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#### MULTI-FUNCTIONAL MATERIALS BY POWDER PROCESSING FOR A THERMAL PROTECTION SYSTEM WITH SELF-COOLING CAPABILITY: PERSPIRABLE SKIN

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## MULTI-FUNCTIONAL MATERIALS BY POWDER PROCESSING FOR A THERMAL PROTECTION SYSTEM WITH SELF-COOLING CAPABILITY: PERSPIRABLE SKIN

By

LI SUN

#### A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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**Mechanical Engineering** 

2009

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#### ABSTRACT

## MULTI-FUNCTIONAL MATERIALS BY POWDER PROCESSING FOR A THERMAL PROTECTION SYSTEM WITH SELF-COOLING CAPABILITY: PERSPIRABLE SKIN

By

#### LI SUN

Aerodynamic heating generated by the friction between the atmosphere and the space vehicle's surface at reentry can enhance the temperature on the surface as high as 1700°C. A Thermal Protection System (TPS) is needed to inhibit the heat entering into the vehicle. Presently, the completely passive thermal protection is used for TPS. The thermal ablation/erosion and oxidization reaction of the current TPS is the major threat to the safety of the space vehicle. Therefore, a new design for TPS with actively self-cooling capability was proposed by bio-mimicking the perspiration of the human body, henceforth called Perspirable skin. The design of Perspirable Skin consists of core material shrink-fitted into a skin panel such as Reinforced Carbon-Carbon (RCC) Composite. The core material contains a very small Coefficient of Thermal Expansion (CTE) compared to the panel material. As temperature increases, the gap between the core and the skin are produced due to the CTE difference. Compressed gas on board the space vehicle will blow out from the gap once the

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surface temperature reaches a critical value. The cold gas flows over the surface and mixes with the atmospheric air to compensate for the frictional heat. With Perspirable Skin, the highest temperature on the surface is expected to decrease, and we assumed it to be around half of the present temperature.

This dissertation focuses on the selection of the core materials and their manufacturing by powder processing. Based on a series of experiments, several results were obtained: 1) the effect of powder mixing on the compaction capability and sintering capability was determined; 2) a flat 3-layered Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> Functionally Graded Material (FGM) without cracks was fabricated; 3) the factors contributing to the cracks in the multi-layered materials were investigated; 4) an isotropic negative thermal expansion material, ZrW<sub>2</sub>O<sub>8</sub>, as well as its composites with ZrO<sub>2</sub> were processed by in-situ reaction of WO<sub>3</sub> and ZrO<sub>2</sub>; 5) several CTE prediction models on composites containing ZrW<sub>2</sub>O<sub>8</sub> were studied and proposed as a better scheme for applying the contiguity of phase; 6) a novel processing technique to produce  $ZrW_2O_8$ -  $ZrO_2$  continuous FGMs was developed; and 7) the thermal and mechanical properties of the various materials were measured. Finally, using finite element analysis (FEA), the complete design of Perspirable Skin has been accomplished.

To LiangCai, Jing, and our parents

#### ACKNOWLEDGEMENTS

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#### **CHAPTER 1**

#### INTRODUCTION

#### **1.1 BACKGROUND AND MOTIVATION**

Space vehicles that enter a planetary atmosphere like the Space Shuttle Orbiter (i.e. earth) require the use of a Thermal Protection System (TPS) to protect them from aerodynamic heating, which is generated at the surface of a space vehicle due to the combination of compression and surface friction of the atmosphere [1]. A TPS mainly is used to inhibit the heat entering into the vehicle [1, 2]. Due to the wide variation of temperatures, the TPS selected for a space shuttle is composed of many different materials. Each material's temperature capability, durability, and weight determine the extent of its application on the vehicle [2]. The orbiter's nose cone, including the chin panel, and the leading edge of the wings are the hottest areas during re-entry [3]. During the reentry back into the atmosphere, the maximum heating occurs about 20 minutes before touchdown, the maximum temperature on these surfaces can reach as high as 1700°C [2. 3]. Reinforced Carbon-Carbon composite (RCC), a light gray composite, along with Inconel foil insulators and quartz blankets, protect these areas from the highest temperatures and aerodynamic forces [3,4].

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Considering the oxidizing environments, the RCC must have oxidation protection coating [4]. The common coating materials include SiC,  $Si_3N_4$  and  $SiO_2$  [4]. However, when temperature is as high as 1700°C, the thermal ablation/erosion speed is considerably high. If the coating layer erodes, the whole TPS will be damaged, therefore jeopardizing the safety of a space vehicle. To increase the safety of a space vehicle, new designs of TPS are needed.

Biomimetics, the application of methods and systems, found in nature, to engineering and technology, has spawned a number of innovations far superior to what the human mind alone could have devised. Today, the gecko's powerful ability to cling to vertical surfaces is inspiring new types of adhesion. Exploring photosynthesis in leaves has led to the creation of transparent photocells that can absorb solar rays passing through a window. And Japanese Express Train picked up speed and reduced energy consumption after modifying the shape of its nose from the tip of a bullet to that of a kingfisher's beak [5].

In humans, Perspiration/sweating is primarily means of thermoregulation. Evaporation of sweat from the skin surface has a cooling effect. In hot weather, or when the individual's muscles heat up due to exertion, hypothalamus, the temperature-regulating area of the brain, sends nerve impulses to the sweat glands stimulating them to increase the size and release sweat. Until the skin receptors detect that the skin's temperature is back to normal. The brain then

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sends messages to stop the release of sweat and the sweat glands will shrink to regular size [6]. Mimicking the process of perspiration, a new designed TPS, named Perspirable Skin, was proposed by Patrick Kwon group at Michigan State University in 2005, which is mainly aimed to be used at the hottest areas of Space Shuttles to reduce their surface temperature at reentry and reduce the TPS damage chance. By applying Perspirable Skin, the temperature of those hottest areas is expected to decrease to the half of the present temperature (1700°C), that is, around 800°C.



