrowing the pore size distribution was also predicted to result in inhibition of grain growth initially and to increase the densification rate indirectly.

In the last decade, Cocks and co-workers [41], [1], [42], [43] examined the structure of constitutive laws and developed a general framework of constitutive models for the sintering of fine-grained materials for situations where power-law creep, grain-boundary diffusion and interface reaction are dominant mechanisms of deformation and densification. In their studies, the material response is expressed in terms of scalar stress and strain-rate potentials. General bounds have been developed for these potentials, which incorporate a description of the coupling relationship between the different mechanisms. The parameters of the material can be expressed in terms of two internal state variables, relative density and grain size. The relationships for densification and deformation were derived from the work of Needleman and Rice [44], Arzt *et al.* [45], Helle *et al.* [33], Hsueh *et al.* [46], Ashby [47], McMeeking and Kuhn [34]. The relationships for grain growth were developed from the studies of Shewmon [36] and Ashby [47]. The full range of models was used to analyse the response of inhomogeneous sintering and HIP to determine the material response. The models proposed by Du and Cocks [1] were micro-mechanical models that were obtained from both macroscopic and microscopic approaches. Unlike empirical models, these kinds of constitutive models are based on rigorous mathematical deduction and objective physical examination. These models critically succeed the outcomes obtained by other researchers and they are the quintessence of the constitutive laws for sintering. Almost all the sintering mechanisms were dealt with by the models, such as power-law creep, grain boundary diffusion and interface reaction. Although they are simple in form, the models can give detailed description of the evolution of the materials during sintering. Furthermore, one feature of the

stated models is that the state variables occurred in the models, such as grain size and relative density, can be obtained from experiments. Therefore, the constitutive models proposed by Cocks and co-workers are considered to be the most appropriate models and are selected to form the basis of the present work.

3.2 Constitutive equations for densification

The first constitutive equation used to describe the relationship of strain rate between stress when the powder compact is under a uniaxial load is give by Norton in 1929 [29]. The strain rate $\dot{\epsilon}$ can be experssed as an exponetial function of stress σ , can be described by the constitutive law as

$$\dot{\epsilon} = \dot{\epsilon}_0 \left(\frac{\sigma}{\sigma_0} \right)^n \quad (3.7)$$

where $\dot{\epsilon}_0$ is the strain rate at a given stress σ_0 , and n is the creep exponent, which depends on the deformation mechanism. For the case of a multiaxial stress state, Eq 3.7 becomes [1]

$$\dot{\epsilon}_{ij} = \frac{3}{2} \dot{\epsilon}_0 \left(\frac{\sigma_e}{\sigma_0} \right)^{n-1} \frac{S_{ij}}{\sigma_0} \quad (3.8)$$

where σ_e and S_{ij} are Von Mises effective stress and deviatoric stress tensor respectively, and they satisfy the relationship

$$\sigma_e = \sqrt{\frac{3}{2} S_{ij} S_{ij}} \quad (3.9)$$

The deviatoric stress tensor can be expressed as

$$s_{ij} = \sigma_{ij} - \sigma_m \delta_{ij} \quad (3.10)$$

and

$$\sigma_m = \frac{1}{3} \sigma_{kk} = \frac{1}{3} (\sigma_1 + \sigma_2 + \sigma_3) \quad (3.11)$$

Where $\sigma_1, \sigma_2, \sigma_3$ are principle stress, σ_m is the mean stress and δ_{ij} is the Kroneker delta, which

$$\delta_{ij} = \begin{cases} 0 & (i \neq j) \\ 1 & (i = j) \end{cases} \quad (3.12)$$

If the material body is porous, the constitutive relationship turns out to be more complicated. This is because the creep response of the compact not only has a

deviatoric component, but also a volumetric component. Thus the material compact would both deform and densify when loaded.

Densification and deformation have long been recognized as fundamental processes that occur during the sintering of materials. Deformation occurs when a uniaxial stress is applied to the component. As a result, models for the sintering processes must take into account the volumetric strain rate as well as the shear strain rate. For deformation, a parameter, termed the von Mises effective strain rate, $\dot{\epsilon}_e$, is introduced to indicate the extent of shear deformation. Volumetric strain rate and effective strain rate can be expressed as

$$\dot{\epsilon}_v = \dot{\epsilon}_{kk} \quad (3.13)$$

and

$$\dot{\epsilon}_e = \sqrt{\frac{2}{3} \dot{\epsilon}_{ij} \dot{\epsilon}_{ij}} \quad (3.14)$$

where $\dot{\epsilon}_{ij}$ is deviatoric strain-rate tensor, which is related to strain rate

$$\dot{\epsilon}_{ij} = \dot{\epsilon}_{ij} - \frac{1}{3} \dot{\epsilon}_{kk} \delta_{ij} \quad (3.15)$$

Based on the state analysis of stress and strain rate, the mean stress, effective stress, volumetric strain rate and effective strain rate can be expressed

$$\dot{\epsilon}_v = (\dot{\epsilon}_1 + \dot{\epsilon}_2 + \dot{\epsilon}_3) \quad (3.16)$$

where the subscripts 1, 2 and 3 refer to the principal components of the strain rate and the stress tensors.

In 1994, Cocks [41] examined the general structure of constitutive laws for the sintering of fine-grained materials and analyzed three mechanisms of densification in detail: power-law creep, grain-boundary diffusion, and interface reaction. Based on his work, it is convenient to describe the creep response in term of the strain-rate potential, ϕ , which is a function of the applied stress σ_{ij} , and a stress potential, φ , which is a function of strain-rate $\dot{\epsilon}_{ij}$. These two potentials are related to each other in the following manner

$$\sigma_{ij} \dot{\epsilon}_{ij} = \phi + \varphi \quad (3.17)$$

Kinetic and statical bounds have been developed for these potentials, which provide a systematic method of developing constitutive laws for the sintering process.

Differentiation of Eq 3.19 gives

$$\sigma_{ij} = \frac{\partial \phi}{\partial \dot{\epsilon}_{ij}} \quad (3.18)$$

and

$$\dot{\epsilon}_{ij} = \frac{\partial \phi}{\partial \sigma_{ij}} \quad (3.19)$$

For fully dense material, the detailed forms of the strain-rate potential and stress potential can be obtained from Eq 3.8 as

$$\phi = \frac{1}{n+1} \dot{\epsilon}_0 \sigma_0 \left(\frac{\sigma_e}{\sigma_0} \right)^{n+1} \quad (3.20)$$

and

$$\varphi = \frac{n}{n+1} \dot{\epsilon}_0 \sigma_0 \left(\frac{\dot{\epsilon}_e}{\dot{\epsilon}_0} \right)^{\frac{n+1}{n}} \quad (3.21)$$

Most ceramic powders show high yield strengths at room-temperature. Even at high temperature, ceramic powders hardly deform nor densify by plastic deformation, so time independent plastic deformation of a ceramic powder is not usually considered, proposed by Kown and Kim [48] [49]. Therefore, the component is regarded as densifying by creep. If the total strain rate is identified with the symmetric part of the deformation-rate tensor, then the general structure of the constitutive relationship can be written as

$$\dot{\epsilon}_{ij} = \dot{\epsilon}_{ij}^e + \dot{\epsilon}_{ij}^c \quad (3.22)$$

where $\dot{\epsilon}_{ij}^e$ and $\dot{\epsilon}_{ij}^c$ are the elastic and inelastic (or creep) strain rates. The elastic strain rate can be expressed as

$$\dot{\epsilon}_{ij}^e = C_{ijkl} \dot{\sigma}_{kl} + \dot{C}_{ijkl} \sigma_{kl} \quad (3.23)$$

where C_{ijkl} is the elastic compliance matrix, σ_{ij} represents the true or Cauchy stress and $\dot{\sigma}_{ij}$ is the Jaumann rate of Cauchy stress. The second term in Eq 3.23 takes into account the change of the elastic compliance matrix with relative density, that is

$$\dot{C}_{ijkl} = \dot{\rho} \frac{\partial C_{ijkl}}{\partial \rho} \quad (3.24)$$

In creep and sintering studies, it is generally observed that the inclusion of the elastic strain rate does not influence the analytical results significantly especially for the case where the creep deformation is large. Therefore, the elastic strain rate can be ignored when analyzing the densification. The plastic strain rate of the material during sintering is a function of applied stress, relative density and grain size

$$\dot{\epsilon}_{ij}^c = \dot{\epsilon}_{ij}^c(\sigma, \rho, L) \quad (3.25)$$

The densification rate can be determined as

$$\dot{\rho} = -\rho \dot{\epsilon}_v \quad (3.26)$$

where $\dot{\epsilon}_v$ is the volumetric strain rate.

The structure of this constitutive law of densification can be employed to describe any of the mechanistic models relating to the sintering process. For a fixed sintering mechanism and sintering stage, governing equations could be selected according to this framework.

It is now widely accepted that there are a number of possible mechanisms for the densification of a powder compact. In a given sintering experiment, it is possible for the dominant mechanism to change as the material densifies and, therefore, for the form of constitutive relationship which describes the response to also change. Ashby *et al.* [3] have identified the different mechanisms of the densification during sintering and developed micro-mechanical models for simple applied stress states. Subsequently, constitutive models for arbitrary stress states have also been developed for the various mechanisms by Fleck *et al.* [50], McMeeking *et al.* [34], Duva *et al.* [51]. In an attempt to verify the constitutive laws developed by these authors, Liu *et al.* [52] and Kwon *et al.* [53] have performed experimental studies on porous alumina. At high homologous temperature, densification can proceed by power-law creep or the direct diffusional transport of the material. It was also shown that at low pressure and in fine-grained materials, diffusional mechanism tends to be favoured. In most situations, grain-boundary diffusion is considered to be the dominant mechanism of deformation sintering and void growth. In fine-grained materials, classical diffusion models tend to over predict the rate of deformation and sintering. These classical models assume that internal surfaces and grain boundaries act as perfect sources and sinks for the diffusing species. However, in practice, some of the work which drives

the overall diffusion process must be used to drive the sources and sinks [41]. As the diffusion distance becomes smaller, an increasing proportion of the work is used to drive the sources and sinks. As a result, in fine-grained materials, it is the rate at which the sources and sinks operate that determine the overall rate of process. We refer to this limit as interface reaction controlled sintering. It is evident from the above discussion that we can identify two limiting situations, where either grain-boundary diffusion or an interface reaction dominates the response. Based on the research aim, the constitutive laws under grain-boundary diffusion and interface reaction dominance are described below.

3.2.1 Grain-boundary diffusion controlled sintering

Grain-boundary diffusion is one of the mechanisms contributing to the densification of ceramic powders and it can be regarded as the most important densification mechanism under certain conditions.

The analysis of a grain-boundary diffusion controlled process tends to be more straightforward as the strain rate has been described as a linear response of stress. Therefore, constitutive models of a grain-boundary diffusion controlled sintering have been investigated extensively. Numerical schemes and models have been described by many researchers, they are: Swinkels and Ashby [32], Nichols and Mullins [54], German and Lathrop [55], Bross and Exner [56] Exner [57], Riedel and Svoboda [58], Zhang and Schneibel [59], and Pan and Cocks [42] [43]. While Riedel *et al.* [58] have discussed how finite element procedures for steady state heat conduction problems can be used for the analysis of kinematically determinate situations, McMeeking and Kuhn [34], Du and Cocks [1], and Cocks [41] have developed models and employed them in the development of constitutive laws for the sintering of materials.

When grain-boundary diffusion is the controlling sintering process, Cocks gave the stress potential and strain-rate potential as

$$\varphi_b = \frac{1}{2} \dot{\epsilon}_{0b} \sigma_0 \left(\frac{L}{L_0} \right)^3 \left[\frac{1}{c_b(\rho)} \left(\frac{\dot{\epsilon}_e}{\dot{\epsilon}_{0b}} \right)^2 + \frac{1}{f_b(\rho)} \left(\frac{\dot{\epsilon}_v}{3\dot{\epsilon}_{0b}} \right)^2 \right] \quad (3.27)$$

and

$$\phi_b = \frac{1}{2} \dot{\epsilon}_{0b} \sigma_0 \left(\frac{L_0}{L} \right)^3 \left[c_b(\rho) \left(\frac{\sigma_e}{\sigma_0} \right)^2 + 9 f_b(\rho) \left(\frac{\sigma_m - \sigma_s}{\sigma_0} \right)^2 \right] \quad (3.28)$$

for both Stages 1 and 2, where the subscript ‘b’ indicates grain-boundary diffusion controlled sintering. $\dot{\epsilon}_{0b}$ is the uniaxial strain rate under an applied stress σ_0 for a fully dense material of grain size L_0 . $f_b(\rho)$ and $C_b(\rho)$ are dimensionless functions of the relative density, and σ_e , σ_m and σ_s are effective stress, mean stress and sintering potential respectively.

By differentiating the strain-rate potential with respect to the effective stress, σ_e , and mean stress, σ_m , respectively, the expressions for the effective and volumetric strain-rates of the material can be obtained as

$$\dot{\epsilon}_e = \frac{\dot{\epsilon}_{0b}}{\sigma_0} \left(\frac{L_0}{L} \right)^3 c_b(\rho) \sigma_e \quad (3.29)$$

and

$$\dot{\epsilon}_v = 9 \frac{\dot{\epsilon}_{0b}}{\sigma_0} \left(\frac{L_0}{L} \right)^3 f_b(\rho) (\sigma_m - \sigma_s) \quad (3.30)$$

3.2.2 Interface reaction controlled sintering

Based on a uniaxial creep law of Arzt *et al.* [4], Besson and Abouaf [60] [61] [10] have developed an empirical model of interface reaction controlled sintering for general multi-axial loading. Adopting a micromechanical approach, Cocks [41] extended a variational principle originally proposed by Needleman and Rice [62] for the analysis of grain-boundary diffusion to include the effect of an interface reaction. In a more recent review, Pan and Cocks [42] [43] have further developed constitutive models for situations where an interface reaction controls the rate of sintering in terms of scalar potential functions for both stage 1 and stage 2.

Following Cocks’ works [41], the stress potential and strain-rate potential in stage 1 for interface reaction controlled sintering, can be written as

$$\varphi_r = \frac{2}{3c_r(\rho)f_r(\rho)} \dot{\varepsilon}_{0r} \sigma_0 \sqrt{\frac{L}{L_0}} \sqrt{f_r^2(\rho) \left(\frac{\dot{\varepsilon}_e}{\dot{\varepsilon}_{0r}} \right)^3 + c_r^2(\rho) \left| \frac{\dot{\varepsilon}_v}{3\dot{\varepsilon}_{0r}} \right|^3} \quad (3.31)$$

and

$$\phi_r = \frac{1}{3} \dot{\varepsilon}_{0r} \sigma_0 \frac{L_0}{L} \left[c_r(\rho) \left(\frac{\sigma_e}{\sigma_0} \right)^{\frac{3}{2}} + f_r(\rho) \left(\frac{|3(\sigma_m - \sigma_s)|}{\sigma_0} \right)^{\frac{3}{2}} \right]^2 \quad (3.32)$$

where the subscript ‘ r ’ indicates interface reaction controlled sintering and $\dot{\varepsilon}_{0r}$ is the strain rate in a uniaxial test at a stress σ_0 on a fully dense material of mean grain size L_0 and the other parameters have the same meaning as Eq 3.28. The effective and volumetric strain rates are given by

$$\dot{\varepsilon}_e = \dot{\varepsilon}_{0r} \left(\frac{L_0}{L} \right) c_r(\rho) \left[c_r(\rho) \left(\frac{\sigma_e}{\sigma_0} \right)^{\frac{3}{2}} + f_r(\rho) \left(\frac{|3(\sigma_m - \sigma_s)|}{\sigma_0} \right)^{\frac{3}{2}} \right] \sqrt{\frac{\sigma_e}{\sigma_0}} \quad (3.33)$$

and

$$\dot{\varepsilon}_v = 3\dot{\varepsilon}_{0r} \left(\frac{L_0}{L} \right) f_r(\rho) \left[c_r(\rho) \left(\frac{\sigma_e}{\sigma_0} \right)^{\frac{3}{2}} + f_r(\rho) \left(\frac{|3(\sigma_m - \sigma_s)|}{\sigma_0} \right)^{\frac{3}{2}} \right] \sqrt{\frac{\sigma_0}{|3(\sigma_m - \sigma_s)|}} \left[\frac{3(\sigma_m - \sigma_s)}{\sigma_0} \right] \quad (3.34)$$

In stage 2 of sintering, Pan and Cocks gave the stress potential and strain-rate potential as

$$\varphi_r = \frac{2}{3} \dot{\varepsilon}_{0r} \sigma_0 \sqrt{\frac{L}{L_0}} \left[c_r^{-\frac{2}{3}}(\rho) \left(\frac{\dot{\varepsilon}_e}{\dot{\varepsilon}_{0r}} \right)^{\frac{5}{3}} + f_r^{-\frac{2}{3}}(\rho) \left| \frac{\dot{\varepsilon}_v}{3\dot{\varepsilon}_{0r}} \right|^{\frac{5}{3}} \right]^{0.9} \quad (3.35)$$

and

$$\phi_r = \frac{1}{3} \dot{\varepsilon}_{0r} \sigma_0 \frac{L_0}{L} \left[c_r(\rho) \left(\frac{\sigma_e}{\sigma_0} \right)^{2.5} + f_r(\rho) \left(\frac{|3(\sigma_m - \sigma_s)|}{\sigma_0} \right)^{2.5} \right]^{1.2} \quad (3.36)$$

which gives

$$\dot{\varepsilon}_e = \dot{\varepsilon}_{0r} \left(\frac{L_0}{L} \right) c_r(\rho) \left[c_r(\rho) \left(\frac{\sigma_e}{\sigma_0} \right)^{2.5} + f_r(\rho) \left(\frac{|3(\sigma_m - \sigma_s)|}{\sigma_0} \right)^{2.5} \right]^{0.2} \left(\frac{\sigma_e}{\sigma_0} \right)^{1.5} \quad (3.37)$$

and

$$\dot{\epsilon}_v = 3\dot{\epsilon}_{0r} \left(\frac{L_0}{L} \right) f_r(\rho) \left[c_r(\rho) \left(\frac{\sigma_e}{\sigma_0} \right)^{2.5} + f_r(\rho) \left(\frac{|3(\sigma_m - \sigma_s)|}{\sigma_0} \right)^{2.5} \right]^{0.2} \sqrt{\frac{|3(\sigma_m - \sigma_s)|}{\sigma_0}} \left[\frac{3(\sigma_m - \sigma_s)}{\sigma_0} \right] \quad (3.38)$$

after differentiating the strain-rate potential with respect to effective stress, σ_e and mean stress, σ_m , respectively. It is also noted that grain-boundary diffusion and interface reaction can operate at the same time. When both grain-boundary diffusion and interface reaction contribute to the material response, the stress potentials for each individual process can be added together to give the coupled response.