Figure 1.1 Schematics of Perspirable Skin TPS

F	F
fash	fashi
core	cores
sma	smal
tem;	temp
CTE	CTE
ωm	comp
The	The
ωm	œmp
keep	keepi
lands	lands
who;	whole
F	Fr
vehic	vehicl
selec	select
as th	as th€
FEAT	FEA (i
and 6	and 6)
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For the design of Perspirable Skin, TPS is arranged in a 'Peg and Hole' fashion, as shown in Fig. 1.1. The skin panels are with numerous holes, in which cores (pegs) made of another material are assembled. The core material has smaller Coefficient of Thermal Expansion (CTE) than that of the skin. As temperature increases, a gap is produced between the skin and cores due the CTE difference. Once the temperature reaches the working temperature, a compressed gas contained in tank inside the space vehicle blow out from the gap. The cold gas flows over the surface and mixes with the atmospheric air to compensate the frictional heat between the vehicle and the atmospheric air, keeping the surface temperature at relatively low temperature. After the vehicles lands and its surface temperature decreases, the gaps close again. Therefore, the whole design is an autonomous, reusable cooling system.

From the design idea to the application of Perspirable Skin on the space vehicles, a series of studies are needed to be performed: 1) core material selection, 2) materials fabrication, 3) materials properties test, which will be used as the input parameter of Finite Element Analysis (FEA), 4) structure design by FEA (including gap and stress analysis), 5) core pieces and RCC panel assembly, and 6) test at simulated reentry environment.

By three and half years efforts, now Steps 1-4 are almost achieved. This dissertation presents all research results of Steps 1-3 as well as part results of

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#### **1.2 MODERN CERAMICS**

Ceramics have demonstrated to be the most important materials used in a wide variety of high temperature applications despite of their inherent brittleness. Ceramics also are used in those application areas where high hardness, wear resistance, corrosion resistance and temperature stability, low specific weight, and low CTE are needed [7,8]. Therefore, considering the high temperature working environment and the low CTE requirement of core materials of Perspirable Skin, ceramics are ideal candidates.

#### **1.2.1 Monolithic Polycrystalline Ceramics**

New and improved ceramics are now available that have much higher strength and toughness than prior ceramics. Modern engineering ceramics such as alumina ( $Al_2O_3$ ), zirconia ( $ZrO_2$ ), silicon carbide ( $Si_3N_4$ ), are making more usages in aerospace, automotive and electronics industry [8].

#### 1.2.1.1 Alumina

Alumina, or aluminum oxide  $(Al_2O_3)$ , is the most mature high-technology ceramic in terms of quantity produced and variety of industrial uses. Approximately five million metric tons were produced in 1999 for wear, chemical, electrical, medical and other applications [9].  $Al_2O_3$  is used in these applications

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because of its excellent combination of properties, including high hardness and wear resistance, chemical resistance, smooth surface, reasonable strength and moderate thermal conductivity.

## 1.2.1.2 Zirconia

Zirconia, or zirconium oxide (ZrO<sub>2</sub>), is another important high-strength, high toughness ceramic that has been developed during the last 30 years [10, 11]. Partially stabilized zirconia (PSZ) has fracture toughness values ranging from 6-15 MPa•m<sup>1/2</sup>, compared to conventional ceramics with fracture toughness of about 2-3 MPa•m<sup>1/2</sup> [11]. The mechanism of toughening in PSZ involves a volume increase due to a polymorphic transformation that is triggered when an applied stress causes a crack to form in the ZrO<sub>2</sub>.

Transformation toughening was a breakthrough in achieving high-strength, high-toughness ceramic materials. For the first time in history a ceramic material was now available with an internal mechanism for actually inhibiting crack propagation. A crack in a normal ceramic travels all the way through the ceramic with little inhibition, resulting an immediate fracture. PSZ has fracture toughness three to six times higher than most other ceramics. ZrO<sub>2</sub> often can provide sufficient increased life to justify its use on a life cycle cost basis. Therefore, it is now wildly used as dies for hot extrusion of metals, wire-drawing capstans, golf cleats, and so on [10, 11].

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# 1.2.1.3 Silicon Nitride

Silicon Nitride (Si<sub>3</sub>N<sub>4</sub>) has a favorable combination of properties that includes high strength over a broad temperature range, high hardness, low coefficient of thermal expansion, moderately high elastic modulus, and unusually high fracture toughness for a ceramic [12, 13]. This combination of properties leads to excellent thermal shock resistance, ability to withstand high structural loads at high temperatures, and superior wear resistance. Si<sub>3</sub>N<sub>4</sub> ceramics have reached large-scale production for cutting tools, bearings, turbocharger totors, diesel pre-chambers and variety of custom wear parts [14, 15].

All Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and Si<sub>3</sub>N<sub>4</sub> are for structural applications. Table 1.1 lists typical mechanical and thermal properties for the three ceramics.

Material Properties	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	Si <sub>3</sub> N <sub>4</sub>
Density (g/cm <sup>3</sup> )	3.975	6.04	3.48
Young's Modulus (GPa)	300	200	310
Fracture toughness (MPa•m <sup>1/2</sup> )	4-5	11-13	6
Flexural strength (MPa)	358	200-360	700
CTE (10 <sup>-6</sup> •°C <sup>-1</sup> )	8.2	8.2-10	3.1
Thermal Conductivity (W/mK)	24.7	27	26

Table 1.1 Typical properties of Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and Si<sub>3</sub>N<sub>4</sub> [8, 10]

# 1.2.1.4 Negative Thermal Expansion Ceramics

Most materials exhibit positive thermal expansion with increasing temperature.