3.2.3 Expressions for the sintering potential, dimensionless density functions and activation energy

Sintering potential

In 1973, Gregg and Rhines [63] proposed an expression for the sintering potential of the form

$$\sigma_s = \alpha \gamma P H \quad (3.39)$$

where α is a proportionality factor taken to be 1, γ is the surface tension, P is the porosity, and H is the mean curvature of the pore surface. They measured σ_s for a copper powder compact as the uniaxial stress needed to stop uniaxial shrinkage, and found that the sintering potential increased with density up to a relative density of 0.95. Beere [64] predicted that the sintering potential is inversely proportional to grain size, but that its relation to density was very complicated. Rahaman *et al.* [65] have performed experiments to determine the sintering potential by measuring the shear and volumetric component of strain when powder compacts are densified under a uniaxial load. They found that the sintering potential decreases with increasing density when grain growth occurs. Ashby [3] has proposed that sintering potential is a function of relative density and grain size, and different functional relationships are required for different stages of sintering due to the different structures of the porosity. Theoretical studies of the sintering potential by Ashby suggested a functional relationship of the form:

$$\sigma_s = \frac{\gamma_s}{L} g(\rho) \quad (3.40)$$

where $g(\rho)$ is a density function, γ_s is the surface free energy per unit area and L is the grain size. The specific forms of sintering potential proposed by Ashby in 1990 for stage 1 and stage 2 are

$$\sigma_s = \frac{6\gamma_s}{L} \rho^2 \left(\frac{2\rho - \rho_0}{1 - \rho_0} \right) \quad (3.41)$$

and

$$\sigma_s = \frac{4\gamma_s}{L} \left(\frac{6\rho}{1 - \rho} \right)^{\frac{1}{3}} \quad (3.42)$$

respectively, where ρ_0 is the initial green relative density of the component. Based on the work of Coble and co-workers [42] [43], McMeeking and Kuhn [34] have also proposed an expression for the sintering potential for Stage 1 as

$$\sigma_s = \frac{24\gamma_s}{L} \rho^2 \left(\frac{\rho_0}{\rho} \right)^{\frac{1}{3}} \quad (3.43)$$

Dimensionless density function

Like sintering potential, dimensionless density functions also play an important role in the constitutive relationship. Eq 3.44 and 3.45 show the connection of these density functions with bulk viscosity, κ , and shear viscosity, μ , when grain-boundary diffusion is the controlling process.

$$\kappa = \frac{\frac{\sigma_0}{\dot{\epsilon}_{0b}} \left(\frac{L}{L_0} \right)^3}{9f_b(\rho)} \quad (3.44)$$

and

$$\mu = \frac{\frac{\sigma_0}{\dot{\epsilon}_{0b}} \left(\frac{L}{L_0} \right)^3}{3c_b(\rho)} \quad (3.45)$$

The Poisson's ratio, ν , defined as the ratio of the radial deformation rate to the axial deformation rate during sinter forging, can also be expressed by the two density functions as

$$v = \frac{c(\rho) - 2f(\rho)}{2(c(\rho) + f(\rho))} \quad (3.46)$$

For the grain-boundary diffusion controlled sintering, following Helle *et al.*, Du and Cocks [1] proposed the following expressions for $f_b(\rho)$ and $C_b(\rho)$ during stage 1

$$f_b(\rho) = \frac{0.54(1 - \rho_0)^2}{\rho(\rho - \rho_0)^2} \quad (3.47)$$

and

$$c_b(\rho) = \frac{1.08(1 - \rho_0)^2}{\rho(\rho - \rho_0)^2} \quad (3.48)$$

where ρ_0 is the green density of the sample.

When examining the forms of $f_b(\rho)$ and $C_b(\rho)$ for stage 2, Helle *et al.* [33] proposed that

$$f_b(\rho) = \frac{3.2(1 - \rho)^{\frac{1}{2}}}{\rho} \quad (3.49)$$

Analyzing the shear deformation of a compact containing a regular array of spherical pores, Cocks approximated the expression for $C_b(\rho)$ in stage 2 as

$$c_b(\rho) = \frac{1}{\left[1 - 2.5(1 - \rho)^{\frac{2}{3}}\right]} \quad (3.50)$$

For the interface reaction controlled sintering, the dimensionless density functions $C_b(\rho)$ and $f_b(\rho)$ for stage 1 proposed by Du and Cocks [1] are:

$$f_r(\rho) = \frac{1}{3} \frac{(1 - \rho_0)}{\rho^{\frac{3}{2}} \rho_0^{\frac{1}{2}} (\rho - \rho_0)} \quad (3.51)$$

and

$$c_r(\rho) = \frac{2}{3} \frac{(1 - \rho_0)}{\rho^{\frac{3}{2}} \rho_0^{\frac{1}{2}} (\rho - \rho_0)} \quad (3.52)$$

for stage 2

$$f_r(\rho) = \frac{0.042}{\left[1 - 1.53(1 - \rho)^{\frac{2}{3}}\right]^{\frac{5}{3}}} \quad (3.53)$$

and

$$c_r(\rho) = \frac{1}{\left[1 - 1.84(1 - \rho)^{\frac{2}{3}}\right]^{\frac{5}{3}}} \quad (3.54)$$

Activation energy

Whether grain-boundary diffusion or interface reaction dominates the process, the connection of kinetic constant $\dot{\epsilon}_0$ with activation energy, Q , can be generalized as

$$\dot{\epsilon}_0 = \frac{\dot{\epsilon}_{00}}{T} \exp\left(\frac{-Q}{RT}\right) \quad (3.55)$$

where $\dot{\epsilon}_{00}$ is a material constant, and R and T are the gas constant and absolute temperature, respectively. In this work, we will examine two kinds of activation energy, namely, activation energy of densification and activation energy of grain growth.

3.3 Grain-growth equations

During high temperature sintering of ceramic powders, grain growth is inevitable and has a significant effect on densification. As a component densifies, grain size increases. In order to understand the densification behaviour of ceramic powders, the study of grain growth model during sintering is necessary.

The rate of grain growth depends on the state of the material, measured in terms of ρ and L , and the temperature T . Thus

$$\dot{L} = f(\rho, L, T) \quad (3.56)$$

Based on the studies of Hillert [37], Shewmon [36], Brook [38] and Ashby [3], Du and Cocks [1] have also proposed constitutive laws for grain growth. In stage 1, the porosity is considered to consist of an interconnected network of pores, and the equation for the rate of grain growth is

$$\dot{L} = \dot{L}_0 \left(\frac{L_0}{L}\right)^3 (1 - \rho)^{-\frac{3}{2}} \quad (3.57)$$

where $\dot{L}_0$ is a temperature-dependent kinetic constant, termed the grain-growth rate constant in this work. In stage 2, where the pores are assumed to be isolated, the corresponding expression for grain growth rate is

$$\dot{L} = \dot{L}_0 \left(\frac{L_0}{L} \right)^3 (1 - \rho)^{-\frac{4}{3}} \quad (3.58)$$

The transition from stage 2 to stage 3 occurs when the largest grains break away from their attached pores and spread quickly through the compact leading to abnormal grain growth. The grain growth rate expression at this stage is

$$\dot{L} = \dot{L}_0 \left(\frac{L_0}{L} \right) \left[1 - 5.5(1 - \rho)^{\frac{2}{3}} \right] \quad (3.59)$$

3.4 Concluding remarks

In this chapter, a series of constitutive equations for densification and grain growth have been presented. The models proposed by Cocks and co-workers are selected for subsequent investigation in this work. The advantage of the selected models is that they are simple in structure, but provide a detailed description of the development of the microstructure in the material. When developing any material model it is important to assess the predictive capability of the model by evaluating the response of components and to compare these results with experimental studies. Another feature of the presented models is that the state variables are related to physically measurable quantities, relative density and grain size, allowing a direct comparison to be made between theory and experiment.

The constitutive laws will be employed to determine the densification mechanism and grain-growth behavior of the material under investigation in the next two chapters, Chapters 4 and 5, and at the same time, the models employed can also be examined.

Chapter 4. Constitutive Modeling for Free Sintering of Near Nano-sized Material

In Chapter 3, the constitutive laws of densification for both grain boundary diffusion and interface reaction controlled sintering were discussed. The governing equations of grain growth were also described. In this chapter, experiments are designed to obtain the data needed to determinate the dominant sintering mechanism and evaluate several essential parameters, such as activation energy. This chapter focuses on sintering of near nano-sized (150 nm) material, which is also the first attempted report on the constitutive modeling of such fine-grained material. With experimental results, such as relative density, grain size and strain, the appropriate mechanism was found.

4.1 Experiment

4.1.1 Raw material characterization

High purity α -Al₂O₃ powder (99.9%, TM-DAR, Taimei Chemical Co., Ltd., Tokyo Japan) was used as starting raw material. The particle size of the powder was analyzed using a Brookhaven BI-XDC nano-sizer and the mean particle size is around 150 nm, shown in Table 4.1. Chemical composition of the powder was characterized as α phase alumina oxide by a Shimazu XRD, as the three major peaks shown in Fig 4.1. The microstructure of loose powder was also observed using a JSM-6340F Field Emission Scanning Electronic Microscope (FESEM), and the scale bar in graph is 100 nanometer in Fig 4.2. Form the FESEM image , it could be noticed that TM-DAR powder has a near-spherical microsture, which has been proved to be easy to densify.

Table 4.1: Result of particle size analysis for TM-DAR powder.

Raw Powder	Particle Size		Specific Surface (m ² /g)
	Volume Mean (μm)	Geometric Mean (μm)	
TM-DAR	0.174	0.157	16.43

Fig 4.1: XRD analysis of raw TM-DAR powder.

Fig 4.2: Microstructure of TM-DAR powder observed by FESEM.

4.1.2 Powder processing

A 'wet' process, slip casting, was adopted to prepare green compacts with high green density and homogenous microstructure. In this section, the procedure of powder processing were introduced and green compacts of high density, which RD was about 65%, were produced for sintering.

Preparation of gypsum mould with good capillary properties and precise concave is the first essential process for slip casting. The plaster of paris powder was weighed and mixed with deionized water, then the mixture stirred to make the slurry and degassed before cast in a plastic mould. After drying, the gypsum bulk was removed

from mould and further processed into the required shape, shown in Fig 4.3. The details of making gypsum mould are summarized below:

1. 150 grams plaster of paris powder was weighed using a Precisa-2200C balance and deionized water was added to make a slip. The weight ratio of plaster paris powder to deionized water is 1:1, not normally 3:2, which is necessary to prevent over fast drying of slurry during mixing and degas process.
2. The mixing process was taken on the RW20DZM mixer for 2 minutes to ensure all the powders are solved in water.
3. The degas process was on the vacuum chamber for 3 minutes to get rid of air bubbles in slurry.
4. The slurry was then cast into a plastic mould ($100 \times 100 \times 80 \text{ mm}^3$) and dried at drying/warming cabinet at 40°C for 24 hours.
5. For demoulding convenience, the dried gypsum bulk was cut into two pieces and cylindrical holes were drilled on the upper piece with 10.5 mm diameter driller. The contact surfaces of two parts were smoothened with a 180 grade SiC sand paper.

Fig 4.3: Gypsum mould for slip casting.

As mentioned in literature review, to obtain powder compacts with high green density and homogeneous microstructure, the slurry must have such properties as, high solid content with low viscosity, uniformly dispersed and thoroughly degassed. To make such slurry, several processing steps were adopted as follows:

1. 60wt% powder was mixed with deionized water.

2. 5% HNO_3 was added to keep the pH value between 3.5~4.0, at which the *Zeta*-potential is at the highest peak.
3. The slurry was then put into an ultrasonic disturbing bath for 30 minutes to break up the soft agglomerates.
4. A thoroughly degassing was then carried out in a vacuum chamber for 10 minutes.
5. Before casting into the gypsum mould, the pH value was measured and adjusted again to ensure the slurry's stability during ultrasonic disturbing.

It was discussed in Chapter 2 that result of slip casting depends on slurry's stability, thus the *Zeta*-potential, which is the most important parameter affecting slurry's stability, must be measured. The pH value of the slurry was measured using a MP220 pH meter, the *Zeta*-potential was measured using a DT1200 acoustic spectrometer and the viscosity of the slurry was measured using a HAAKE VT-550 viscosity meter at 800 rpm of shearing rate. Figure 4.4 shows *Zeta*-potential and viscosity of the slurry at different pH value. It was observed that the *Zeta*-potential reached its maximum value at pH of 3.3 where the slurry is most stable. It was also found that viscosity is lowest at pH value ranging form 3.2 to 5.0, at which highest casting rate can be achieved. Based on the discussion made in early section, the pH value between 3~4 was chosen to obtain the best dispersion condition.

Fig 4.4: Viscosity of TM-DAR slurry at different pH value.

4.1.3 Sintering profile

The powder compacts were sintered in a high-temperature furnace without pressure. The sintering profile started with a heating rate of $2^{\circ}\text{C}/\text{min}$ until the temperature reached 500°C , at which nitrate and other organic impurities can be eliminated. To make sure all impurities were burned off, 1 hour dwelling was required. Then the samples were heated to the sintering temperature of 1200°C , 1250°C , 1300°C and 1400°C , respectively, with a rate of $10^{\circ}\text{C}/\text{min}$. At the sintering temperature, the samples were held with different dwelling times, varies from 5 minutes to 2 hours. Finally, the sintered bodies were cooled to room temperature at a rate of $5^{\circ}\text{C}/\text{min}$. The samples at 1200°C , 1250°C were used to investigate the sintering mechanisms for both Stage 1 and Stage 2. Those samples sintered at different temperature with similar density were used to evaluate the activation energy of the material system. The sintering profile is shown in Fig 4.5.

Fig 4.5: Sintering profile of alumina.

4.1.4 Sample preparation for FESEM

The cross section of sintered sample was observed by FESEM to study the grain size. The procedure to prepare the samples for FESEM is presented bellow:

1. The sintered pellets were cross-sectioned using an ISO MET2000 diamond cutter.
2. The cut-offs were cold-mounted for polishing.

3. After mounting, the samples are ground and polished with a Buehler Metaserv grinder and polisher. During grinding, different grades of grinding papers were used to level up the surface. Then different grades of diamond pastes, from 9 μm to 0.25 μm , were used to polish the surfaces of samples.
4. After the samples were removed from the resin by heat (or acetone), they were put into a high-temperature furnace for thermal etching, which is necessary for FESEM observation. The heating schedule for thermal etching is always at a temperature that is 100°C lower than the sintering temperature.

4.2 Results

The net weight of samples was weighed using a Scientech SA510 analytical balance and diameters and thicknesses are measured by a Vernier caliper. The relative density ρ , volume strain ε_v and effective strain ε_e of the sample were obtained by the following equations

$$\rho = \frac{\rho_{\text{measured}}}{\rho_{\text{theoretical}}} \quad (4.1)$$

$$\varepsilon_v = 2\varepsilon_d + \varepsilon_h \quad (4.2)$$

$$\varepsilon_e = \frac{2}{3}|\varepsilon_h - \varepsilon_d| \quad (4.3)$$

where ε_d is strain in diameter and ε_h is strain in thickness. The theoretical density of alumina is taken as 3.98 g/cm³ for calculation of the relative density. In the present work, effective strain ε_e is zero because all samples were sintered without pressure applied, thus ε_d equals to ε_h . In order to examine the reliability of the present density experimental data, the values of ε_d and ε_h are treated as time dependent variables. It is found that the value of ε_d and ε_h is comparable at a given holding time, which means the shrinkage is isotropic for the sintered compacts (figures are attached in Appendix I). Therefore, it can be concluded that the present density experimental data is suitable for modeling study.

In the SEM pictures, the grain size is determined by counting the number of grains traversed by different straight lines of known length. About 150~200 grains are measured for each sample. The final grain size was taken as 1.56 times the average

grain size measured [65]. The experimental results, such as relative density, grain size and volumetric strain, ε_v , under different sintering temperatures obtained directly from the sintered samples, are shown in Table 4.2~4.5 and Fig 4.6~4.8.

Table 4.2: Experimental grain size and density obtained from 1200°C sintering.

Time (min)	5	10	30	60	120
Density (g/cm ³)	3.056	3.184	3.345	3.552	3.661
Grain size (μm)	0.210	0.219	0.245	0.280	0.301
ε_v	0.1465	0.1722	0.2218	0.2663	0.2959

Table 4.3: Experimental grain size and density obtained from 1250°C sintering.

Time (min)	5	10	30	60	120
Density (g/cm ³)	3.330	3.475	3.623	3.761	3.845
Grain size (μm)	0.210	0.246	0.307	0.366	0.489
ε_v	0.2461	0.2873	0.3331	0.3889	0.4178

Table 4.4: Experimental grain size and density obtained from 1300°C sintering.

Time (min)	5	10	30	60	120
Density (g/cm ³)	3.642	3.760	3.879	3.898	3.955
Grain size (μm)	0.243	0.248	0.435	0.465	0.547
ε_v	0.3325	0.3931	0.4112	0.4127	0.4232

Table 4.5: Experimental grain size and density obtained from 1400°C sintering.