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However, there exist some materials, almost all are ceramics, with anomalous Negative Thermal Expansion (NTE), meaning they shrink when heated. The thermal contraction of most NTE ceramics is anisotropic. That is, those materials show positive thermal expansion in one or two dimensions that is coupled with negative thermal expansion in the other two or one dimensions. For example, both cordierite (Mg<sub>2</sub>Al<sub>2</sub>Si<sub>5</sub>O<sub>8</sub>) and  $\beta$ -eucryptite (LiAlSiO<sub>4</sub>) show thermal expansion in two dimensions coupled with thermal contraction in one dimension; but NZP (NaZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>) shows thermal expansion in one dimension coupled with thermal contraction in the other two dimensions [16-19]. When these materials are heated, some bonds expand (For B-eucryptite, Li-O bonds) driving one or two-dimensional expansion. However, the rigidity of the other bonds (For β-eucryptite, Al-O and Si-O bonds) forcing the contraction in the other two or one dimension(s) [16].

Isotropic negative thermal expansion is very rare. Table 1.2 summarizes five ceramic materials with isotropic negative thermal expansion.

Material	CTE range (10 <sup>-6</sup> •K <sup>-1</sup> )	Temperature range of NTE (K)
ThP <sub>2</sub> O <sub>7</sub>	-9.3 to 4.3	573-480
UP <sub>2</sub> O <sub>7</sub>	-7.1 to 3.1	773-1773
ZrV <sub>2</sub> O <sub>7</sub>	-11.1 to 15.4	380-875
ZrW <sub>2</sub> O <sub>8</sub>	-13.2 to -6.5	3-1050
HfW <sub>2</sub> O <sub>8</sub>	-12.9 to -6.4	3-1050

Table 1.2 Isotopic negative thermal expansion materials [16, 18-23]

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Figure 1.2 Dependence of relative expansion on temperature of NCTE materials As Fig. 1.2 shown, ThP<sub>2</sub>O<sub>7</sub>, UP<sub>2</sub>O<sub>7</sub>, and ZrV<sub>2</sub>O<sub>7</sub> shows positive thermal expansion when temperatures are lower than the corresponding range listed in Table 1.2. Only ZrW<sub>2</sub>O<sub>8</sub> and HfW<sub>2</sub>O<sub>8</sub> feature negative CTE over the whole solid state. However, Hf is a much rare element than Zr. So ZrW<sub>2</sub>O<sub>8</sub> has been the most intense study subject of isotropic negative thermal expansion material.



Figure 1.3 Schematic of thermal contraction caused by thermal motion (filled

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circles are cations, and open circles are oxygen atoms. The solid line shows low temperature bonds position, dash line shows bonds at high temperature and arrows show the vibration direction of oxygen atoms) [16].

The M-O-M linkage is the basis for the isotropic negative thermal expansion of the ceramics in Table 1.2. For ZrW<sub>2</sub>O<sub>8</sub>, the M-O-M linkage is Zr-O-Zr or W-O-W. The five materials share several structural characteristics: 1) the crystal structure is an open, low-density framework structure; 2) the coordination of oxygen is only twofold; and 3) the M-O bond is very strong. These characteristics have two intimately related consequences: 1) The thermal expansion of the M-O bond will be very low, and the thermal vibration of oxygen will be very low in the directions of the M atoms; and 2) thermal vibration of oxygen perpendicular to the M-O-M linkage must be very high. With these unique thermal motions, as oxygen atoms vibrate, M cations are pulled together as shown in Fig. 1.3, resulting in the negative thermal expansion of the materials [16, 18, 20].

Several studies on the synthesis of ZrW<sub>2</sub>O<sub>8</sub> substrates have been performed [24, 25]. One possible application of ZrW<sub>2</sub>O<sub>8</sub> is to combine it with positive thermal expansion materials to produce composites with controllable thermal expansion. ZrW<sub>2</sub>O<sub>8</sub>/Cu [26], ZrW<sub>2</sub>O<sub>8</sub>/Al [27], ZrW<sub>2</sub>O<sub>8</sub>/Cement [28], and ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> [29-31] have been studied. However, the large disparity in the thermal expansion behavior between different components may present major problems in practical

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applications for some of the aforementioned composites [26, 27].

A ZrW<sub>2</sub>O<sub>8</sub>-containing composite with a CTE of zero can be used as ceramic substrate of optical fiber Bragg gratings as well as components of microelectronics. One advantage of using this kind of composite is the reduction of both decomposition and deterioration due to the temperature change of the material system.

#### **1.2.2 Ceramic Matrix Composites**

Two primary methods are being used to increase the capability of ceramics for thermal, mechanical, corrosion and structural applications. One method is to refine the monolithic polycrystalline ceramics.  $Si_3N_4$ , for example, had a reported tensile strength around 80 ksi in the 1980s, whereas now it is over 110 ksi [7, 32]. The other method is to combine two or more ceramic components, producing composites that integrate the properties of the constituent materials. There are two categories of ceramic matrix composites: particle-reinforced ceramic matrix composites.

#### 1.2.2.1 Particle-Reinforced Ceramic Matrix Composites

Adding particles of a second ceramic into a ceramic matrix during the fabrication process produces a particle-reinforced ceramic matrix composite (PRCMC). Most second phase ceramic powders are between 0.5 and 40  $\mu$ m in diameter. An important PRCMC is titanium carbide (TiC) reinforced Al<sub>2</sub>O<sub>3</sub>, which

was developed as a cutting tool insert. TiC- Al<sub>2</sub>O<sub>3</sub> has higher hardness and lightly higher toughness than pure Al<sub>2</sub>O<sub>3</sub> and could cut a wider range of alloys including hardened steel and chilled cast-iron [33]. Al<sub>2</sub>O<sub>3</sub> with 15-20% addition of PSZ particles has been reported to have toughness between 6.5 and 15 MPa•m<sup>1/2</sup> (two to three times that of Al<sub>2</sub>O<sub>3</sub>) and flexure strength between 480 and 1200 MPa (higher than both Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>) [34]. This material is more resistant to some forms of wear than both Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>.

#### 1.2.2.2 Fiber-Reinforced Ceramic Matrix Composites

In the search for improved toughness for ceramics, material scientists conceived the idea of reinforcing ceramics with continuous strands of high-temperature fiber. Embedded continuous ceramic fibers reinforce the ceramic matrix by deflecting and bridging fractures. Fiber-reinforced ceramic matrix composites (FRCMC) are composed of a ceramic fiber, a fiber-matrix interface coating and a ceramic matrix. The fiber is converted to useful form by using conventional textile-forming techniques. Common fiber materials include SiC, Al<sub>2</sub>O<sub>3</sub>, SiOC, and SiNC. FRCMCs can be used to manufacture heater tubes, hot-gas filters, heat exchangers, and radiant burner, and so on [35].

#### 1.2.2.3 Micromechanics Prediction Models For Particulate Composites

Many micromechanics models have been presented to predict the effective or bulk physical properties of composite materials [36-42]. For particulate

composites, the Mori-Tanaka method [36] is widely used to determine the effective elastic stiffness tensor [41, 42]. The effective stiffness tensor is given by

$$\mathbf{C}_{c} = \mathbf{C}_{m} + V_{p}(\mathbf{C}_{p} - \mathbf{C}_{m})\mathbf{A}_{p}$$
(1.1)

where the subscripts *c*, *p*, and *m* represent the composite, inclusion materials, and matrix material, respectively, **C** represents stiffness tensor, *V* is volume fraction and  $\mathbf{A}_p$  is the inclusion strain concentrator tensor which relates the average strain in the inclusion to the applied homogeneous boundary strain. The Mori-Tanaka method defines  $\mathbf{A}_p$  to be

$$\mathbf{A}_{p} = \mathbf{T}[V_{m}\mathbf{I} + V_{p}\mathbf{T}]^{-1}$$
(1.2)

where I is the fourth rank identity tensor and T is Wu's Tensor [43] defined as

$$\mathbf{T} = [\mathbf{I} + \mathbf{ES}_m (\mathbf{C}_p - \mathbf{C}_m)]^{-1}$$
(1.3)

where **E** is Eshelby's tensor determined by the shape of the inclusion [44] and **S** represents compliance tensor.

When applying the Mori-Tanaka scheme to a two-phase composite, one needs to assume one phase as the matrix and the other as the second, or reinforcement, phase. In metal matrix composites, the metal phase typically constitutes the matrix and the hard ceramics phase becomes the reinforcement. In case of ceramic-ceramic composites, the distinction between reinforcement and matrix phases may not be so clear. As the volume ratio of the second phase increases, the second phase becomes more and more continuous and the distinction ₩1.

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between matrix and second phases become ambiguous. When the volume ratio reaches a certain threshold, the role of each phase completely reverses. This threshold value depends on the volume ratio, the shape and morphology of each phase and the consolidation characteristic of each phase [45]. In percolation theory, this threshold value is called percolation threshold [46]. In real systems of materials, both phases can be continuous and thus one needs to define the degree of contiguity. By incorporating the continuity  $\eta$  as a weighting function, Kwon *et al.* [42] revised the Mori-Tanaka method, producing the following model that linearly interprets the two extreme cases as

$$C_c = C^+ + \eta (C^- - C^+) \qquad (1.4)$$

where C<sup>+</sup> is the stiffness tensor calculated from Eqation (1.1) by assuming one phase to be the matrix phase and C<sup>-</sup> is the one by assuming that the same phase to be the second phase. The continuity,  $\eta$ , ranging from 0 to 1, has been defined by Nishimatsu and Gurland [47].

For the effective CTE prediction of a composite, the rule of mixture (ROM) is the simplest method based on the CTE and volume fraction of each of its components. The equation for the ROM is

$$\alpha_c = \alpha_p V_p + \alpha_m V_m \tag{1.5}$$

where  $\alpha$  is CTE.

The ROM calculates the effective CTE by assuming a linear relationship

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between the CTE and volume ratio of each phase. However, the thermal strain in one phase within a composite is constrained by the other phase and the magnitude of such strain depends on the shear transfer at the interface. Thus, the thermal strain features strong dependence on the elastic constants [37-40]. Therefore, several other models were presented, which take into account the elastic constants for the CTE estimation, including the Turner model [37], the Kerner model [38], the Rosen-Hashin Bounds model [39] and the Levin model [40]. The calculation formula for each of the models is shown below:

The Turner Model states

$$\alpha_c = \frac{\alpha_m K_m V_m + \alpha_p K_p V_p}{K_m V_m + K_p V_p} \tag{1.6}$$

The Kerner model states

$$\alpha_{c} = \alpha_{m}V_{m} + \alpha_{p}V_{p}$$

$$+ V_{m}V_{p}(\alpha_{p} - \alpha_{m})\frac{K_{p} - K_{m}}{K_{m}V_{m} + K_{p}V_{p} + 3K_{m}K_{p}/4G_{m}}$$
(1.7)

And the Rosen-Hashin bounds model states

$$\begin{cases} \alpha_{c}^{u} = \frac{4V_{m}V_{p}G_{p}(K_{m} - K_{p})(\alpha_{m} - \alpha_{p})}{3K_{m}K_{p} + 4G_{p}(K_{m} + K_{p})/2} + (\alpha_{m}V_{m} + \alpha_{p}V_{p}) \\ \alpha_{c}^{l} = \frac{4V_{m}V_{p}G_{m}(K_{m} - K_{p})(\alpha_{m} - \alpha_{p})}{3K_{m}K_{p} + 4G_{m}(K_{m} + K_{p})/2} + (\alpha_{m}V_{m} + \alpha_{p}V_{p}) \end{cases}$$

(1.8)

where the K is the bulk modulus, G is the shear modulus, the superscript u represents upper bound and I signifies lower bound.