Time (min)	5	10	30	60	120
Density (g/cm ³)	3.751	3.818	3.912	3.957	3.971
Grain size (μm)	0.412	0.452	0.497	0.716	1.12
ε_v	0.4095	0.4161	0.4178	0.4249	0.4273

Fig 4.6: Relative density at different sintering temperatures.

Fig 4.7: Grain size of samples sintered at different temperatures.

Fig 4.8: Volumetric strain of samples sintered at different temperatures.

4.3 Discussion

The experiment data of relative density and grain size at different temperatures were used to verify the dominant densification mechanism for both grain-boundary diffusion mechanism and interface reaction mechanism. The constitutive model was established with the combination of densification equations and grain growth equations. During modeling, two sintering kinetic coefficients, the strain-rate constant $\dot{\epsilon}_0$ and the grain growth rate constant $\dot{L}_0$, were obtained. The most appropriate densification mechanism to describe sintering process was determined by comparing the modeling results of each mechanism with the experimental data.

4.3.1 Grain-boundary diffusion controlled sintering

In this section, grain-boundary diffusion is assumed to be the dominant densification mechanism for sintering. For this mechanism, densification proceeds by the difference in chemical potential on grain boundaries and the flux of material goes along the grain boundaries. The specific equations of strain rate for grain-boundary diffusion controlled sintering are given by Eq 3.30, from which the densification rate equation can be derived as

$$\dot{\epsilon}_v = 9 \frac{\dot{\epsilon}_{0b}}{\sigma_0} \left(\frac{L_0}{L} \right)^3 f_b(\rho) (\sigma_m - \sigma_s) \quad (3.30)$$

$$\dot{\rho} = -9\rho \frac{\dot{\epsilon}_{0b}}{\sigma_0} \left(\frac{L_0}{L} \right)^3 f_b(\rho) (\sigma_m - \sigma_s) \quad (4.4)$$

For free sintering, there is no stress applied on samples, so σ_m and σ_e is zero. Eq 4.4 turns out to be

$$\dot{\rho} = \rho \frac{\dot{\epsilon}_{0b}}{\sigma_0} \left(\frac{L_0}{L} \right)^3 [9f_b(\rho)\sigma_s] \quad (4.5)$$

where $\dot{\epsilon}_{0b}$ is the grain-boundary diffusion controlled strain rate constant, in which the subscript 'b' indicates the grain-boundary diffusion mechanism. In Eq 4.5, the sintering potential σ_s and dimensionless densification function $f_b(\rho)$ is chosen after the work of Du and Cocks [41], shown in Table 4.6.

Table 4.6: Variables for grain-boundary diffusion controlled sintering.

Variables	Stage 1	Stage 2
$f_b(\rho)$	$\frac{0.54(1-\rho_0)^2}{\rho(\rho-\rho_0)}$	$\frac{3.2(1-\rho)^{\frac{1}{2}}}{\rho}$
σ_s	$\frac{6\gamma_s\rho^2(2\rho-\rho_0)}{L(1-\rho_0)}$	$\frac{4\gamma_s\rho^2(6\rho)^{\frac{1}{3}}}{L(1-\rho)}$

Substituting the variables in Table 4.6 into Eq 4.5 with the expressions, we obtained the specific densification rate function for both stage 1 and stage 2 grain-boundary controlled sintering, respectively. For stage 1 sintering, the densification equation is

$$\dot{\rho} = 29.16\dot{\epsilon}_{0b} \left(\frac{L_0}{L} \right)^4 \frac{\rho^2(1+\rho_0)(2\rho-\rho_0)}{(\rho-\rho_0)} \quad (4.6)$$

and for stage 2

$$\dot{\rho} = 209.33\dot{\epsilon}_{0b} \left(\frac{L_0}{L} \right)^4 (1-\rho)^{\frac{1}{6}} \rho^{\frac{1}{3}} \quad (4.7)$$

The densification equation obtained now only contains the density and grain size as the variables, which can be obtained directly from experiments. The densification rate of whole sintering process can also be obtained from experiments. Eq 4.6 and Eq 4.7

were used to model the densification rate both stage 1 and stage 2 when grain-boundary diffusion is the controlling mechanism.

4.3.2 Interface reaction controlled sintering

As derived in Chapter 3, the interface reaction controlled densification equation for stage 1 is given by Eq 3.28

$$\dot{\rho} = 27\dot{\epsilon}_{0r}\rho\left(\frac{L_0}{L}\right)(f_r(\rho))^2\left(\frac{\sigma_s}{\sigma_0}\right)^2 \quad (4.8)$$

and for stage 2 is given by Eq 3.34 as

$$\dot{\rho} = 27\dot{\epsilon}_{0r}\rho\left(\frac{L_0}{L}\right)(f_r(\rho))^{1.2}\left(\frac{\sigma_s}{\sigma_0}\right)^2 \quad (4.9)$$

where $\dot{\epsilon}_{0r}$ is strain rate constant, the subscript 'r' indicates the interface reaction mechanism. The dimensionless density function $f_r(\rho)$ which represents volumetric component. The expressions for $f_r(\rho)$ σ_s are proposed as shown in Table 4.7.

Table 4.7: Variables for interface reaction controlled sintering

Variables	Stage 1	Stage 2
$f_r(\rho)$	$\frac{(1-\rho_0)}{3\rho^{\frac{3}{2}}\rho_0^{\frac{1}{2}}(\rho-\rho_0)}$	$\frac{0.042}{\left[1-1.53(1-\rho)^{\frac{2}{3}}\right]^{\frac{5}{3}}}$
σ_s	$\frac{6\gamma_s\rho^2(2\rho-\rho_0)}{L(1-\rho_0)}$	$\frac{4\gamma_s\rho^2(6\rho)^{\frac{1}{3}}}{L(1-\rho)}$

Replacing $f_r(\rho)$ and σ_s using the expressions in Table 4.7, the densification rate equations for interface reaction controlled sintering can be obtained. For stage 1, the rate expression is

$$\dot{\rho} = 108\dot{\epsilon}_{0r}\left(\frac{L_0}{L}\right)^3 \frac{\rho^2(2\rho-\rho_0)^2}{\rho_0(\rho-\rho_0)^2} \quad (4.10)$$

For stage 2, the expression is

$$\dot{\rho} = 31.76\dot{\epsilon}_{0r}\left(\frac{L_0}{L}\right)^3 \frac{\rho^{\frac{5}{3}}}{\left[1-1.53(1-\rho)^{\frac{2}{3}}\right]^2 (1-\rho)^{\frac{2}{3}}} \quad (4.11)$$

4.3.3 Modeling results

A simple Euler scheme was adopted to approximate the densification function and grain growth equations, where the changes of the relative density and grain size depend on the interval of time, Δt . The density and grain size can be expressed as

$$\rho_{t+1} = \rho_t + \dot{\rho}_t \cdot \Delta t \quad (4.12)$$

$$L_{t+1} = L_t + \dot{L}_t \cdot \Delta t \quad (4.13)$$

where $\dot{\rho}_t$ and $\dot{L}_t$ is the densification rate and grain growth rate respectively. Combining these two Euler equations with grain growth function, Eq 3.57 and 3.58, and densification function, Eq 4.10 and 4.11, a constitutive model was established for densification and also grain growth. The grain growth rate constants $\dot{L}_0$ at 1200°C, 1250°C, 1300°C and 1400°C were modelled by linear fitting by plotting $\dot{L} \cdot (1 - \rho)^{\frac{3}{2}}$ against $\left(\frac{L_0}{L}\right)^3$ from experiment data, as shown in Fig 4.9 and Fig 4.10.

$$\dot{L} = \dot{L}_0 \left(\frac{L_0}{L}\right)^3 (1 - \rho)^{-\frac{3}{2}} \text{ (stage 1)} \quad (3.57)$$

$$\dot{L} = \dot{L}_0 \left(\frac{L_0}{L}\right)^3 (1 - \rho)^{-\frac{4}{3}} \text{ (stage 2)} \quad (3.58)$$

Fig 4.9: linear fitting for grain growth constant at 1200°C and 1250°C from experiment data directly.

Fig 4.10: linear fitting for grain growth constant at 1250°C, 1300°C and 1400°C from experiment data.

Base on above result, the grain growth constant $\dot{L}_0$ at 1200°C is obtained as $1.50 \times 10^{-5} \text{ um} \cdot \text{s}^{-1}$ and that of 1250°C is $1.67 \times 10^{-5} \text{ um} \cdot \text{s}^{-1}$. To compare, the grain growth constant of stage 2 sintering is also modelled by Eq 3.58, shown in Fig 4.10. It is found that $\dot{L}_0$ at 1250°C is also $1.67 \times 10^{-5} \text{ um} \cdot \text{s}^{-1}$, as same as stage 1 modelling, which indicates that Du and Cocks grain growth function is appropriate for current experiment. At 1300°C and 1400°C, the grain growth constant $\dot{L}_0$ is found to be $1.01 \times 10^{-5} \text{ um} \cdot \text{s}^{-1}$ and $1.06 \times 10^{-4} \text{ um} \cdot \text{s}^{-1}$.

Based on grain growth constant $\dot{L}_0$ value obtained from above calculations, the densification and grain growth at 1200°C and 1250°C was modeled. Fig 4.11 shows the results of densification modeling for 1200°C sintering. It could be found that interface reaction mechanism can provide a better agreement with the experimental data than grain boundary diffusion model at this temperature. This observations can be understood that for current near nano-sized powder, grain size is small that results in an abundance short-ranged diffusion path. The diffusion process along such short-ranged grain boundaries is much faster. As discussed in Chapter 2, interface reaction and grain boundary diffusion are two sequential processes in mass transportation, and the slower mechanism will be the bottle neck, dominating the whole process. The present investigation shows that interface reaction process dominate grain boundary diffusion process. Thus, interface reaction model will be used to determine the rate of

densification for the sintering of near nano-sized materials. Identifying interface reaction as the dominant densification mechanism, the strain rate constant $\dot{\epsilon}_{0r}$ was obtained as $4.60 \times 10^{-8} \text{ s}^{-1}$. For grain boundary diffusion model, the strain rate constant $\dot{\epsilon}_{0b}$ was obtained as $2.56 \times 10^{-6} \text{ s}^{-1}$.

Fig 4.11: IR and GB modelling result of 1200°C densification.

The same trend is found in modeling of 1250°C sintering. Experimental results showed that sintering at 1250°C began at stage 1 and then entered stage 2 after 30 minutes. Therefore, the model is adjusted to cover both stage 1 and stage 2 sintering. Since different densification equations are employed for different sintering stages, a transition period is necessary because that densification is a physically continuous process, when relative density is closed to critical point, 91% in present study. Thus, during the transitional period, the density employed was expressed as

$$\dot{\rho} = k \cdot \dot{\rho}_{stage1} + (1 - k) \cdot \dot{\rho}_{stage2} \quad (4.14)$$

where k is a variable depending on the density. Fig 4.12 shows the result of densification modeling for 1250°C sintering. The same trend as 1200°C sintering is observed. The sintering process covers both stage 1 and 2, as a result, there is inflexion for both modeling curves, which indicates the different expressions of density and grain size for two stages. It is obvious that the discrepancy by grain-boundary diffusion is more severe in stage 2 sintering. Based on the present result, interface reaction mechanism is considered as the dominant densification mechanism

for 1250°C sintering. The strain rate constant $\dot{\epsilon}_{0r}$ is obtained by interface reaction model as $9.80 \times 10^{-8} \text{ s}^{-1}$. Also, $\dot{\epsilon}_{0b}$ is obtained as $2.80 \times 10^{-6} \text{ s}^{-1}$.

Fig 4.12: IR and GB modeling result of 1250C densification.

4.4 Grain growth study

It has been discussed in Chapter 2 that the grain growth and densification are two interconnected process. In this section, we focus on the comparison of interface reaction and grain boundary diffusion mechanism on grain growth process for both 1200°C and 1250°C sintering. For stage 1, the interface reaction model is:

$$\dot{L}_t = \dot{L}_0 \left(\frac{L_0}{L_t} \right)^3 (1 - \rho_t)^{\frac{3}{2}} \quad (3.57)$$

$$\dot{\rho}_t = 108 \dot{\epsilon}_{0r} \left(\frac{L_0}{L_t} \right)^3 \frac{\rho_t^2 (2\rho_t - \rho_0)^2}{\rho_0 (\rho_t - \rho_0)^2} \quad (4.10)$$

and for stage 2, the model is:

$$\dot{L}_t = \dot{L}_0 \left(\frac{L_0}{L_t} \right)^3 (1 - \rho_t)^{\frac{4}{3}} \quad (3.58)$$

$$\dot{\rho}_t = 31.76 \dot{\epsilon}_{0r} \left(\frac{L_0}{L_t} \right)^3 \frac{\rho_t^{\frac{5}{3}}}{\left[1 - 1.53(1 - \rho_t)^{\frac{2}{3}} \right]^2 (1 - \rho_t)^{\frac{2}{3}}} \quad (4.11)$$

where subscript 't' represents time, and subscript 'r' represents interface reaction mechanism. Base on the above equations and Eq 4.12 and Eq 4.13 below, the grain growth processes at 1200°C and 1250°C were modelled, and results are shown in Fig 4.12 and Fig 4.13 respectively.

$$\rho_{t+1} = \rho_t + \dot{\rho}_t \cdot \Delta t \quad (4.12)$$

$$L_{t+1} = L_t + \dot{L}_t \cdot \Delta t \quad (4.13)$$

It should be noted that for grain growth at 1250°C, transitional expressions, Eq 4.14 is also applied.

$$\dot{\rho} = k \cdot \dot{\rho}_{stage1} + (1 - k) \cdot \dot{\rho}_{stage2} \quad (4.14)$$

For comparison, the results of grain boundary diffusion model were also shown in Fig 4.13 and Fig 4.14. The grain boundary diffusion model employed in current modeling follows Eq 4.6 and 4.7 for both stage 1 and stage 2.

$$\dot{\rho} = 29.16 \dot{\epsilon}_{0b} \left(\frac{L_0}{L} \right)^4 \frac{\rho^2 (1 + \rho_0) (2\rho - \rho_0)}{(\rho - \rho_0)} \quad (4.6)$$

$$\dot{\rho} = 209.33 \dot{\epsilon}_{0b} \left(\frac{L_0}{L} \right)^4 (1 - \rho)^{\frac{1}{6}} \rho^{\frac{1}{3}} \quad (4.7)$$

Fig 4.13: IR and GB modeling result of 1200°C grain growth.

Fig 4.14: IR and GB modeling result of 1250°C grain growth.

In Fig 4.13 and 4.14, it is found that interface reaction model is more appropriate than grain boundary diffusion model. At 1200°C, this trend is more obvious, while at 1250°C, the results of two mechanisms are quite close. This observation may indicate that at higher temperature, when microstructure is coarse the operating mechanism is shifting from interface reaction to grain boundary diffusion mechanism. The rate constants of densification and grain growth used in current grain growth modeling were obtained from densification study and were shown in Table 4.8.

Table 4.8: Rate constants for densification and grain growth obtained at different sintering temperatures.

Temperatures	$\dot{L}_0 \text{ (um}\cdot\text{s}^{-1}\text{)}$	$\dot{\epsilon}_{0r} \text{ (s}^{-1}\text{)}$	$\dot{\epsilon}_{0b} \text{ (s}^{-1}\text{)}$
1200°C	1.50×10^{-5}	4.60×10^{-8}	9.80×10^{-8}
1250°C	1.67×10^{-5}	2.56×10^{-6}	2.80×10^{-6}

4.5 Evaluation of activation energy

Determination of the activation energy could shed light in the identification of the dominant mechanism during the process. In this section, the activation energies of both densification and grain growth processes were determined respectively using the experimental results. The results obtained are compared with thoes reported in the literature.

4.5.1 Activation energy for densification

The activation energy for densification of alumina materials has been widely investigated in resent years. It is well reported that the activation energy for densification for both powder-law creep and lattice diffusion mechanisms were both 477 kJ/mol [66]. For grain-boundary diffusion mechanism, the activation energy was reported to be 419 kJ/mol [66]. The activation energy for interface reaction was 290 kJ/mol, reported by McCoy and Wills [67]. From the strain rate equations, it is noted that the strain rate is a function of density and grain size. Hence, $\dot{\epsilon}_v$ can be express as

$$\dot{\epsilon}_v = \dot{\epsilon}_0 G(\rho, L) \quad (4.15)$$

Combining with Eq 3.55, the above expression can be rewritten as

$$\dot{\epsilon}_0 = \frac{\dot{\epsilon}_{00}}{T} \exp\left(\frac{-Q}{RT}\right) \quad (3.55)$$

$$\dot{\epsilon}_v = \frac{\dot{\epsilon}_{00}}{T} \exp\left(\frac{-Q}{RT}\right) \cdot G(\rho, L) \quad (4.16)$$

In Eq 4.16, if the function $G(\rho, L)$ can be ignored or remain constant for different temperatures, the activation energy, Q , can be easily obtained by the logarithm of both sides of Eq 4.16, Rearranging the Eq 4.16, we have

$$\ln(T\dot{\epsilon}_v) = -\frac{Q}{RT} + C \quad (4.17)$$

where C is a constant contains both function $G(\rho, L)$ and constant $\dot{\epsilon}_{00}$. Noted function $G(\rho, L)$ only depends on density and grain size, we make an assumption that grain size is similar between samples if they have similar density, no matter how they are sintered. This assumption is validated in later section of this chapter.

Based on the above analysis, we calculated activation energy by Eq 4.17 if the volumetric strain rate $\dot{\epsilon}_v$ is known. Experimentally, we can calculate $\dot{\epsilon}_v$ by differentiating the fitting function with time in Fig 4.8, shown in Fig 4.15. Then the as-calculated $\dot{\epsilon}_v$ is plotted versus relative density in Fig 4.14. At a certain density, for instance, 90% RD, we can locate $\dot{\epsilon}_v$ value at three different sintering temperatures.

Fig 4.15: Volumetric strain rate of samples sintered at different temperatures is plotted versus density.

To improve accuracy, an empirical relation between $\dot{\epsilon}_v$ and temperature is established, shown in Fig 4.16. The value of strain rate at other temperatures can be estimated, results are shown in Table 4.9. Then, the values of $\ln(T\dot{\epsilon}_v)$ were then plotted against the reciprocal of the absolute temperatures in Fig 4.16. The activation energy of densification can be obtained from the slope of the fitted straight line as shown in Fig 4.17. From the above analysis and calculation, the activation energy was obtained as 314 kJ/mol, which is close to the value of 290 kJ/mol proposed by McCoy and Wills [67] for interface reaction mechanism. This result also demonstrates that the dominant mechanism of sintering process is probably interface reaction.

Fig 4.9: Empirical volumetric strain rate at different temperatures.

Table 4.9: Results of Volumetric strain rate at different temperatures.

Temperature (°C)	1200	1225	1250	1275	1300
$\dot{\epsilon}_v$ (min ⁻¹)	0.00087	0.00146	0.00326	0.00627	0.01049

Fig 4.10: Logarithm of $T\dot{\epsilon}_v$ as a function of reciprocal absolute sintering temperature.

It should be noticed that the above analysis is only appropriate when the grain size and density of the samples sintered at different temperatures were not significantly different. We have checked it using the SEM pictures (Fig 4.18~4.20). This confirms our early assumption; that is all samples which have nearly the same RD show similar grain size of around 240 nm.

Fig 4.11: SEM picture of sample sintered at 1200°C dwell 30 minutes with 87% relative density.

Fig 4.19: SEM picture of sample sintered at 1250°C dwell 10 minutes with 89% relative density.

Fig 4.20: SEM picture of sample sintered at 1300°C dwell 5 minutes with 90% relative density.

4.5.2 Activation energy of grain growth

The investigation for activation energy for grain growth also helps to identify the mechanism of grain growth as in the case of densification. There are several mechanisms for grain growth of solid-state materials and the mechanisms can be largely divided into two categories, namely, boundary controlled and pore controlled grain growth, shown in Table 4.10. For high purity solid-phase alumina materials, the most likely mechanism is surface diffusion. It was reported by Frost and Ashby [66] that the activation energy of grain growth is 500 kJ/mol when surface diffusion dominates the grain growth process.

Table 4.10: Grain growth mechanisms.

Boundary control	Pore control
Pure system	Vapor transport (interface control)
Impurity drag	Vapor transport (diffusion control)
Solution of solid second phase	Lattice diffusion
Coalescence of solid second phase	Surface diffusion
Continuous liquid phase (interface control)	
Continuous liquid phase (diffusion through film)	

Following a similar derivation as that in the earlier section, the grain growth equation can be rewritten as

$$\ln(TL) = -\frac{Q}{RT} + C \tag{4.20}$$

The grain growth rate can be obtained from the plot of grain size against dwelling time at different temperature, shown in Fig 4.20. Three grain growth rate values are chosen from experimental results of 1200°C, 1250°C and 1300°C at 238 nm. Next, an empirically fitted function was used to obtain the grain growth rate at other temperature, shown Table 4.11.

Fig 4.20: Grain growth rate against grain size at different sintering temperature.

Table 4.11: Empirically evaluated results of grain growth rate at different temperatures.

Temperature (°C)	1200	1225	1250	1275	1300
$\dot{L}$ (μm/min)	0.01075	0.01365	0.02048	0.03595	0.06172

Fig 4.21: Empirical grain growth rate at different temperatures.

According to the results shown in Table 4.11, the activation energy can be calculated from the slope of logarithm of $T \cdot \dot{L}$ against the reciprocal of absolute sintering temperature, as shown in Fig 4.22.

Fig 4.22: Logarithm of $T \cdot \dot{L}$ as a function of reciprocal of absolute sintering temperature.

The activation energy of grain growth work was evaluated to be 436 kJ/mol in the present work. This value is close to the value of the surface diffusion mechanism controlled grain growth. It is hence concluded that surface diffusion is the dominant grain growth mechanism for the present material system.

4.6 Concluding remarks

In this chapter, constitutive modeling for both grain-boundary diffusion and interface reaction controlled sintering were carried out based on the designed experiments. The grain growth was also studied and conclusions are given as follows:

1. It was found that interface reaction mechanism provides the most reasonable agreement with the experimental densification result for present near nano-sized material.
2. Rate constants for densification $\dot{\epsilon}_{0r}$ obtained for interface reaction controlled sintering are $4.60 \times 10^{-8} \text{ s}^{-1}$ at 1200°C, and $9.80 \times 10^{-8} \text{ s}^{-1}$ at 1250°C. The grain

growth constant $\dot{L}_0$ is $1.50 \times 10^{-6} \mu\text{m}\cdot\text{s}^{-1}$ at 1200°C and $1.67 \times 10^{-6} \mu\text{m}\cdot\text{s}^{-1}$ at 1250°C respectively.

3. Activation energies for both densification and grain growth are 314 kJ/mol and 443 kJ/mol, respectively, indicating that densification of near nano-sized alumina powder used in present work is controlled by interface reaction mechanism and grain growth is dominated by the surface diffusion mechanism.

Chapter 5. Constitutive Models for Free Sintering of 3Y-TZP Nano-Material

In chapter 4, a constitutive model for sintering of near nano-sized Al_2O_3 material was developed and interface reaction mechanism was shown to be the dominant densification mechanism for densification of near nano-sized alumina material. In this chapter, we focus on the study of the free sintering of nano-sized ceramic powder in this chapter. With similar approaches, sintering mechanisms were investigated and the material constants are also determined.

5.1 Introduction

3Y-TZP (3% mole yttria stabilized tetragonal Zirconia polycrystalline) material is currently widely used for its superior fracture toughness among ceramic materials. In the application of high toughness requirement, tetragonal phase is preferred because tetragonal phase tends to transform into monoclinic phase when stress is loaded. Such phase transformation is always accompanied with remarkable volume expansion which stops the growth of micro crack within ceramic material. However, this phase transformation can only take place when the grain size of 3Y-TZP material is within a critical value, 0.8 μm normally [68]. Thus, the understanding of densification and grain growth for 3Y-TZP material is very important in the fabrication of this material. In this chapter, nano-sized 3Y-TZP powder was processed and sintered to nearly full density. Then the densification and grain growth mechanisms of this material were studied by constitutive models. Activation energies and kinetic variables were also calculated during modeling.

5.2 Experiment procedures

5.2.1 Powder characterization

A commercially available 99.9 wt% 3Y-TZP powder is used as the raw material. The particle size of the powder is measured by means of a Brookhaven BI-XDC particle

size analyzer and FESEM, and the particle was found to be granular in shape with a mean particle size of 58 nm, shown in Fig 5.1 and Fig 5.2.

Fig 5.1: Particle size distribution for the present 3Y-TZP nano powder, it is found that 100 wt% powder is smaller than 78 nm.

Fig 5.2: SEM picture of nano-sized 3Y-TZP powder.

Cylinder shape powder compacts are prepared by die-pressing under stress of 50 MPa. Then the powder compact was sintered to 1400°C with heating rate of 2°C/min and then cooled down naturally using a dilatometer. The relative shrinkage of sample during sintering was obtained, shown in Fig 5.3. It is found that the volumetric shrinkage start around 950°C, which indicates the densification initiates at this temperature.

Fig 5.3: Relative shrinkage during heating, the heating rate is 2°C/min and the finishing temperature is 1400°C.

5.2.2 Isothermal sintering

Cylinder shape powder compacts were formed by die pressing with a pressure of 50 MPa, and then the as-formed powder compacts were subjected to an ABB42260 Cold Isostatic Pressing (CIP) for 20 minutes with a pressure of 400 MPa. Powder compacts with 51.8% RD were obtained as green compacts. Several batches of green compacts were sintered in air atmosphere without pressure at different sintering temperatures of 1200°C, 1250°C, 1300°C and 1350°C. At each temperature, the samples were sintered with different dwelling times. The density of a sintered compact was calculated by mass-volume method, and the relative density was obtained, taking the theoretical density (6.08 g/cm³ for 3Y-TZP), shown in Fig 5.4. In order to study the grain size of the sintered compacts, the cross section of the samples was polished and then subjected with thermal etching (heated at 100°C lower than sintering temperature). The as prepared surface was then investigated with the JEOL SM-31160 Field Emission Scanning Microscope (FESEM). From the FESEM images, grain size of sintered samples was obtained, plotted against time in Fig 5.5. The SEM pictures are attached in Appendix II. The volumetric strain ε_v was calculated using Eq 4.2, ε_d and ε_h which were obtained directly from measuring sintered samples, and result is shown in Fig 5.6.

$$\varepsilon_v = 2\varepsilon_d + \varepsilon_h \quad (4.2)$$

From raw data of volumetric strain, the volumetric strain rate $\dot{\epsilon}_v$ can be analyzed by differentiating the strain with time. The result is shown in Fig 5.7.

Fig 5.4: Relative density of sintered compacts at different temperatures.

Fig 5.5: Grain size of sintered compacts obtained at different temperatures.

Fig 5.6: Volumetric strain of sintered compacts at different sintering temperatures.

Fig 5.7: Strain rate data was obtained from differentiating strain against time at different temperatures.

5.3 Constitutive models

In this chapter, the constitutive model for sintering combines both the densification model and the grain growth model. As discussed in Chapter 4, from Eq 4.6 and Eq 4.7 with Eq 4.14, the densification model for grain boundary diffusion is developed as

$$\dot{\rho}_{stage1} = 29.16 \dot{\epsilon}_{0b} \left(\frac{L_0}{L} \right)^4 \frac{\rho_{stage1}^2 (1 + \rho_0) (2\rho_{stage1} - \rho_0)}{(\rho_{stage1} - \rho_0)} \quad (\rho_0 < \rho < \rho_1) \quad (5.1)$$

$$\dot{\rho}_{stage2} = 209.33\dot{\varepsilon}_{0b} \left(\frac{L_0}{L} \right)^4 (1 - \rho_{stage2})^{\frac{1}{6}} \rho_{stage2}^{\frac{1}{3}} \quad (\rho_2 < \rho < 1) \quad (5.2)$$

and the densification model for interface reaction is

$$\dot{\rho}_{stage1} = 108\dot{\varepsilon}_{0r} \left(\frac{L_0}{L} \right)^3 \frac{\rho^2 (2\rho_{stage1} - \rho_0)^2}{\rho_0 (\rho_{stage1} - \rho_0)^2} \quad (\rho_0 < \rho < \rho_1) \quad (5.3)$$

$$\dot{\rho}_{stage2} = 31.76\dot{\varepsilon}_{0r} \left(\frac{L_0}{L} \right)^3 \frac{\rho_{stage2}^{\frac{5}{3}}}{\left[1 - 1.53(1 - \rho_{stage2})^{\frac{2}{3}} \right]^2 (1 - \rho_{stage2})^{\frac{2}{3}}} \quad (\rho_2 < \rho < 1) \quad (5.4)$$

In the above equations, ρ_0 is the green density, was taken as 51.8% from experiments. There is a transitional region between stage 1 and stage 2 to obtain smooth curve when $\rho_1 < \rho < \rho_2$ ($\rho_1=0.88$ and $\rho_2=0.92$), thus a transitional densification rate is defined and k is an effective constant, shown in Eq 5.5 and Eq 5.6.

$$\dot{\rho}_{transition} = k \cdot \dot{\rho}_{stage1} + (1 - k) \cdot \dot{\rho}_{stage2} \quad (\rho_1 < \rho < \rho_2) \quad (5.5)$$

$$k = \frac{\rho - \rho_2}{\rho_1 - \rho_2} \quad (\rho_1 < \rho < \rho_2) \quad (5.6)$$

The grain growth is coupled with the density and microstructure of the sintered samples in the current study. At stage 1, the porosity of sintered body is considered to consist of an interconnected network of pores, and the equation for the rate of grain growth is

$$\dot{L} = \dot{L}_0 \left(\frac{L_0}{L} \right)^3 (1 - \rho)^{-\frac{3}{2}} \quad (\rho_0 < \rho < 0.9) \quad (5.7)$$

For stage 2 sintering, where the pores are assumed to be isolated, the corresponding expression for grain growth rate is

$$\dot{L} = \dot{L}_0 \left(\frac{L_0}{L} \right)^3 (1 - \rho)^{-\frac{4}{3}} \quad (0.9 < \rho < 1) \quad (5.8)$$

In the above equations, L_0 is the initial grain size which is taken as particle size of powder, and 0.9 is the transitional point of relative density between stage 1 and stage 2. To combine densification model and grain growth model, a simple Euler scheme is adopted to approximate the densification function and grain growth equation, where the changes of the relative density and grain size depend on the time interval, Δt . The density and grain size can be expressed as

$$\rho_{t+1} = \rho_t + \dot{\rho}_t \cdot \Delta t \quad (5.9)$$

$$L_{t+1} = L_t + \dot{L}_t \cdot \Delta t \quad (5.10)$$

Combining the above two equations with densification functions and grain growth functions, the constitutive modeling of density and grain size is carried out for nano-scale material in the current study.

5.4 Results and discussions

In the following section, we apply the early established grain boundary diffusion and interface reaction model to predict the densification and grain growth processes. The modeling prediction is then compared with experimental data to verify the most appropriate mechanism for densification of nano-materials. During this process, two sintering kinetic coefficients, the strain rate constant $\dot{\epsilon}_0$ and the grain growth rate constant $\dot{L}_0$ are obtained and the relationship between these coefficients and the temperature is also studied.

5.4.1 Densification mechanism study

The trajectory of density against time is plotted using the models of two mechanisms of densification process of 1200°C, 1250°C, 1300°C and 1350°C, as shown in Fig 5.8~5.11. It is found that the trajectory of the interface reaction is much closer to experimental results than that of the grain boundary diffusion at 1200°C, a same trend is also observed at the other three temperatures. Thus, the interface reaction model is again shown to provide more appropriate prediction than the grain boundary diffusion model.

Fig 5.8: Densification modeling result of 1200°C sintering.

Fig 5.9: Densification modeling result of 1250°C sintering.

Fig 5.10: Densification modeling result of 1300°C sintering.

Fig 5.11: Densification modeling result of 1350°C sintering.

The evaluation of activation energy for densification was also carried out to provide information of the dominant sintering mechanism. It is reported that for both power-law creep and lattice diffusion mechanisms, the activation energy for densification is 477 kJ/mol; for grain-boundary diffusion mechanism, the activation energy is 419 kJ/mol [66]. For interface reaction mechanism, the activation energy of densification

is 290 kJ/mol [67]. In the following section, the activation energy of densification was determined using experimental volumetric strain rate data obtained at different temperatures to compare with constitutive modeling results. It can be seen from Eq 4.17 that the effect of density and grain size on strain rate can be normalized. Thus the activation energy Q can be determined by plotting $\ln(T\dot{\epsilon}_v)$ against $-\frac{1}{RT}$ where R is the ideal gas constant and T is absolute temperature. Applying the volumetric strain rate $\dot{\epsilon}_v$ obtained from Fig 5.5, the trajectory of strain rate against relative density at different temperatures was plotted in Fig 5.12. Table 5.1 shows the $\dot{\epsilon}_v$ value at various temperatures at 94% RD. Finally, $\ln(T\dot{\epsilon}_v)$ are calculated and plotted against $-\frac{1}{RT}$, as shown in Fig 5.13. The activation energy of densification, which is the slope of the fitted line, is found to be 292 kJ/mol. This result is consistent with that reported in literature [67].

$$\ln(T\dot{\epsilon}_v) = -\frac{Q}{RT} + C \tag{4.17}$$

Fig 5.12: Experimental volumetric strain rate.

Table 5.1: Volumetric strain rate obtained from different temperature at 94% RD.

Temperature (°C)	1200	1250	1350
$\dot{\epsilon}_v$ (min ⁻¹)	0.000406281	0.00140292	0.00212897

Fig 5.13: Activation energy of densification was obtained as slope of the fitting line.

The above results show that the interface reaction is an appropriate dominant densification mechanism for fine-grained materials. This can be understood as when grain size is as small as in nano scale, the vast amount of grain boundaries results in significant enhanced diffusion rate along the grain boundaries. Hence the total densification process is largely controlled by adding or removing atoms at grain boundaries or free surfaces, which is much slower compared to the grain boundary diffusion. Using the interface reaction model, the strain rate constant $\dot{\epsilon}_{0r}$ was obtained as 1.15×10^{-7} , 5.58×10^{-7} , 7.51×10^{-7} and $1.09 \times 10^{-6} \text{ s}^{-1}$ respectively for the four different temperatures investigated.

5.4.2 Grain growth study

Grain growth is an important process during sintering as the mechanical properties can be very sensitive to the grain size for ceramic material. There are several processing parameters which affect grain growth. It has been known that significant grain growth in 3Y-TZP ceramics took place during high-temperature heat treatments. As well as temperature, heating rate also plays a big role in grain growth. Nightingale *et al.* [69] and Burggraaf *et al.* [70] found that grain growth mechanism in 3Y-TZP during microwave sintering differed from that obtained by conventional pressureless sintering. However, their investigations were concentrated mainly on stage 1 sintering. It is important to understand the science underlying the sintering mechanisms and microstructure evolution of the whole sintering process. Many mechanical properties

are determined by the final microstructure. The grain size generated mainly by the grain growth during the final stage, stage 2, is therefore significant. Stevens *et al.* [71] reported that grain growth is controlled by solute drag in the final sintering stage, as was also reported by Burggraaf *et al.* [70]. In the present study, the grain growth mechanism of stage 1 and stage 2 are investigated by the evaluation of the activation energy. The grain growth model established is then integrated with interface reaction densification model to predict the full description of the process.