Equations (1.5-1.8) are only suitable for the isotropic two-phase composites. A more general equation was presented by Levin [40].

$$\alpha_{c} = \alpha_{m} + (\alpha_{p} - \alpha_{m})(S_{p} - S_{m})^{-1}(S_{c} - S_{m})$$
(1.9)

where the effective compliance tensor, S<sub>c</sub>, can be calculated by the Mori-Tanaka approach [36].

These micromechanics models have been used widely to predict the mechanical/thermal properties of composites. The predictions from the models have successfully applied in some cases. However, the main drawback has been that the applicability of these models is usually limited to the composite with the volume fraction below 0.6 of reinforce phase. Beyond 0.6 value, one need to use contiguity concept to reverse the role of each phase in the calculation [42, 47].

#### **1.2.3 Ceramic Functionally Graded Materials**

The term Functionally Graded Materials (FGMs) describes a class of engineering materials exhibiting gradually changed properties with position [48, 49]. The property gradient in FGMs, which can be continuous or stepwise, is caused by a position-dependent chemical composition or microstructure [49, 50]. FGMs, especially Ceramic Functionally graded materials (CFGMs), were originally conceived as TPS materials for space structures and fusion reactors



[48]. CFMGs can be designed to withstand severe temperature gradients of a TPS whilst retaining mechanical toughness and oxidation resistance. Several thermal-barrier coating FGMs for TPS have been investigated, including ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> FGM and ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> FGM [51]. Another important application of FGMs is to join dissimilar materials with different thermal expansion properties. Thermal residual stresses developed if directly join two materials with different CTE, which may result in premature joint failure. Due to the components variation at different position, the CTE of a FGM can change along one direction. By matching one end CTE of the FGM to one material and the other end to the second material, the thermal stress caused by CTE difference or thermal gradient loading can be reduced [52].

A large variety of production methods have been developed for the processing of FGMs, such as powder metallurgy (P/M), sheet lamination, laser cladding, and Chemical Vapor Deposition (CVD), to name a few. Among these methods, P/M is widely used to fabricate metallic as well as ceramic FGMs [53-55].

A zirconia/alumina ( $ZrO_2/Al_2O_3$ ) FGM has been of great interest for its potential application as thermal-barrier coating and high-temperature heat exchanger [51, 56]. By incorporation of  $ZrO_2$  phase, the tensile strength and fracture toughness of  $Al_2O_3$  increases [56, 57]. Cai et al. [58] produced as many as 23 successive layers of  $ZrO_2/Al_2O_3$  laminate. Mott and Evans [59] used an ink

jet printing method to produce ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> FGMs. Chang et al. [60] and Moon et al. [61] produced multi-layered ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> composites by sequential centrifugal consolidation.

A critical problem in the manufacturing of FGMs by P/M is the formation of cracks and/or distortion in the samples [58, 62]. These defects are due to the residual stress caused by mismatches in thermal expansion and sintering among the constituent components [58, 63, 64]. Since ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> feature distinct sintering behavior and disparate CTE, cracks and/or camber were present in many ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> FGM samples as evidenced in the aforementioned research work [58, 60-62]. Hillman et al. [62] found that differences in sintering kinetics result in cracks with a large opening displacement (>30µm), while thermal expansion mismatch produces cracks with a small opening displacement (<2µm). Cai et al. [58] summarized three different crack modes: channeling in tensile layers, debonding and edge-effect cracks. Some reports [58, 62] show that the number of cracks can be reduced by controlling heating and cooling rates and layer composition. Torrecillas et al. [65] studied an FGM system featuring zircon and molybdenum, concluding that a nearly similar transient shrinkage state for each layer can lead to the final fully-sintered specimen being free of cracks.

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# **1.3 POWDER METALLURGY**

### **1.3.1 Introduction**

Powder Metallurgy (P/M) is the study of the processing of powders. It is the most common fabrication method for most ceramic and some metal engineering components [66]. Compared to most other processing methods, P/M is cheaper. Therefore, P/M was considered to be the best candidate method to fabricate core materials for Perspirable Skin.

The three main steps of P/M to convert powders into useful objects are 1) powder processing, 2) forming operations, and 3) sintering [66]. The powder processing may involve 1) milling, which is the mechanical agitation used to break particles or agglomerates into smaller particles and 2) mixing, which is the process of thorough incorporating of two or more powders [67]. Many methods are being used in forming operations of powders such as injection molding, slurry techniques and compaction [66]. Conventional uniaxial powder compaction, which is performed with the pressure applied along one axis using hard tooling of die and punches, is the most widely used method to compact powders. Samples after compaction are called "greens". In pharmacology, green samples can be used immediately as pharmaceutical tablets. In the case of ceramics or metals, green samples are the precursor for attaining a dense body by sintering. Sintering describes the formation of bonds between particles close to their melting point. It

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can occur at temperatures below the melting point by solid-state atomic transport phenomenon. However, some instances involve the formation of a liquid phase [66, 68]. On a microstructural scale, the bonding occurs as cohesive necks grow at the particle contacts [66-68].