It is well know that during the sintering process, grain growth can be expressed as [72]

$$L^n - L_0^n = k \cdot t \tag{5.11}$$

where L_0 is the initial grain size, k is the kinetic constant, t is time and n (with value of 1~4) is the exponential constant which connects the grain growth mechanism. Table 5.2 shows n value for different mechanisms. The mechanism will have some shift for different materials.

Table 5.2: different grain growth mechanisms.

n value	Possible mechanisms
1	Anomalous grain growth [71]
2	Volume diffusion, Normal grain growth [71]
3	Surface diffusion, Lattice diffusion [70], Solid-solution drag controlled grain growth [71]
4	Pore drag controlled grain growth [71]

From the experiment data, possible grain growth mechanisms of the two sintering stages were studied using Eq 5.11. The value of $L^n-L_0^n$ was plotted against time t , shown in Fig 5.14 and Fig 5.15. In the early stage, a linear relation was found between $L^n-L_0^n$ and t when n equals 3 and in final stage linear relationship was found when n equals 4. This result indicated that for the current material, grain growth mechanism may be surface diffusion or solid solution-dragged controlled where n equals 3, in stage 1, and grain growth maybe pore drag controlled where n equals 4, for stage 2 sintering. In order to verify the dominant mechanism of grain growth for stage 1 and 2 sintering, the activation energy is calculated.

Fig 5.14: Grain growth in early stage of sintering of 1200°C and 1250°C, $L^3 - L_0^3$ was plotted against time t and linear relationship was found.

Fig 5.15: Grain growth in final stage of sintering of 1200°C, 1250°C, 1300°C and 1350°C, $L^4 - L_0^4$ was plotted against time t and linear relationship was found.

In the Eq 5.11, k is a kinetic constant and after using an Arrhenius for k ($k = k_0 \cdot \exp(-Q/RT)$), we obtained Eq 5.12

$$\ln(G^n - G_0^n) = -\frac{Q}{RT} + \ln(t) + C \quad (5.12)$$

where Q is the apparent activation energy for grain growth and C a constant independent of temperature. For the early stage of sintering, the value of Q was

calculated as 558 kJ/mol with $n = 3$, shown in Fig 5.16; for the final stage of sintering, the value of Q was calculated as 325 kJ/mol with $n = 4$, shown in Fig 5.17.

Fig 5.16: Activation energy of early sintering stage, grain size data was chosen at 30 min dwelling at 1200°C, 1210°C, 1230 and 1250°C.

Fig 5.17: activation energy of final sintering stage, grain size data was chosen at 120 min dwelling at of 1200°C, 1250°C, 1300°C and 1350°C.

Burggraaf *et al.* [71] reported that the activation energy of solid-solution drag-controlled grain growth is 510 ± 25 kJ/mol when $n = 3$. Compared with the activation energy obtained in the present work, one may conclude that this solid-solution drag controlled grain growth is dominant in the stage 1 sintering for 3Y-TZP nano powder.

In the stage 2 sintering, our grain size experiment data are best fitted by the linear fitting with $n = 4$, which could be most likely related to a pore-drag controlled grain growth. However, there is no activation energy value reported for this mechanism to be compared. This work shows that the activation energy of grain growth mechanism is 325 kJ/mol.

The present results of n equals to 3 for early sintering stage and n equals 4 for final stage enhance the validity of Du and Cocks grain growth model, Eq 3.57 and Eq 3.58. Integrate Du and Cocks grain growth function into interface reaction model, the grain growth at 1200°C, 1250°C, 1300°C and 1350°C was studied at the same time. The results are shown in Fig 5.18. It was found that the present interface reaction model can provide reasonable prediction on grain size. It was also noted that the agreement between model and experiment is better in lower temperature and early stage. In later sinter stage, discrepancy was found. It was also noted that the discrepancy tended to increase with arising temperature, and such discrepancy is remarkable at 1350°C, which cannot be attributed to experiment error. The discrepancy between model and experiments at higher temperature and later sintering stage can be understood as following reason. In the present study, Du and Cocks grain growth model used was actually coupled densification-grain growth equations, *i.e.*, the calculated density value was input to calculate the grain size using interface reaction controlled model. In higher temperature and later sintering stage, as grain size has grown quite large, the interface reaction model is no longer providing accurate density values, hence resulted in discrepancy of grain size.

Although some discrepancy exists, the current interface reaction model is still operative for early stage sintering and lower temperature. Comparing with experiment data, the grain growth rate constant $\dot{L}_0$ at four different temperatures were obtained as 1.39×10^{-3} , 8.52×10^{-3} , 1.28×10^{-2} and 1.67×10^{-2} nm·s⁻¹ respectively.

Fig 5.18: Grain growth modeling results at four temperatures.

5.4.3 Densification rate constant and grain growth rate constant

In the study of densification and grain growth, we have already obtained the densification rate constant and grain growth rate constant using the interface reaction model. At different sintering temperatures, these constants were found to be different, as shown in Table 5.3. From Eq 3.55, we obtained

$$\ln(\dot{\epsilon}_{0r}T) = -\frac{Q}{RT} + \ln(\dot{\epsilon}_{00}) \quad (5.13)$$

where the material constant $\dot{\epsilon}_{00}$ can be determined by plotting the trajectory of $\ln(\dot{\epsilon}_0T)$ against $-\frac{1}{RT}$. The strain rate constant data used in this evaluation were taken from the modeling results, shown in Table 5.3. As the result, is obtained from the intercept of the fitting line as $7.33 \times 10^6 \text{ s}^{-1}$ for the current material, shown in Fig 5.19. Combine this result with Eq 3.49, we have

$$\dot{\epsilon}_{0r} = \frac{7.33 \times 10^6}{T} \exp\left(-\frac{Q}{RT}\right) \quad (5.14)$$

which shows the relationship between temperature and strain rate constant. With this relation, the strain rate constant of 1000°C is calculated as $2.98 \times 10^{-8} \text{ s}^{-1}$.

In the similar approaches, the temperature dependence of grain growth constant was also obtained. From the physics of the grain growth rate constant, an exponential

relationship between the grain growth rate constant and temperature was adopted and plotted in Fig 5.20, then at 1000°C the $\dot{L}_0$ was obtained as $1.20 \times 10^{-2} \text{ nm} \cdot \text{s}^{-1}$.

Table 5.3: Densification and grain growth rate constants were obtained by interface reaction model.

Temperature(°C)	1200	1250	1300	1350
$\dot{\epsilon}_{0r} \text{ (s}^{-1}\text{)}$	1.15×10^{-7}	5.58×10^{-7}	7.51×10^{-7}	1.09×10^{-6}
$\dot{L}_0 \text{ (nm} \cdot \text{s}^{-1}\text{)}$	1.39×10^{-3}	8.52×10^{-3}	1.28×10^{-2}	1.67×10^{-2}

Fig 5.19: The material constant $\dot{\epsilon}_{00}$ was obtained from the intercept of the fitting line.

Fig 5.20: Relation of grain growth rate constant and sintering temperature.

With these two constants determined, the interface reaction model for 1000 °C sintering was then generated. In order to confirm the validity of the model, several

samples were sintered at 1000 °C for 30, 60 and 120 minutes dwelling time, respectively. The experimental results are then compared with modeling results in Fig 5.21. As shown in Fig 5.21, satisfactory agreement is found between model's prediction and experiment observation, which gives the credibility to the present interface reaction model.

Fig 5.21: Compare of modeling prediction with experiment data for 1100°C densification.

5.4.4 Mechanism study by rate constant

To further validate the conclusion on densification mechanism study in previous sections, the densification rate constant $\dot{\epsilon}_0$ obtained from grain boundary model and interface reaction model are compared with that obtained from activation energy Q . The better agreement between $\dot{\epsilon}_0$ obtained from model and that obtained from activation energy may also indicate the dominant mechanism.

From Eq 3.55, we have

$$\dot{\epsilon}_0 = \frac{\dot{\epsilon}_{00}}{T} \exp\left(-\frac{Q}{RT}\right) \quad (3.55)$$

We know that $\dot{\epsilon}_0$ can be treated as a temperature dependent variable, because that $\dot{\epsilon}_{00}$ is a temperature independent constant and Q has been obtained from experiment data as 292 kJ/mol in section 5.4.1.

In other hand, $\dot{\epsilon}_0$ is obtained from constitutive modeling at different temperatures by curve fitting for different operating mechanisms, shown in Table 5.4. Thus, $\dot{\epsilon}_0$ from Eq 3.55 can be compared with $\dot{\epsilon}_0$ obtained from interface reaction model and grain boundary model. The result was shown in Fig 5.22.

Table 5.4: Densification and grain growth rate constants obtained by constitutive modelling.

Temperature (°C)	1200	1250	1300	1350
$\dot{\epsilon}_0$ IR model (s ⁻¹)	1.15×10^{-7}	5.58×10^{-7}	7.51×10^{-7}	1.09×10^{-6}
$\dot{\epsilon}_0$ GB model (s ⁻¹)	5.31×10^{-6}	7.85×10^{-6}	1.09×10^{-5}	1.15×10^{-5}
$\dot{L}_0$ IR model (nm· s ⁻¹)	1.39×10^{-3}	8.52×10^{-3}	1.28×10^{-2}	1.67×10^{-2}
$\dot{L}_0$ GB model (nm· s ⁻¹)	9.11×10^{-3}	1.23×10^{-3}	1.95×10^{-2}	1.95×10^{-2}

Fig 5.22: Comparison of $\dot{\epsilon}_0$ obtained from IR, GB and activation energy.

As shown in Fig 5.22, it is found that the value of $\dot{\epsilon}_0$ obtained from interface reaction model is closer to $\dot{\epsilon}_0$ obtained from activation energy. Therefore, the conclusion of densification mechanism for the present work is thus strengthened.

5.5 Conclusion remarks

In this chapter, a constitutive densification model that describes sintering process of 3Y-TZP nano-material was developed. This model couples the density and the grain

size so that it gives more appropriate prediction on the sintering process. The sintering mechanisms of present material system were also studied, and two important rate constants were calculated.

1. It was found that interface reaction controlled diffusion dominates mechanism of the densification process for the current nano-material. The activation energy of densification was obtained as 292 kJ/mol.
2. In the study of grain growth, the mechanism of stage 1 could be solid-solution drag controlled grain growth and $n = 3$, the activation energy was obtained as 558 kJ/mol which is also comparable to the value of this mechanism from literature. The mechanism of grain growth of stage 2 could also be pore-drag controlled with $n = 4$, and the activation energy was obtained as 325 kJ/mol for this mechanism.
3. The current model combines interface reaction densification model and Du and Cocks grain growth model which gives good prediction on densification; the model also provides good grain growth prediction in the early stage of sintering. The discrepancy between the present model and experiment data at higher temperature and later sintering stage may imply the limitation of interface reaction model and the possible involvement of other densification mechanisms.
4. The kinetic constants, such temperature independent constant, $\dot{\epsilon}_{00}$, was obtained as $7.33 \times 10^6 \text{ s}^{-1}$. The strain rate constants and grain growth constants at different temperatures were also obtained by empirical equations.
5. To enhance the validity of interface reaction model, the densification rate constants, $\dot{\epsilon}_0$, which were obtained from interface reaction model and grain boundary diffusion model, were compared with that obtained from activation energy. It was found that the $\dot{\epsilon}_0$ obtained from interface reaction model is closer to that obtained from activation energy. Therefore, the conclusion that the interface reaction controls the densification of present material was strengthened.

Chapter 6. Constitutive Modeling of Sinter-forging for 3Y-TZP Nano-material

A constitutive model to predict the densification and grain growth of nano-sized ceramic powder compact during sinter-forging is developed in this chapter. The effect of applied stress on both densification and grain growth is incorporated as an independent state variable in the model. The involvement of applied stress also provides another way to study the densification mechanism. This chapter builds up the constitutive model with three state variables, density, grain size and applied stress, to study the densification and grain growth mechanism. Then the model's predictions are compared with experimental data and several kinetic constants are obtained via the comparison.

6.1 Introduction

In the past few years, a plethora of techniques have been shown to be capable of producing large quantities of nano powder. The next stage following such development is to consolidate these nano powders into fully dense material. Conventional pressureless sintering fails to fully densify these powders while retaining a nanocrystalline grain size, due to occurrence of anomalous grain growth in the final sintering stage; however, sinter-forging has been shown to be quite effective in this regard. It is a sintering technique where simultaneous densification and deformation are achieved in porous ceramics at elevated temperature under a uniaxial stress.

As mentioned in the beginning, the constitutive model with applied stress shows another way to study the densification mechanism. This is because when powder compact is sinter-forged the shearing stress during densification is no longer zero, thus the deformation contains both volumetric shrinkage and shear deformation, so that we can use volumetric strain and effective strain together to evaluate the densification mechanism. The evaluation result can be compared with chapter 5 result to verify the dominant mechanism.

Besides constitutive models, many empirical models have been also proposed to study the densification during sinter-forging of 3Y-TZP nano powder. Mayo *et al.* [74] has developed a densification model in which an exponential relationship between densification driving force and stress is proposed. In their work, stress-assist diffusion coupled with a strain-controlled pore closure has been identified as the dominant densification mechanism. In this chapter, the constitutive model which combines interface reaction model and Du and Cocks grain growth model [1] will be used to analyze the sinter-forging of 3Y-TZP nano powder.

6.2 Experiments

It is known that tetragonal zirconia (TZP) ceramics have high strength and toughness. Nano-sized 3Y-TZP powder was chosen in the present experiment because it has been widely used in modern industries. For the current model, it should be noted that the sintering process of the chosen material should not have any phase transformation which can involve inaccuracy to density calculation. Despite 3Y-TZP being a well known phase-transform strengthening material, the phase transformation can be prevented in the experiment by controlling the grain size after sintering, *i.e.*, by keeping the grain size below the critical size of 0.8 μm .

6.2.1 Experiment procedure

The same commercial nano-sized 3Y-TZP powder with mean particle size of 58 nm was used as the starting material. Tablet-shaped green powder compacts with 50.4 % RD were prepared by 50 MPa uniaxial pressing to give shape and strength to the compacts. The dimensions of the powder compacts are approximately $\Phi 16\text{mm} \times 2\text{mm}$, measured by a digital vernier calliper, and each weighed around 2 gram. The compacts were sintered in a Centorr hot-pressing furnace inside a graphite die. The sintering temperature was 1000°C. The heating schematic of the sinter-forging process is shown in Fig 6.1. During the sintering-forging cycle, the heating chamber was first evacuated to a vacuum of 5×10^{-5} Torr. Then pre-pressed compacts were heated to 1000°C with a rate of 15°C/min without any applied stress. After the sintering temperature was reached, the uniaxial stress was applied onto the samples gradually at a rate of 5kg/min until the required loading. For the present experiment, several

loadings, such as 50 kg, 100 kg, 200 kg and 400 kg were chosen. Three samples placed in 120° symmetry were sintered for each sintering run. The stress on each sample was estimated as 0.8 MPa, 1.6 MPa, 3.2 MPa and 6.4 MPa taking the diameter of compacts is 16 mm. After holding the samples at the sintering temperature for desired time period, the applied load was taken off slowly with 5 kg/min and the sintered compacts were allow to cool to room temperature again at $15^\circ\text{C}/\text{min}$ simultaneously. During the whole sinter-forging cycle, the high vacuum is kept below 5×10^{-5} Torr. Several powder compacts were sintered in the hot-pressing furnace without applied stress for comparison.

Fig 6.1: Schematic of hot-press sintering (sinter-forging).

6.2.2 Experiment results

The relative density and grain size of the sinter-forged compacts were obtained. The sintered density was calculated by dividing the measured mass by the volume (obtained by measuring diameter and thickness). The relative density (RD) was calculated as the ratio of sintered density to the theoretical density, the latter being taken as 6.08 g/cm^3 for pure 3Y-TZP material. The sintered density of five different loadings is below 90% which means all compacts were in stage 1 sintering, shown in Fig 6.2.

Fig 6.2: sintered density obtained from five different loadings, temperature is 1000°C.

The grain size of the sinter-forged compacts was investigated by studying the image of microstructure using a Field Emission Scanning Electronic Microscope (FESEM). The sintered compacts were cut using a diamond cutter, and the cross section was polished and thermally etched, then observed under a JOEL FESEM. In the SEM image, the grain size was determined by counting the number of grains traversed by a straight line of known length and the final grain size was taken as 1.56 times the average intercept length. The experimental grain size data obtained from different loading batches were shown in Fig 6.3. It was found that the grain size of all the compacts were in submicron scale and less than 400 nm. The SEM pictures are attached in Appendix II.

The volumetric strain and the effective strain were also obtained experimentally by measuring the volume shrinkage and extend of deformation of the samples. Follow the Eq 4.2 and Eq 4.3, ε_v and ε_e of the compacts were calculated. It should be noted that ε_d and ε_h have the same meaning as previous chapters. The experimental strain data of different loadings calculated are shown in Fig 6.4 and Fig 6.5. Noted that the value of ε_e at zero loading is zero, thus it was absent in Fig 6.5.

$$\varepsilon_v = 2\varepsilon_d + \varepsilon_h \quad (4.2)$$

$$\varepsilon_e = \frac{2}{3} |\varepsilon_h - \varepsilon_d| \quad (4.3)$$

Fig 6.3: Experimental grain size obtained from sample of different loading batches.

Fig 6.4: Experimental volumetric strain obtained at different loading stress.

Fig 6.5: Experimental effective strain obtained at different loading stress.

As shown in Chapter 5, the volumetric strain rate and effective strain rate were obtained and the results are shown in Fig 6.6 and Fig 6.7. The value of effective strain at zero loading stress is zero because there is no deviatory deformation for free sintering samples.

Fig 6.6: Volumetric strain rate obtained at different stress by differentiating volumetric strain with time.

For 0 MPa series, the 1000 minutes' data was obtained by numerical fitting.

Fig 6.7: Effective strain rate obtained at different stress by differentiating effective strain with time, noted that the value for free sintering is zero.