The three steps of P/M are closely related to each other. Each step affects the subsequent step(s). The initial powder characteristics, such as average particle size [69-72], particle shape [73], particle size distribution [70-72, 74, 75] and specific surface area [70] achieved during powder milling and mixing, influence the compaction and sintering capability. The pressure [71, 76] and the die wall friction [77] of the compaction step can affect the shape of green body due to different density distribution [77-80].

#### 1.3.2 Compaction

#### 1.3.2.1 Procedure

Fig. 1.4 shows the detailed compaction process of a uniaxial die set. The loose, free flowing powder is introduced into the die cavity in the filling step. The upper surface of the powder was flattened. Then the top punch is forced into the die to compact the powder. After compaction ( $\sim$ 80MPa), the relative density of compact is around 50% for most ceramic powders. In the ejection step, the forces acting upon the punches are removed and the top punch is used to eject the sample from the confines of the die [54, 66].

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Figure 1.4 The process of die set compaction.

#### 1.3.2.2 Powder Mixing Effect on Compaction

Several studies have already been preformed investigating the powder mixing effect on the compaction/packing of particles [69, 73, 81]. By adding single-sized fine sand/metal balls into single-sized coarse sand/metal balls, Westman et al. [69] and McGeary [81] determined that the mixtures have reduced porosity, thus showing better compaction capabilities. For ceramic powders, however, this conclusion may not always be accurate since ceramic powders are quite different. Firstly, the particle size of a ceramic powder is usually much smaller than that of the sand or metal balls. The average particle size of a ceramic powder usually is on the order of submicron/micron, while the size of sand or metal balls is on the order of millimeter to centimeter. Secondly, by chemical/physical treatment, some ceramic powders can have much better compaction capability than other ceramic powders even if their material compounds are nearly identical. Thirdly and most importantly, most ceramic powders have a continuous distribution of particles. Finally, due to the small particle size and large surface energy, agglomerations

prevail in ceramic powders. Compared to the sand or metal balls, these unique characteristics may result in a unique relationship between the compaction capability and powder mixing for ceramic powders.

# 1.3.2.3 Dimensional and Density Variation by Compaction

Due to the series of operation steps of compaction, the green samples contain a degree of structural inhomogeneity of two kinds, namely, density distributions as the variation of the internal form and the dimensional variability as manifest in the external shape of the compact [78-80, 82-84]. The former is the non-homogeneous density distribution within the compact. Some regions have higher densities than others. The latter is the geometry of the external surface of the ceramic green body that is invariably not exactly the same as, or a simple linear scale transformation of the shape of the terminal geometry of die cavity after the green ejection.

The densities of a green sample are not even everywhere. Aydin et al [78, 79] designed an experiment, in which they used lead balls as tracers to detect the densification. Their results are similar to others' report [82-84]. The high-density regions exist at the near the bottom central region and on the central axis. And the low-density regions are at the bottom edges and near the top center. However, the density distribution range varies as different powders. The limitation of Aydin's method is only putting the tracers in several positions, not in a continuous way.
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By finite element analysis, Aydin et al [80] found after compaction, the green samples inside the die have large residual radial stress at about the middle of the compact, and small redial residual stress on the top and bottom surface. After the ejection of the green sample, the compact is free in the radial direction. Therefore, the high stress regions relax radically, resulting larger diameter regions in the final greens. So finally the lateral shape of a green sample is similar to a barrel.

#### 1.3.2.4 Constitutive Models for Powder Compaction

Historically, ceramic component manufacturers have relied heavily on trail-and-error to minimize density gradients in powder compacts. More recently, finite element method (FEM) modeling has been used to predict powder compaction response and to provide insight into the causes of density gradients in green powder compacts [76, 78, 79, 85]. A critical component of any predictive model for powder compaction is the constitutive model that describes the mechanical behavior of the granulated powder. A series of continuum plasticity models, originally developed in soil mechanics, have been applied to ceramic powder compaction [86-89]. In those models, modified Drucker-Prager/cap elasto-plasticity model (modified D-P model) has been identified for successful modeling the compaction of granulated Al<sub>2</sub>O<sub>3</sub> powder during uniaxial die pressing [78-80, 90]. This model has already been included in the internal library of commercial FEM code ABAQUS [91] for the simulation of powder compaction.

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Modified D-P model is expressed in a stress space of the mean stress ( $\sigma_m$ ) and the second invariant of the deviatoric stress  $J'_2^{1/2}$ . By the principal stresses  $\sigma_1$ ,  $\sigma_2$ , and  $\sigma_3$ ,  $\sigma_m$  and  $J'_2^{1/2}$  are expressed as:

$$\sigma m = \frac{1}{3}(\sigma 1 + \sigma 2 + \sigma 3) \tag{1.10}$$

$$J_{2} = \frac{1}{6} \left[ (\sigma_{1} - \sigma_{2})^{2} + (\sigma_{2} - \sigma_{3})^{2} + (\sigma_{1} - \sigma_{3})^{2} \right]$$
(1.11)

As shown in Fig. 1.5, modified D-P model consists principally of two parts: 1) a linear shear failure surface showing increasing shear stress with increasing mean stress, and 2) a curved cap that intersects both the shear failure surface and the mean stress axis. There is also a transition region between the two segments, which is introduced to provide a smooth surface [78, 87, 89].



Figure 1.5. Illustration of modified Drucker-Prager/cap elasto-plasticity model. (*d* is the material cohesion, and  $\beta$  is the internal angle of friction).