Non-isothermal sintering was designed to calculate activation energy. In order to normalize the grain size and applied stress effects, several samples were sintered at different temperatures with different holding times, as shown in Table 6.1. From the discussion of Chapter 4, we have known that samples with similar density have comparable grain sizes. Another batch of samples was also sintered at different temperatures with same holding time. The grain size of these samples was measured. The results are shown in Table 6.2. These data were used to calculate activation energy of grain growth.

Table 6.1: Non-isothermal sinter-forging, stress is 3.2 MPa.

Temperature (°C)	Time (min)	Density (%)	Grain size (nm)
900	120	70.7	164
950	100	70.1	175
1000	30	69.5	169
1100	10	71.7	178

Table 6.2: Grain size obtained as different temperature sinter-forging, the applied stress is 3.2 MPa and dwelling time is one hour.

Temperature(°C)	Grain size (nm)	Time (min)
900	145	60
950	168	60
1000	214	60
1100	296	60

6.3 Discussions

In this section, the densification and grain growth mechanisms of current nano powder are under study. First, the activation energies of both densification and grain growth are calculated based on non-isothermal experiment data, from which the dominant mechanisms are deduced. Then, the constitutive model for sinter-forging is developed and used to perform mechanism study in another aspect. With the model catering dominant mechanism was established, several kinetic constants are obtained.

6.3.1 Activation energy for densification

The densification of a powder compact during a certain sintering stage can be generally described by the Arrhenius equation, which can be given as

$$\left[\frac{\Delta l / l_0}{t} \right] = C \cdot \exp\left(\frac{-Q}{RT}\right) \quad (6.1)$$

where Q is the activation energy for densification, $\Delta l / l_0$ is the relative shrinkage, t is holding time and RT has its usual meaning. The relative shrinkage can be related to the volumetric strain of sintered compacts and it can be substitute by relative density due to

$$\varepsilon_v = \Delta l / l_0 \quad (6.2)$$

$$\dot{\rho} = -\rho \cdot \dot{\varepsilon}_v \quad (6.3)$$

Integrating both sides of Eq 6.3 gives

$$\varepsilon_v = -\ln(\rho) \quad (6.4)$$

Substitute Eq 6.2 and Eq 6.4 into Eq 6.1, we have

$$\left[\frac{-\ln(\rho)}{t} \right] = C \cdot \exp\left(\frac{-Q}{RT}\right) \quad (6.5)$$

Linearization of Eq 6.4 results in

$$\ln\left[\frac{-\ln(\rho)}{t} \right] = -\frac{Q}{RT} + C_1 \quad (6.6)$$

From Eq 6.6, activation energy of densification can be obtained from the plot of the trajectory of $\ln[-\ln(\rho)/t]$ versus $1/T$. If there is only one operating mechanism, the trajectory will be linear and the activation energy Q is the slope of the fitted line. On the other hand, a curved trajectory indicates that several mechanisms may be operative. Such a plot is shown in Fig 6.8 giving a straight line. The activation energy of densification is thus obtained from the slope of fitted line as 161 kJ/mol for the stage 1 sintering.

Fig 6.8: Arrhenius plots of the intermediate sintering stage for current nano material, the activation energy was obtained as the slope of straight line.

It is well accepted that diffusional mechanism tends to dominate the densification of fine-grained ceramic materials. The calculation of activation energy can provide the first evaluation on the dominant mechanism. Many investigations have been focused in this area. It is well reported that for 3Y-TZP material, the activation energy for densification is around 500~700 kJ/mol when grain boundary diffusion is the only active densification mechanism. For example, Stevens *et al.* [72] reported that in 3Y-TZP ceramics, the activation energy of oxygen diffusion is 100 kJ/mol and the activation energy for diffusion of Zr^{4+} is 387 kJ/mol; the combined activation energy for diffusion is about 587 kJ/mol. It should be noticed for grain boundary diffusion,

the atoms or ions which have the smaller activation energy always diffuse faster. As discussed in earlier chapters, for diffusion process involving both interface reaction and grain boundary diffusion controlled by slower process. Thus, the bottle neck of grain boundary diffusion for 3Y-TZP material is that of Zr^{4+} ions. Under certain conditions, the activation energy can be reduced by the involvement of other densification mechanisms. In chapter 5, we obtained that the activation energy of interface reaction controlled diffusion is 292 KJ/mol for free sintering of nano-sized 3Y-TZP powder compacts, which is much lower than grain boundary diffusion. Burggraaf *et al.* [71] reported a surface diffusion-assisted grain boundary slip mechanism for densification of fine-grained 3Y-TZP, of which the activation energy of this mechanism is 100 kJ/mol. All these reports show the possibility of activation energy reduction by means of other factors, such as to reduce particle size and the presence of applied load, which can enhance densification.

In chapter 5, we found that interface reaction controlled diffusion is dominant for the free sintering of nano-sized 3Y-TZP powder compacts. Although the activation energy for sinter-forging is lower than that of free sintering being 161 kJ/mol, this result is much closer to that of interface reaction mechanism than grain boundary diffusion reported in literature. So that interface reaction mechanism is more likely to dominate in the present case. Based on the obtained activation value and above analysis, we can also infer that the applied stress plays a role in promoting interface reaction mechanism in sinter-forging. We shall discuss this further in the last part of this chapter.

6.3.2 Densification mechanism study

As mentioned at the beginning of this chapter, the involvement of the applied stress can produce effective strain during sintering in powder compacts, which provides another approach to investigate densification mechanism. In this section, elaborated procedures to study the densification mechanism during sinter-forging will be presented. Our goal is to use both free sintering and sinter-forging data to shed light on whether grain boundary diffusion or interface reaction can better explain the current experimental observations for densification of nano-sized 3Y-TZP material.

Firstly, we applied the experiment data to determine the sintering stress of current material. Then the as-determined sintering stress was used to analyze the densification mechanism for sinter-forging. Two approaches were presented for both mechanisms. In the first approach which is termed as ‘method 1’ in this report, sintering stress can be evaluated by comparing the volumetric strain rate with effective strain rate of compacts prepared by sinter-forging. Alternatively, we can also solve the sintering stress by comparing the volumetric strain rate of sinter-forged samples with that of free sintering samples. This provides the second approach which is termed ‘method 2’ in this report. It is noted the suitable mechanism should show good agreement on sintering stress obtained by both approaches.

In the present work, we have taken both density and grain size as state variables in the expression of sintering stress. It is noticed that the externally applied stress may influence the detailed shape of the necks that are formed between the contacting particles, which could be a variable in the function. However, Bouvard and McMeeking [76] have demonstrated in their study that the shrinkage rate resulting from the changes in neck size are essentially independence of each other and the geometry of neck does not significantly affect the densification rate. In a powder compact, the neck size can be expressed in terms of density and grain size. Therefore, we can give the sinter stress expression as

$$\sigma_s = \frac{g(\rho)}{L} \gamma_s \quad (6.7)$$

For a more general expression, the sintering stress was expressed in terms of normalized grain size. Equation 6.6 can be deduced as

$$\bar{\sigma}_s = \frac{\gamma_s}{L_0} g(\rho) = \sigma_s \frac{L}{L_0} \quad (6.8)$$

As the samples have same initial grain size and density, the grain size normalized sintering stress is a function of sintered density only. In the case of sinter-forging, the values of σ_m and σ_e are $\frac{1}{3}\sigma_{kk}$ and σ_{kk} , respectively. The initial grain density is determined as 50%. For a certain density, the data of volumetric strain rate, effective strain rate and grain size achieved at different applied stress are required for calculation, and they are shown in Table 6.3 to 6.6.

Table 6.3: Volumetric strain rate obtained from experiments at different applied stresses.

	Volumetric strain rate $\dot{\epsilon}_v$ (min ⁻¹)				
<i>RD</i>	0 MPa	0.8 MPa	1.6 MPa	3.2 MPa	6.4 MPa
0.65	0.00178	0.00265	0.00506	0.00703	0.0126
0.68	0.0000445	0.000919	0.00216	0.00425	0.00830
0.71	0.0000449	0.000160	0.000245	0.00154	0.00549
0.74	0.0000469	0.000174	0.000166	0.000328	0.00302

Table 6.4: Effective strain rate obtained from experiments at different applied stresses.

	Effective strain rate $\dot{\epsilon}_e$ (min ⁻¹)			
<i>RD</i>	0.8 MPa	1.6 MPa	3.2 MPa	6.4 MPa
0.65	0.00117	0.00197	0.00281	0.00757
0.68	0.000431	0.000900	0.00173	0.00594
0.71	0.0000633	0.000120	0.000580	0.00436
0.74	0.0000617	0.0000793	0.000172	0.00262

Table 6.5: Grain size obtained from experiments at different applied stresses.

	Grain size (nm)				
<i>RD</i>	0 MPa	0.8 MPa	1.6 MPa	3.2 MPa	6.4 MPa
0.65	182.6	169.6	167.7	147	109.7
0.68	309.5	196.2	187.2	162.7	120.2
0.71	435.0	266.4	203.1	173.3	132.9
0.74	577.7	344.2	304.6	210	149

Table 6.6: Grain growth rate date obtained from experiments at different applied stresses.

	Grain growth rate (nm·min ⁻¹)				
<i>RD</i>	0 MPa	0.8 MPa	1.6 MPa	3.2 MPa	6.4 MPa
0.65	2.4062	2.01533	2.41355	2.55139	3.03386
0.68	0.494811	1.29442	2.00107	2.24738	2.78069
0.71	0.212384	0.363701	1.14819	1.65895	2.55139
0.74	0.212384	0.325544	0.364486	0.87876	2.24738

Grain boundary diffusion evaluation

First, we assume that the densification of the present material is only controlled by grain boundary diffusion, and the effective strain rate and the volumetric strain rate can be obtained from Eq 3.29 and Eq 3.30. Also sintering stress is normalized by grain size and given in Eq 6.8. Therefore, we obtain the ratio of $\dot{\epsilon}_v$ to $\dot{\epsilon}_e$ for method 1 calculation as

$$\dot{\epsilon}_e = \frac{\dot{\epsilon}_{0b}}{\sigma_0} \left(\frac{L_0}{L} \right)^3 c_b(\rho) \sigma_e \quad (3.29)$$

$$\dot{\epsilon}_v = 9 \frac{\dot{\epsilon}_{0b}}{\sigma_0} \left(\frac{L_0}{L} \right)^3 f_b(\rho) (\sigma_m - \sigma_s) \quad (3.30)$$

$$\frac{\dot{\epsilon}_v}{\dot{\epsilon}_e} = 9 \frac{\bar{\sigma}_s \cdot L_0 \cdot f_b(\rho)}{\sigma \cdot L \cdot C_b(\rho)} + 3 \frac{f_b(\rho)}{C_b(\rho)} \quad (6.9)$$

In Eq 6.9, the value of $C_r(\rho)/f_r(\rho)$ is taken as 2 [41], and grain size normalized sintering stress $\bar{\sigma}_s$ for method 1 can be calculated since the value of $\frac{\dot{\epsilon}_v}{\dot{\epsilon}_e}$ and $\frac{L_0}{\sigma L}$ can be obtained from experiment data, as shown in Table 6.3 to 6.6. On the other hand, we obtain the ratio of sinter-forging volumetric strain rate $\dot{\epsilon}_{vp}$ to free sintering volumetric strain rate $\dot{\epsilon}_{vf}$ from Eq 3.30, which gives method 2 Equation as

$$\frac{\dot{\epsilon}_{vp}}{\dot{\epsilon}_{vf}} \left(\frac{L_p}{L_f} \right)^4 = \frac{\sigma \cdot L_p}{3\bar{\sigma}_s \cdot L_0} + 1 \quad (6.10)$$

where the subscript 'p' stands for sinter-forging expressions and 'f' for free sintering.

Equation 6.10, $\bar{\sigma}_s$ for method 2 can be solved because the value of $\frac{\dot{\epsilon}_{vp}}{\dot{\epsilon}_{vf}} \left(\frac{L_p}{L_f} \right)^4$ and

$\frac{\sigma \cdot L_p}{L_0}$ can be calculated from experiment data listed in Table 6.3 to 6.6. In the

calculation, $\bar{\sigma}_s$ at the same RD was obtained. The results are shown in Table 6.7.

Table 6.7: $\bar{\sigma}_s$ obtained in grain boundary diffusion evaluation for method 1 and 2.

$\bar{\sigma}_s$ (MPa)	Relative density (%)			
	65	68	71	74
Method 1	0.68	0.99	3.30	8.59
Method 2	21.10	15.72	13.14	53.19

Interface reaction evaluation

In this section, we assume that the interface reaction is the dominant mechanism. Similar to grain boundary evaluation, the method 1 equation for interface reaction mechanism is obtained from stage 1 strain rate equations, as the present experiments are all in stage 1. By dividing Eq 3.34 by Eq 3.33, we have

$$\dot{\epsilon}_e = \dot{\epsilon}_{0r} \left(\frac{L_0}{L} \right) c_r(\rho) \left[c_r(\rho) \left(\frac{\sigma_e}{\sigma_0} \right)^{\frac{3}{2}} + f_r(\rho) \left(\frac{|3(\sigma_m - \sigma_s)|}{\sigma_0} \right)^{\frac{3}{2}} \right] \sqrt{\frac{\sigma_e}{\sigma_0}} \quad (3.33)$$

$$\dot{\epsilon}_v = 3\dot{\epsilon}_{0r} \left(\frac{L_0}{L} \right) f_r(\rho) \left[c_r(\rho) \left(\frac{\sigma_e}{\sigma_0} \right)^{\frac{3}{2}} + f_r(\rho) \left(\frac{|3(\sigma_m - \sigma_s)|}{\sigma_0} \right)^{\frac{3}{2}} \right] \sqrt{\frac{\sigma_0}{|3(\sigma_m - \sigma_s)|}} \left[\frac{3(\sigma_m - \sigma_s)}{\sigma_0} \right] \quad (3.34)$$

$$\frac{\dot{\epsilon}_v}{\dot{\epsilon}_e} = 3 \frac{f_r(\rho)}{C_r(\rho)} \sqrt{\frac{3\bar{\sigma}_s L_0}{\sigma L} + 1} \quad (6.11)$$

In Eq 6.11, $\bar{\sigma}_s$ can be obtained because the value of $\left(\frac{\dot{\epsilon}_v}{\dot{\epsilon}_e} \right)^2$ and $\frac{L_0}{\sigma L}$ can be calculated base on experiment data, as shown in Table 6.3 to 6.6. Thus, $\bar{\sigma}_s$ for method 1 at different densities is obtained and shown in Table 6.8. Alternatively, the equation for method 2 is obtained by dividing the sinter-forging volumetric strain rate by that of free sintering volumetric strain rate, giving

$$\frac{\frac{L_p}{L_f} \cdot \frac{\dot{\epsilon}_{vp}}{\dot{\epsilon}_{vf}}}{\frac{L_p}{L_f} \cdot \frac{\dot{\epsilon}_{vp}}{\dot{\epsilon}_{vf}}} = \frac{\frac{C_r(\rho)}{f_r(\rho)} \sigma^{1.5} \left(\sigma + 3\bar{\sigma}_s \frac{L_0}{L_p} \right)^{0.5} + \left(\sigma + 3\bar{\sigma}_s \frac{L_0}{L_p} \right)^2}{9\bar{\sigma}_s^2 \left(\frac{L_0}{L_f} \right)^2} \quad (6.12)$$

Where the subscripts ‘*p*’ and ‘*f*’ have same meaning as in Eq 6.10. It is noticed that Eq 6.12 is a polynomial function of $\bar{\sigma}_s$ and $\bar{\sigma}_s$ can be solved based on experiment data. In the above calculation, the value of $C_r(\rho)/f_r(\rho)$ is taken as 2 [41], and all data needed is taken from Table 6.3 to 6.6. The calculated results of $\bar{\sigma}_s$ for method 2 at different densities are also shown in Table 6.8.

Table 6.8: $\bar{\sigma}_s$ obtained in interface reaction evaluation for method 1 and 2.

$\bar{\sigma}_s$ (MPa)	Relative density (%)			
	65	68	71	74
Method 1	2.46	3.09	11.84	35.66
Method 2	1.33	1.82	7.16	31.75

From the results shown in Table 6.7 and Table 6.8, it is found that the grain size normalized sintering stresses $\bar{\sigma}_s$ obtained from the two methods for interface model are close to each other, while those of grain boundary diffusion model differ widely to each other, as shown in Fig 6.9. This can be concluded that interface reaction model is more appropriate than grain boundary diffusion to describe densification during sinter-forging. In Fig 6.9, it is also noticed that $\bar{\sigma}_s$ tends to increase with sintered density which is consistent with reports in literatures [5].

Fig 6.9: Variation of grain size normalized sintering stress with relative density, was obtained from two methods for each mechanism (IR and GD represent interface reaction and grain boundary diffusion respectively).

Based on the above analysis and calculations, we obtain experimental sintering stress σ_s as the average value of two methods, given by models of interface reaction mechanism, as shown in Fig 6.10. This figure shows that the sintering stress varies from 1 to 10 MPa with proceed of densification for the current interface reaction controlled sintering.

Fig 6.10: Sintering stress was obtained as the average value of two methods from IR model.

In the above discussion, we have found that interface reaction mechanism is more appropriate for the sintering of current material by two methods approach. Therefore, we can derive densification model for current stage 1 sinter-forging as

$$\dot{\rho} = \dot{\epsilon}_{0r} \rho \frac{L_0}{\sigma_0^2 L} \left[f_r(\rho) C_r(\rho) \sigma^{\frac{3}{2}} (\sigma - 3\sigma_s)^{\frac{1}{2}} + f_r^2(\rho) (\sigma - 3\sigma_s)^2 \right] \quad (6.13)$$

where σ is applied stress and other symbols have the usual meaning.

6.3.3 Grain growth study

Mechanism study

With the grain size data of sinter-forging experiment, the possible grain growth mechanism is studied using Eq 5.11.

$$L^n - L_0^n = k \cdot t \quad (5.11)$$

The values of $L^n - L_0^n$ obtained at different applied stress are plotted against time t in Fig 6.11 to Fig 6.13.