The shear failure surface function  $F_s$  is written as:

$$F_{s} = \sqrt{J'^{2} - (\tan\beta)\sigma m} - d = 0 \qquad (1.12)$$

where d is the material cohesion, and  $\beta$  is the internal angle of friction. Intersection of the load path with the shear failure surface defines the onset of permanent, plastic deformation by shearing. Intersection of the load path with the cap marks the onset of permanent, plastic deformation by a combination of shear and volumetric strain. Loading along the mean stress axis is in hydrostatic compression, and intersection with the cap produces permanent volumetric strain along. Loading within the wedge-shaped region defined by the shearing failure surface, the cap, and the coordinate axis is elastic. Plastic hardening occurs with the application of increasing mean stress. As the material hardens, the cap curve expands gradually from the dotted curves to the solid curve in Fig. 1.5. The shape of the cap (Fc) is controlled by a shape factor R (0<R<1) and a transition parameter  $\alpha$  (typically 0.01< $\alpha$ <0.05 [78]).  $\alpha$  is used to provide a smooth transition surface between the shear failure surface and cap.

$$F_{c} = \sqrt{\left[\sigma m - p_{a}\right]^{2} + \left[\frac{R\sqrt{J'2}}{1 + \alpha - \frac{\alpha}{\cos\beta}}\right]^{2}} - R(d + p_{a}\tan\beta) = 0 \quad (1.13)$$

where  $P_a$  is an evolution parameter that represents the volumetric plastic stain driven hardening effects, which relates to the hydrostatic compaction yield stress P<sub>b</sub> in the following equation [91]:

$$p_a = \frac{p_b - Rd}{\left(1 + R \tan \beta\right)} \tag{1.14}$$

The transition surface between the shear failure surface and the cap is described as

$$F_{t} = \sqrt{\left[\sigma m - p_{a}\right]^{2} + \left[\sqrt{J'^{2}} - \left(1 - \frac{\alpha}{\cos\beta}\right)(d + p_{a}\tan\beta)\right]^{2}}$$

$$-\alpha (d + p_{a}\tan\beta) = 0$$
(1.15)

Totally, the modified D-P model requires seven material parameters as input, including: bulk modulus (*K*), shear modulus (*G*), Young's modulus (*E*), Poisson's ratio (*v*), angle of internal friction ( $\beta$ ), cohension (*d*), cap shape parameter (*R*), and transition surface parameter (*a*). One important point is that ceramic powders are pressure sensitive. So those materials depend on the ambient mean stress. Aydin *et al* [78-80] applied modified D-P model to model the compaction of an alumina powder. They indirectly measured most of the seven input parameters. And the remaining parameters were estimated from data published in the open literature. Zeuch *et al* [89] designed a series of experiments and measured all seven parameters directly for an alumina powder.

#### 1.3.3 Sintering

#### 1.3.3.1 Sintering Kinetics

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The macroscopic driving force of sintering is the reduction of excess energy associated with surfaces by a) the increase in the average size of particles (coarsening), and b) the elimination of solid/vapor interfaces and the creation of grain boundary areas, followed by grain growth (densification). The five basic atomic mass transport mechanisms in sintering are: 1) Evaporation-condensation (coarsening); 2) Surface diffusion (coarsening); 3) Volume diffusion (densification, dependent on location of the source); 4) Grain boundary diffusion (densification); and 5) Viscous or creep flow (densification) [92].

Coble [93] proposed three stages in sintering. During each stage, different sintering kinetics takes place.

- The initial stage: The inter-particle contact area increases by neck growth.
   The relative density increases to 65%.
- 2. The intermediate stage: Continuous pore channels are seen at the triple points (three-grain junctions) and relative density increases from 65 to 90%.
- 3. The final stage: Pore phase is eventually pinched off. Continuous pore channels disappear. Individual pores are either lenticular on grain boundaries, or rounded within a grain. Pore and grain boundary mobility increases dramatically at this stage.

Sintering kinetics is dependent on many variables [92], listed as follows,

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- 1. Temperature: Increasing temperature enhances sintering kinetics as the potential for diffusion mechanism increases [66, 92].
- 2. Green density: The higher the green density, the less pore volume that has to be eliminated, the densification rate decreases [66, 70].
- 3. Uniformity of green microstructure: Non-uniformity caused by agglomerate can lead to abnormal grain growth. Non-uniformity after cold die compaction will lead to shape distortion [70, 80, 84, 93].
- 4. Atmosphere: In some cases, the atmosphere can enhance or reduce diffusivity [66, 92].
- 5. Impurities: Impurities can be introduced into powders in the powder process or during compaction step. Some impurities can form a liquid phase or low-temperature eutectics with main powder during sintering and then enhance sintering kinetics of main powder. Some compounds, on the other hand, can lower surface diffusion and grain boundary mobility, finally decrease the sintering kinetics of main powder [95].
- 6. Particle size: Finer particles have more surface area than coarser particles, and thus in principal the use of finer particles favors sintering. In practice, however, very fine particles may lead to agglomeration. The agglomerates tend to sinter together into larger particles, which not only dissipate the driving force for densification but also produce large pores among the

partially sintered agglomerates.

- 7. Phase transition: Densification rate changes due to phase transition [96].
- 8. Size distribution and porosity: Narrow size distribution will reduce abnormal grain growth. However, wide size distribution enables a denser initial particle packing [97], reducing sintering kinetics due to less porosity [98]. The effect of size distribution is also investigated by Ting *et al.* [74, 75] and Darcovich *et al.* [99, 100]. Ting *et al.* [74, 75] concluded that prior to the occurrence of grain growth, the densification rate increases as the particle size distribution width increases. After growth occurs, the rate decreases as the particle size distribution width of the staring powder increases.