Fig 6.11: When $n = 2$, the relationship between $L^n-L_0^n$ and t is obviously non-linear.

Fig 6.12: When $n = 3$, the relationship between $L^n-L_0^n$ and t is linear for all series can be regarded as linear which indicates the possibility of solid solution-drag controlled grain growth mechanism for sinter-forging of nano-sized 3Y-TZP.

Fig 6.13: When $n = 4$, the relationship between $L^n - L_0^n$ and t is linear for all series can be regarded as linear which indicates the possibility of pore-drag controlled grain growth mechanism for sinter-forging of nano-sized 3Y-TZP powder compacts.

It is found that the relation between $L^n - L_0^n$ and t is non-linear when $n = 2$ (Fig 6.14), and tends to be linear when $n = 3$ and $n = 4$ in the stage 1. This result indicates that for the current material the dominant grain growth mechanism is probably solid solution-drag ($n = 3$) or pore-drag controlled ($n = 4$) grain growth. As our investigation focus on the stage 1 sintering, the pore-drag controlled mechanism is not very likely due to the large fraction of open porosity. Thus we propose that the appropriate dominant grain growth mechanism for the present case is solid solution-drag controlled grain growth, and $n = 3$. Eq 5.11 is hence written as

$$L^3 - L_0^3 = kt \quad (6.14)$$

where k is a kinetic constant related to activation energy ($k = k_0 \exp(-Q/RT)$) and t is dwelling time.

The activation energy of grain growth can be obtained from the linear plot of Eq 6.15.

$$\ln(L^3 - L_0^3) = -\frac{Q}{RT} + \ln(t) + C \quad (6.15)$$

Several compacts are sinter-forged at 900°C, 950°C, 1000°C and 1100°C to obtain necessary grain size (Table 6.2). The plot of $\ln(L^3 - L_0^3)$ verse $-\frac{1}{RT}$ is shown in Fig 6.14.

Fig 6.14: the activation energy of grain growth of current sinter-forging was obtained as the slope of linear line as 150 kJ/mol.

In Fig 6.14, the activation energy of grain growth is obtained as 150 kJ/mol. This result is much lower than 510 ± 25 kJ/mol which is reported for solid-solution drag-controlled grain growth. From many literature [70] [72], for stage 1 sintering of 3Y-TZP material, the most likely grain growth mechanism is surface diffusion and solid-solution drag-controlled grain growth at $n = 3$. Since the current activation energy is much smaller than that of solid-solution drag-controlled mechanism, we can propose that surface diffusion is operative in the current stage 1 sinter-forging. The value of activation energy is also comparable to 275 kJ/mol in literature [71].

The current activation energy is lower than that of stage 1 free sintering. This indicates that the grain growth occurs more readily during sinter-forging and the grain growth rate at a given RD could be faster than that of free sintering. This can be understood as the applied stress could increase the neck area between the particles, which in turn provides increased possibility for grains immersing (bigger grains consume smaller grains) during grain growth by diffusion.

Applied stress incorporated grain growth model

In the previous study, we have found that the applied stress plays an active role in the grain growth during sinter-forging. In the following, we try to analyze this effect of

applied stress on grain growth rate by establishing a grain growth model coupled with applied stress as one of variables.

Fig 6.15 shows the microstructure for a powder compact during sinter-forging. Σ_{ij} is the macroscopic applied stress and $\dot{E}_{ij}$ is the strain rate respond for Σ_{ij} . For a single grain or unit cell, the macroscopic applied stress will result in a localized stress response σ_{ij} , as shown in Fig 6.15. From this geometry configuration, we derived grain growth model incorporated with σ_{ij} .

Fig 6.15: Microstructure for a powder compact in sinter-forging. Σ_{ij} is applied stress and $\dot{E}_{ij}$ is the strain rate respond for Σ_{ij} [41].

During grain growth, the pores are dragged along grain boundaries and grain interface as the same velocity as the migrating grain boundaries. Brook [38] showed that if F_b is the driving pressure for grain growth and M_b and M_p are the mobility of the grain boundaries and the pores, respectively, the grains grow at a rate

$$\dot{L} = \frac{M_b M_p}{M_p + M_b N} F_b \quad (6.16)$$

where N is the number of pores per unit length of grain boundary

$$N = \frac{1}{L} \quad (6.17)$$

Hillert [37] postulated a steady stage process and obtained the driving pressure for the rate of growth of the mean grain size as

$$F_b = \frac{\gamma_b}{L} \quad (6.18)$$

where γ_b is the grain boundary energy per unit area. However, the driving pressure result from energy change but also localized applied stress. In the present work, it is

$$F_b = \frac{\gamma_b}{L} + \sigma_{ii} \quad (6.19)$$

where σ_{ii} is the local stress caused by applied stress of sinter-forging. Du and Cocks [1] developed the mobility of pores and grain boundaries. For stage 1 sintering

$$M_p = \frac{\dot{\mu}_p}{L_0 \sigma_0} \left(\frac{L_0}{r} \right)^{\beta-1} \quad (6.20)$$

$$M_b = \frac{\dot{\mu}_b}{\sigma_0} \quad (6.21)$$

where $\dot{\mu}_p$ is the velocity of a pore of radius L_0 (equals to initial grain size) at a driving force $\sigma_0 L_0^2$, and β is a constant that depends on the mechanism (for the current system $\beta=n=3$). The variable r is the mean radius of pores, giving

$$r = \frac{1}{\pi} (1 - \rho)^{\frac{1}{2}} L \quad (6.22)$$

Substituting Eq 6.18 to Eq 6.21 into Eq 6.16, giving

$$\dot{L} = \frac{\dot{\mu}_b \left(\frac{L_0}{L} \right)}{1 + f(\rho, L/L_0)} \cdot \frac{\gamma_b + \sigma L}{\sigma_0 L_0} \quad (6.23)$$

where

$$f(\rho, L/L_0) = \pi^{1-\beta} \frac{\dot{\mu}_b}{\dot{\mu}_p} \left(\frac{L}{L_0} \right)^{\beta-2} (1 - \rho)^{\frac{\beta-1}{2}} \quad (6.24)$$

As $f(\rho, L/L_0) \gg 1$ [1] and $\beta=n=3$ in Eq 6.24, Eq 6.23 approximately equals to

$$\dot{L} = \dot{L}_0 \left(\frac{L_0}{L} \right)^2 (1 - \rho)^{-1} + \dot{L}_0^* \left(\frac{L_0}{L} \right) (1 - \rho)^{-1} \cdot \sigma \quad (6.25)$$

where $\dot{L}_0$ and $\dot{L}_0^*$ are material kinetic constants

$$\dot{L}_0 = \pi^2 \frac{\dot{\mu}_p \gamma_b}{\sigma_0 L_0} \quad (6.26)$$

$$\dot{L}_0^* = \frac{\pi \mu_p}{2 \sigma_0} \quad (6.27)$$

Eq 6.25 describes the grain growth behaviours in sinter-forging. It is noticed that when there is no applied stress the sinter-forging model becomes stage 1 Du and Cocks' model [1]. In order to examine the validity of the newly proposed model, Eq 6.25, experiment data as shown in Table 6.6 are applied.

Fig 6.16 shows the variation of grain growth rate with density at different applied stresses. It is found that at given relative densities, higher applied stress gives high grain growth rate which indicates applied stress can increase grain growth rate at stage 1 sintering for compacts with same densities.

Fig 6.16: Experimental grain growth varies with relative density at different applied stress.

Fig 6.17 shows the variation of grain growth rate with applied stress, in which linear relationship is found at a same relative density. This observation supports Eq 6.25, in which we have suggested a simple linear relationship between grain growth rate and applied stress when the RD and grain size are same. From the physical meaning of $\dot{L}_0^*$ in Eq 6.27, we know that it is a temperature dependant material constant which does not change with the applied stress. Thus, we obtained it as the average value of four stresses in analyzing the slope of fitting lines in Fig 6.17. In the present calculation, the kinetic constant $\dot{L}_0^*$ was obtained as 2.585×10^{-7} nm/min·Pa, and another constant $\dot{L}_0$ can be obtained in the grain growth modeling.

Fig 6.17: Grain growth rate increase linearly with applied stress at same density on observation early stage sinter-forging.

It should be noted that Eq 6.25 only suits the stage 1 sinter-forging, because when the applied stress is approaches to zero the relationship between grain growth rate and applied stress at a given RD cannot be regarded to be linear, as shown in Fig 6.17.

6.3.4 Constitutive model for sinter-forging

In the earlier discussion on densification and grain growth mechanisms, we have obtained a suitable model to describe the current sinter-forging experiment. In this section, the constitutive model combining interface reaction densification model and presently derived extend stress effect incorporated grain growth model is developed, and the sinter-forging process was modelled. The densification equation comes from Eq 6.13 and $f_r(\rho)$ and $C_r(\rho)$ are followed Du and Cocks' expressions [1] as

$$f_r(\rho) = \frac{1}{3} \frac{(1 - \rho_0)}{\rho^{3/2} \rho_0^{1/2} (\rho - \rho_0)} \quad (6.28)$$

$$C_r(\rho) = \frac{2}{3} \frac{(1 - \rho_0)}{\rho^{3/2} \rho_0^{1/2} (\rho - \rho_0)} \quad (6.29)$$

and

$$\sigma_0 L_0 = \gamma_s \quad (6.30)$$

where γ_s is surface energy. Douglas *et al.* [74] has reported that the surface energy of 3Y-TZP materials can be represented as $1.428 - (0.000431) \times T$ where T is absolute

temperature. Substituting Eq 6.28 and Eq 6.29 into the densification model, Eq 6.13 becomes

$$\dot{\rho} = \frac{1}{9} \frac{\dot{\epsilon}_{0r} \gamma_s^2}{LL_0} \frac{(1-\rho_0)^2}{\rho^2 \rho_0 (\rho - \rho_0)} [\sigma^{\frac{3}{2}} (\sigma - 3\sigma_s)^{\frac{1}{2}} + (\sigma + 3\sigma_s)^2] \quad (6.31)$$

where ρ is the current density and ρ_0 the initial density (both are relative density), L and L_0 are current grain size and initial grain size respectively, $\dot{\epsilon}_{0r}$ is a materials constant and σ is the applied stress. The value of sintering stress in Eq 6.31 was obtained from experiment data, shown in Fig 6.13. The grain growth is determined by Eq 6.25. A simple Euler function (Eq 4.12 and 4.13) is used to integral densification rate and grain growth rate with time, thus we obtain density-time and grain size relationships. All these computations are completed using software Matlab 6.5.

Fig 6.18: Densification at four applied stresses was modeled and compared with experiment data. A coupled interface reaction and stress-assisted grain growth model was used (Eq 6.25).

Fig 6.18 shows the densification modeling for the current sinter-forging process at four different applied stresses. It was found the interface reaction model (Eq 6.31) provides good agreement with experiment data. The kinetic constant $\dot{\epsilon}_{0r}$ are $3.48 \times 10^{-12} \text{ s}^{-1}$, $3.52 \times 10^{-12} \text{ s}^{-1}$, $3.45 \times 10^{-12} \text{ s}^{-1}$ and $4.05 \times 10^{-12} \text{ s}^{-1}$ for 0.8 MPa, 1.6 MPa, 3.2 MPa and 6.4 MPa, respectively. It is also found that the value of $\dot{\epsilon}_{0r}$ obtained for different batches are very similar. This result is reasonable because $\dot{\epsilon}_{0r}$ is a kinetic constant and only related to temperature and materials.

Fig 6.19 shows the modeling result of grain growth model incorporated with applied stress. It is found that current model can provide good agreement with experiment data for different applied stress. Compared with Fig 5.18, the current modeling result is closer to the experiment data, which strengthen the conclusion on grain growth mechanism study in section 6.3.3. It is also found that the curves of different applied stress looks like similar in shape, which may indicated the current grain growth is independent with applied stress. However, this is not true because the applied stress has approved to affect grain growth rate in many studies [74, 75]. The reason of similar curves is because that the current applied stress is quite minor compared with sintering stress. For instance, the applied stress is 6.4 MPa at maximum; however, the sintering stress is about fifty times of this value. This is also proved by the discrepancy of current model tends to be larger in low applied stress. Thus it is easy to understand that the current model give better prediction at higher applied stress. For example, the discrepancy between model and experiments in 0.8 MPa series is much bigger than other three series. This observation also shows the scope of Eq 6.25. The kinetic constants $\dot{L}_0$ and $\dot{L}_0^*$ are also obtained after and shown in Table 6.9. It can be seen that for samples obtained at different applied stress, $\dot{L}_0$ value remains reasonably constant, however, $\dot{L}_0^*$ varies dramatically with applied stress as it is a stress related constant.

Table 6.9: Kinetic constants obtained in modeling.

Applied stress	0.8 MPa	1.6 MPa	3.2 MPa	6.4 MPa
$\dot{\epsilon}_{0r} \text{ (s}^{-1}\text{)}$	3.48×10^{-12}	3.52×10^{-12}	3.45×10^{-12}	4.05×10^{-12}
$\dot{L}_0 \text{ (nm}\cdot\text{s}^{-1}\text{)}$	5.46×10^{-2}	4.23×10^{-2}	4.10×10^{-2}	3.16×10^{-2}
$\dot{L}_0^* \text{ (nm}\cdot\text{s}^{-1}\cdot\text{MPa}^{-1}\text{)}$	1.22×10^{-3}	5.08×10^{-4}	2.31×10^{-4}	1.17×10^{-4}

Fig 6.19: Grain growth at four applied stress was modelled and compared with experiment data, the model coupled interface reaction model and as-derived grain growth model.

6.4 Conclusion remarks

In this chapter, the densification and grain growth of nano-sized 3Y-TZP powder compacts prepared by sinter-forging were studied. The study focused on stage 1 sintering and derivation of applied stress incorporated interface reaction densification model and grain growth model. The following conclusions are drawn:

1. It was found that interface reaction controlled diffusion mechanism is more appropriate to describe the densification of sinter-forging of current material system. The activation energy of densification was obtained as 161 kJ/mol.
2. In the grain growth study, the mechanism of stage 1 sintering could be surface diffusion with $n = 3$, with an activation energy of 150 kJ/mol.
3. In the study of applied stress effects on grain growth of current nano-material, a stress-incorporated grain growth model was developed. The new model provides good agreement with experiments. Due to the limitation of current equipment, the applied stress effect of current model was not obviously observed.

Chapter 7. Study of sintering stress for nano-material

In the sintering process of a porous powder compact, the sintering stress is a fundamental parameter. In the earlier chapter, it is observed that the magnitude of sintering stress varies with relative density during sintering. In this chapter, an appropriate sintering-stress expression for stage 1 sintering is developed based on the experiment results given by Chapter 6. Several expressions given in literature are also investigated and compared.

7.1 Introduction

In the previous study, we have noted that the sintering stress affects the hydrostatic component of the present densification model, which results in volumetric shrinkage of the material. The sintering stress, which is also denoted as the intrinsic driving pressure of densification, is a driving force induced by surface tension. It arises from the curvature of the pore surface and can be written as $2\gamma_s/r$ for spherical pores, where γ_s is surface tension (energy) and r is pore radius [76]. In many derivations of models of diffusional densification mechanisms for submicron and larger-grained materials, the sintering stress term is generally ignored since it is less than 1 MPa, which is small compared with typical applied stress (usually 10~300MPa). However, in nano-materials and low pressure sintering, the sintering stress becomes significant and cannot be ignored (for example, $2\gamma_s/r \approx 40\text{MPa}$ for a spherical pore with $r=50\text{ nm}$).

In attempts to calculate the magnitude of sintering stress, a number of experimental studies have been performed by many researchers. Venkatachari and Raj [77] and Rahaman *et al.* [65] have both determined the sintering stress by measuring the shear and volumetric components of strain when powder compacts were sintered under a uniaxially applied stress. Hsueh *et al.* [46] have also provided a direct measure of the sintering stress by comparing the prediction of their constitutive models with their experiment results. Both Rahaman *et al.* [65] and Hsueh *et al.* [46] proposed that sintering stress was nearly a constant during sintering with a value of around 1 MPa.

However, Venkatachari and Raj [77] found that the sintering stress was in the range of 0.4 MPa to 0.8 MPa and it decreased with relative density during stage 1 sintering. However, all these groups of researchers have assumed a linear stress and inverse cubic grain size relationship on strain rate throughout the sintering process, which suggests that grain boundary diffusion is the dominant sintering mechanism. On the other hand, Ma [5] determined the sintering stress of fine-grained alumina material was in the range of 1 to 10 MPa, and in different stages, the sintering stress varies. In stage 1 sintering, the sintering stress increases with relative density, but in stage 2, the sintering stress decreases with increasing relative density.

Theoretical expressions of sintering stress have been studied by many researchers. Gregg and Rhines [63], Bordia and Scherer [78], Kellett and Lange [79], McMeeking and Kuhn [34], Ashby [3], Sovoboda *et al.* [80], Cocks [41], and Shinagawa and Hirashima [81] have proposed different expressions for the sintering potential for different sintering stages. In the present work, several most representative theoretical equations for stage 1 sintering stress are compared with the experiment results. The specific equations of their expressions are shown in Table 7.1. In Shinagawa *et al.*'s [81] expression, K is a parameter representing the initial pore size which approximately equals to 12 in stage 1. Other variables γ_s , L , ρ and ρ_0 have their usual meanings as early chapters.

Table 7.1: Expressions of sintering stress during stage 1 sintering.

Researcher	Expression
Ashby	$\sigma_s = \frac{6\gamma_s}{L} \rho^2 \left(\frac{2\rho - \rho_0}{1 - \rho_0} \right)$
McMeeking <i>et al.</i>	$\sigma_s = \frac{24\gamma_s}{L} \rho^2 \left(\frac{\rho_0}{\rho} \right)^{\frac{1}{3}}$
Shinagawa <i>et al.</i>	$\sigma_s = \frac{4\gamma_s}{KL} \rho^6 \left[\frac{(1 - \rho_0)\rho}{(1 - \rho)\rho_0} \right]^{\frac{1}{3}}$

These theoretical equations are normalized respect to grain size by a product with L/L_0 and compared with the grain size normalized sintering stress obtained from experiments in Chapter 6, as shown in Fig 7.1. In the figure, we found out that both

Ashby [3] and McMeeking *et al.* [34] expressions overestimate sintering stress by an order of magnitude in the case of nano-scaled particles, while the value given by Shinagawa *et al.*'s [81] equation is smaller than experiment result by an order of magnitude. Thus, the development of a most appropriate expression on sintering stress for sintering of nano-sized material will be of significant contribution to this field of study.

Fig 7.1: Several representative theoretical expressions were compared with present experiment grain size normalized (GN) sintering stress.

7.2 Sintering stress study

7.2.1 Geometry configurations

In many studies on establishing theoretical expressions, the two balls model has been commonly used, in which particles were treated as sphere shaped. This assumption brings a lot of convenience in computation and provides acceptable precision in coarse-grained materials. However, it may not be appropriate in the case of nano-scaled particles. For nano-sized particles, there are much more atoms on the grain surface than interior grain, the various parameters are very sensitive to surface structure of the particles. Taking this into consideration, Wigner-Sietz cell is more appropriate for the present study. Normally, the Wigner-Sietz cell is formed by a truncated octahedron which has 6 square faces, and 8 hexagonal faces [80]. However, in the present case, as 3Y-TZP material has f.c.c lattice, so that the Wigner-Sietz cell

of 3Y-TZP particle is made by 12 identical planes and two types of corners at which four and six grains, respectively meet [80]. Fig 7.2 shows a schematic drawing of the said configuration. The possible maximum coordination number, Z , is 12. The volume of the unit cell is calculated by using the sphere (dash line in Fig 7.2) with an effective radius of R , where $2R$ is usually regarded as particle size L .

Fig 7.2: Wigner-Sietz cell of 3Y-TZP particles. Pores can be 3D2 type and appears on the plane of the unit cell. The volume of the unit cell can be taken as $4\pi R^3/3$.

Following the sintering stage definition by Ashby [3], in stage 1a, an open porosity formed by interconnecting network of pores is prominent microstructure. The dihedral angle on free surface (between pore and grain surface) should be rather small, no more than 20° based on the current geometry, as shown in Fig 7.3. In stage 1b sintering, as porosity decreases, pores normally appear on two-grain junctions which are any plane of the cell, as shown in Fig 7.2. As the particles get closer, the porosity structure will change from open porosity to isolated porosity on junctions of grain boundaries. The pores on two-grain junctions in Fig 7.2 are called 3D2 pores, followed the terminology of Riedel and Svoboda [80], where 3D means three-dimensional and 2 means they are located on two-grain junctions. Normally, the dihedral angle of the isolated pore is bigger than that of open porosity, ranges from 20° to 90° [80], as shown in Fig 7.4. If one starts from spherical particles, the maximum packing density is 0.52 for simple cubic, 0.68 for b.c.c lattice and 0.74 for the f.c.c lattice. Thus we can deduce that the maximum packing density for the

present 12-faces cell is between 0.68 and 0.74, which means at this point, Z reaches it maximum value as 12.

Fig 7.3: Open porosity formed and dihedral angel is less than 20 degree.

Fig 7.4: Dihedral angel for 3D2 pores.

7.2.2 Sintering stress expression

The sintering stress, σ_s , is defined as the mechanical hydrostatic stress which just balance the internal surface tension forces so that the porous solid does not shrink. Thus the solid is in equilibrium if

$$\sigma_s dV = \frac{1}{2} \sum F_i du_i \quad (7.1)$$

where F_i is the force acting on grain facet i , and du_i is the virtual displacement across facet I , which is associated with a volume change dV . The sum extends over all facets.

Follow the results given by Svoboda *et al.* [80], Eq 7.1 can be deform to

$$\sigma_s = \frac{1}{2} \gamma_s \sum (2\kappa A_i + L_i \sin \varphi) du_i / dV \quad (7.2)$$

There are two kinds of force in equation 7.2, the first force comes from the stress on the boundary which follows from the continuity of the chemical potential when moving from the surface to grain boundary, and $F_i = 2\gamma_s \kappa_i A_i$ where κ is the mean curvature, A_i is the contact area on facet i ; the second force arises from the surface tension force, which has the normal component $\gamma_s L_i \sin \varphi$, where L_i is the length of the circumference of the contact area on the facet i .

For the present Wigner-Sietz cell of 3Y-TZP particle

$$du = dV / 24a^2 \quad (7.3)$$

where a is the edge length of the unit cell. In this case, the sintering stress can be expressed as

$$\sigma_s = \frac{\gamma_s}{48a^2} \sum_{i=1}^{12} (2\kappa A_i + L_i \sin \varphi) \quad (7.4)$$

Following the work of Svoboda *et al.* [79], the value of A_i and L_i for closed 3D2 pores was taken as

$$A_i = a^2 - \pi \sin^2 \varphi / \kappa^2 \quad (7.5)$$

$$L_i = 2\pi \sin \varphi / \kappa \quad (7.6)$$

The mean curvature κ of the pore surface can be expressed as a function of density, dihedral angle and dimensionless volume of a pore F_v ($F_v = V_p \kappa^3$, V_p is the actual pore volume).

$$\kappa R = \left(\frac{3NF_v}{4\pi} \frac{1-f}{f} \right)^{\frac{1}{3}} \quad (7.7)$$

where f is porosity, R is radius of particles ($R=L/2$) and N is the number of pores per unit cell. For 3D2 pores in f.c.c structure, the V_p was calculated by Clemm and Fisher [82] as

$$V_p = \frac{2\pi}{3} r^3 (2 - 3 \cos \varphi + \cos^3 \varphi) \quad (7.8)$$

where r is pore radius and $r=1/\kappa$. In the present case, $N=6\rho/\rho^*$ (ρ^* is the maximum packing density for the present unit cell) and $f=1-\rho$, thus the sintering stress simplifies to

$$\sigma_s = \frac{2\gamma_s}{L} \left[\frac{3f(\varphi)\rho^2}{\rho^*(1-\rho)} \right]^{\frac{1}{3}} \quad (7.9)$$

where

$$f(\varphi) = 2 - 3 \cos \varphi + \cos^3 \varphi \quad (7.10)$$

It should be noted that the value of $f(\varphi)$ is closely related to the pore structure in the unit cell. For 3D2 closed pores on particle surface, when $\rho > \rho^*$, φ ranges from 60° to 90° [80]. In the case of $\rho_0 < \rho < \rho^*$, open porosity occurs inside the unit cell, it is assumed that φ is smaller than 20° based on its physical interpretation. Incorporating the present determination, it shows that the present-proposed sintering stress fits well with experimental sintering stress, as shown in Fig 7.5. During the above calculation, different dihedral angles are assumed as densification proceeds. The maximum packing density ρ^* is taken as 70%. Thus, when $\rho < 70\%$, the pore structure belongs to open porosity and the dihedral angle, φ , is taken as 20° ; while when $\rho \geq 70\%$, the pore structure is 3D2 isolated pore on surface of two grains junction and φ is taken as $60^\circ \sim 90^\circ$.

Fig 7.5: Present sintering stress equation was compared with experiment data and other expressions from literature.

7.2.3 Conclusion

In this chapter, a sintering stress expression for stage 1 sintering nano-sized powder compacts was developed. In the derivation, a Wigner-Sietz cell was used as the geometry dimension of nano-sized particles instead of the two-ball model. It was found that the present expression can explain the experiment data well. The pore structure during sintering was also explored. When the relative density is below the maximum packing density, 70%, open porosity will occur; whereas for the case that RD is higher than 70%, the pores will be closed and located on the surface of two-grain junctions.

Chapter 8. Conclusion and Future Work

In the present work, elaborate experiments for sintering of near nano-sized alumina and nano-sized 3Y-TZP powders have been designed and performed. The above fine grained powders have been carefully processed, and sintered to nearly full dense. Upon the experiment data obtained, a constitutive model which combines densification and grain growth is applied to study the dominant mechanism for either free sintering or sinter-forging. During modeling, several important variables and constants have been obtained. Based on the observed discrepancy between Du and Cocks model with current experiment data, the constitutive model has been further developed to suit the nano-sized material system better.

8.1 Conclusions for current study

Based on experimental data and modeling analysis, conclusions of present work are obtained as follows:

1. During the densification study of near-nano sized alumina powder, it was found that interface reaction controlled diffusion dominates the densification process. Several kinetic constants, such as volumetric strain rate constant $\dot{\epsilon}_{0r}$ and grain growth rate constant $\dot{L}_0$ were obtained. The values of $\dot{\epsilon}_{0r}$ are $4.60 \times 10^{-8} \text{ s}^{-1}$ at 1200°C and $9.80 \times 10^{-8} \text{ s}^{-1}$ at 1250°C . The values of $\dot{L}_0$ are $1.50 \times 10^{-6} \mu\text{m}\cdot\text{s}^{-1}$ at 1200°C and $1.67 \times 10^{-6} \mu\text{m}\cdot\text{s}^{-1}$ at 1250°C . Activation energies for both densification and grain growth were also calculated as 314 kJ/mol and 443 kJ/mol respectively, which also demonstrated that the dominant mechanism of densification is most appropriate to be interface reaction mechanism.
2. During the study of free sintering of nano-sized 3Y-TZP powder, it was also found that interface reaction controlled diffusion again dominates the densification process. The activation energy of densification was calculated as 292 kJ/mol based on experimental data. In the study of grain growth, the dominant mechanism for stage 1 could be solid-solution drag controlled grain growth with $n = 3$. The activation energy was determined to be 558 kJ/mol

which was also comparable to that in the literature. The mechanism of grain growth in stage 2 could be pore-drag controlled with $n = 4$, and the activation energy was calculated as 325 kJ/mol. The interface reaction model provides good prediction on densification, and also grain growth in early stage. However, in the late period of stage 2, discrepancy between grain growth model and experiment data was observed which implies that other densification mechanisms may involved. Kinetic constants, $\dot{\epsilon}_{00}$, was obtained as $7.33 \times 10^6 \text{ s}^{-1}$.

3. From the sinter-forging study on nano-sized 3Y-TZP powder, it was found that interface reaction mechanism was also dominating. The current study focused on stage 1 sintering and the activation energy of densification was obtained as 161 kJ/mol based, which is much lower than that of grain boundary diffusion reported. In the grain growth study, the mechanism of the stage 1 could be surface diffusion with $n = 3$, where the activation energy was obtained as 150 kJ/mol which is comparable to literature. A grain growth model which takes account of applied stress effect was developed from Brook's model. The model predicted that the grain growth rate is a linear function of applied stress, which was consistent with the current experiment observations. The interface reaction model coupled the stress-incorporated grain growth, which provides good prediction on both densification and grain growth in stage 1 sinter-forging.
4. A sintering stress expression for stage 1 sintering was developed based on experiment data obtained for nanocrystalline 3Y-TZP material. A Wigner-Sietz cell was adopted as the geometry to represent the current nano-sized particles instead of the two-ball model. The current expression established the sintering stress as a function of density, grain size and dihedral angle between pores and free surfaces. It was found that the present expression can provide better agreement with the experiment data. The pore structure during sintering was also explored. When the relative density is below the maximum packing density, i.e., around 70%, open porosity will occur; when RD is higher than 70%, the pores will be closed pores and locate on the surface of two-grain junctions.

8.2 Future work

8.2.1 Quantity analysis on the effect of applied stress in mechanism study

In Chapter 6, we have observed that the involvement of applied stress results in decrease of activation energy. This indicates that interface reaction process is assisted by applied stress. Therefore, it should be studied that how the applied stress acts during atoms diffusion and quantity analysis on its action is also necessary to understand the intrinsic sintering physics behind the phenomenon.

8.2.2 Sintering study of stage 2 sinter-forging

The current sintering study only focused on the early sintering stage. However, the properties of sintering component will mainly affected by the final sintered density and microstructure, thus the modeling analysis on final stage of sintering will complete the present work. A constitutive model for final stage sintering, coupling with grain growth, could be developed and the expression of sintering variables could be improved.

8.2.3 Develop sintering map for nanocrystalline ceramic material

Sintering map is very useful tool in modern ceramic industry. The sintering map for free sintering or sinter-forging alumina and 3Y-TZP nanocrystalline powder would be developed using suitable constitutive models, which can be used as a guidance in cost-efficient fabrication of advanced materials.

Appendix I

In Chapter 4, the near nano-sized alumina powder compacts were sintered at different temperature. Radial strain ε_d and longitude strain ε_h is plotted against dwelling time in below figures. It is found that at 1200°C, 1250°C, 1300°C and 1400°C the value of ε_d and ε_h is quite close which means the shrinkage of sintering is isotropic in both radial and longitude direction. The experimental data of ε_d and ε_h have been plotted as time dependent functions as follows:

Fig 1: ε_d and ε_h at 1200°C sintering.

Fig 2: ε_d and ε_h at 1250°C sintering.

Fig 3: ϵ_d and ϵ_h at 1300°C sintering.

Fig 4: ϵ_d and ϵ_h at 1400°C sintering.

In Chapter 5, nano-sized 3Y-TZP powder was free sinter to full density. The experimental data of ϵ_d and ϵ_h have been plotted as time dependent functions as follows:

Fig 5: ϵ_d and ϵ_h at 1200°C sintering.

Fig 6: ϵ_d and ϵ_h at 1250°C sintering.

Fig 5: ϵ_d and ϵ_h at 1300°C sintering.

Fig 5: ϵ_d and ϵ_h at 1350°C sintering.

It can be noticed that the shrinkage in both radial direction and longitude direction is consistent.

Appendix II

For free sintering of 3Y-TZP material, SEM pictures have been provided to study the microstructure as follows:

Fig 1: 3Y-TZP 1200C sinter for 10 min.

Fig 2: 3Y-TZP 1200C sinter for 30min.

Fig 3: 3Y-TZP 1200C sinter for 60min.

Fig 4: 3Y-TZP 1200C sinter for 120min.

Fig 5: 3Y-TZP 1200C sinter for 240min

Fig 6: 3Y-TZP 1250C sinter for 10min.

Fig 7: 3Y-TZP 1250C sinter for 30min.

Fig 8: 3Y-TZP 1250C sinter for 60min.

Fig 9: 3Y-TZP 1250C sinter for 120min.

Fig 10: 3Y-TZP 1250C sinter for 240min.

Fig 11: 3Y-TZP 1300C sinter for 10min.

Fig 12: 3Y-TZP 1300C sinter for 30min.

Fig 13: 3Y-TZP 1300C sinter for 60min.

Fig 14: 3Y-TZP 1300C sinter for 120min.

Fig 15: 3Y-TZP 1300C sinter for 240min.

Fig 16: 3Y-TZP 1350C sinter for 10min.

Fig 17: 3Y-TZP 1350C sinter for 30min.

Fig 18: 3Y-TZP 1350C sinter for 60min.

Fig 19: 3Y-TZP 1350C sinter for 120min.

Fig 20: 3Y-TZP 1350C sinter for 240min.

Below SEM pictures belong to sinter-forging of 3Y-TZP, sintering temperature is 1000°C.

Fig 21: 3Y-TZP free sinter for 10min.

Fig 22: 3Y-TZP free sinter for 1hr.

Fig 23: 3Y-TZP free sinter for 4 hr.

Fig 24: 3Y-TZP free sinter for 8hr.

Fig 25: 3Y-TZP sinter for 10min with 0.8MPa applied stress.

Fig 26: 3Y-TZP sinter for 30min with 0.8MPa applied stress.

Fig 27: 3Y-TZP sinter for 60min with 0.8MPa applied stress.

Fig 28: 3Y-TZP sinter for 120min with 0.8MPa applied stress.

Fig 29: 3Y-TZP sinter for 400min with 0.8MPa applied stress.

Fig 30: 3Y-TZP sinter for 10min with 1.6MPa applied stress.

Fig 31: 3Y-TZP sinter for 30min with 1.6MPa applied stress.

Fig 32: 3Y-TZP sinter for 60min with 1.6MPa applied stress.

Fig 33: 3Y-TZP sinter for 120min with 1.6MPa applied stress.

Fig 34: 3Y-TZP sinter for 180min with 1.6MPa applied stress.

Fig 35: 3Y-TZP sinter for 360min with 1.6MPa applied stress.

Fig 36: 3Y-TZP sinter for 10min with 3.2MPa applied stress.

Fig 37: 3Y-TZP sinter for 30min with 3.2MPa applied stress.

Fig 38: 3Y-TZP sinter for 60min with 3.2MPa applied stress.

Fig 39: 3Y-TZP sinter for 120min with 3.2MPa applied stress.

Fig 40: 3Y-TZP sinter for 10min with 6.4MPa applied stress.

Fig 41: 3Y-TZP sinter for 30min with 6.4MPa applied stress.

Fig 42: 3Y-TZP sinter for 60min with 6.4MPa applied stress.

Fig 43: 3Y-TZP sinter for 120min with 6.4MPa applied stress.

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Publications

1. Constitutive Modeling for Nanoceramic Materials Sintering, F. XUE and J. MA, International Journal of Nanoscience - Vol. 5, Nos. 4-5 (August & October 2006)
2. Constitutive Modeling for Sintering of Submicron Alumina Material, F. Xue and J. Ma, The 3rd International Conference on Materials Processing for Properties and Performance (MP3), Symposium Nanofabrication and Nanotechnology, Singapore 2004
3. Constitutive grain growth model for 3Y-TZP nanocrystalline powder, Xue Feng and Ma Jan, 2nd MRS-S Conference on Advanced Materials, Jan 18, 2006
4. A Constitutive Densification Model for 3Y-TZP Nano Particles, F. XUE and J. MA, Journal of the American Ceramic Society, Accepted.