#### 1.3.3.2 Sintering Curves and Models

Two types of curves are commonly used to describe the sintering kinetics: the shrinkage rate-sintering temperature curve and the densification rate-relative density curve. For the latter one, the relative density D is the ratio of the mass density of the sample to the theoretical density of the corresponding powder mixture. And the densification rate is defined as:

$$\dot{\varepsilon}^{S}(T) = \frac{\partial \rho}{\rho \,\partial t} = \frac{\dot{D}(T)}{D(T)} \tag{1.16}$$

In the last decades, a lot of research has been devoted to predict the densification kinetics of powder compaction [101-105]. Some of this research

attempted to obtain a description from the modeling of physical mechanisms responsible for sintering. Most of them derived the densification kinetics of a powder aggregate from the sintering of two contacting spheres by viscous flow diffusion phenomena. For example, Su et al [104] proposed a master sintering curve model, and they described the densification rate as:

$$\dot{\varepsilon}^{s}(T) = \frac{\gamma \Omega \Gamma(D) D_{0}}{k T(G(D))^{n}} \exp(-\frac{Q}{RT})$$
(1.17)

where *g* is the surface energy,  $\Omega$  is the atomic volume,  $\Gamma(D)$  relates the driving force and mean diffusion distance, k is the Boltzmann constant, *G* is the mean grain diameter, *Q* is the apparent activation energy,  $D_0$  is the diffusion coefficients and *R* is the gas constant.

Two inherent problems limit the wild application of the physical models for the densification (sintering) process. One problem is the difficulty to exactly measure the physical parameters such as the surface energy g and the apparent activation energy Q in Su's model [104]. Such parameters require a set of very complex experiments, some of which need to be in an extreme environment, such as high vacuum and precise temperature. The other problem is that parameter adjustments are necessary to apply the models from one material to other materials depending on the diffusion mechanism involved [106]. As a result, other researchers used an alternative approach, phenomenological model. The phenomenological model consists of fitting analytical expressions directly from the

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results of sintering experiments. Thus, it provides a constitutive equation describing as precisely as possible the real behavior of the material without regarding the physical meaning of its parameters.

An example of the phenomenological models is presented by Hsueh [107]:

$$\dot{\varepsilon}^{s} = \Omega(T) [D\infty(T) - D]^{n}$$
(1.18)

where  $D_{\infty}(T)$  is the theoretically possible full-sintered density at temperature *T*. and if we compare formulas (1.18) and (1.17), we can know that  $\Omega(T)$  is related to grain size and activation energy. Gillia et al [108] used Hsueh's model to analyze the densification kinetics of WC-Co mixture.

#### **1.4 DISSERTATION OVERVIEW**

There are seven more chapters in this dissertation. Chapter 2 summarizes experimental materials and facilities used in the study; Chapter 3 and 4 discuss compaction and sintering of Powder Metallurgy, respectively, which are the physical foundations of this research. From Chapter 5 to 7, each chapter presents the process and properties of one advanced material, including ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> stepwise FGM, ZrW<sub>2</sub>O<sub>8</sub> and ZrW<sub>2</sub>O<sub>8</sub>-ZrO<sub>2</sub> composites, and ZrW<sub>2</sub>O<sub>8</sub>-ZrO<sub>2</sub> continuous FGMs. Finally, Chapter 8 states conclusions and provides suggestion for future works. Fig. 1.6 illustrates the relationship among the chapters.

- Physical Foundations -

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Figure 1.6. Illustration of the relationship among chapters

## **CHAPTER 2**

## **MATERIALS AND FACILITIES**

### 2.1 MATERIALS

Eight ceramic powders used are listed in Table 2.1, which included four alumina (Al<sub>2</sub>O<sub>3</sub>) powders, two zirconia (ZrO<sub>2</sub>) powders, one tungsten (VI) oxide (WO<sub>3</sub>) powder and one zirconium tungstate (ZrW<sub>2</sub>O<sub>8</sub>) powder.

Powder	Material	Chemical analysis (ppm)						a phoso		
		Na	K	Fe	Ca	Si	Mg	a-phase		
TMDAR	Al <sub>2</sub> O <sub>3</sub>	4	2	5	3	3	1	100	)%	
CR-15		13	22	2	3	13	1	90%		
CR-6		13	22	2	3	14	<1	100%		
GE-1		12	15	5	2	42	<1	100	100%	
TZ3YS	7:00	Stah	ilized	by 5 '	) wrt%	V <sub>2</sub> O	•			
CERAC-2003		Stat	mza	<b>Uy J</b>	2 WI/U	1203	<b>)</b>			
W-Fluka	WO <sub>3</sub>									
ZW-OR	ZrW <sub>2</sub> O <sub>8</sub>									
Powder	Mean particle size (µm)			n)   I	Mean pore size (µn			m)	Bulk density	
TMDAR	0.17			(	0.09				0.9 g/m <sup>2</sup>	
CR-15	0.42			(	0.18				0.45 g/m <sup>2</sup>	
CR-6	0.60			(	0.27				0.6 g/m <sup>2</sup>	
GE-1	9.76			(	0.24				0.45 g/m <sup>2</sup>	
TZ3YS	0.54			(	0.23				0.75 g/m <sup>2</sup>	
CERAC-2003	1.23			(	0.27				0.71 g/m <sup>2</sup>	
W-Fluka	8.22			(	0.29				0.85 g/m <sup>2</sup>	
ZW-OR	12.33			(	0.26				0.66 g/m <sup>2</sup>	

Table 2.1 Characteristics of the ceramic powders used in this study

The four alumina powders are TMDAR (Taimei Chemical CO., LTD., Japan), CR-15, CR-6, and GE-1 (Baikowski Ind. Corp., U.S.A.). The two zirconia powders include TZ3YS (Tosoh Co., Japan) and CERAC-2003 (CERAC Inc., U.S.A.). The tungsten (VI) oxide powder is W-Fluka (Sigma-Aldrich, U.S.A.). And the zirconium tungstate powder is ZW-OR, (Teledyne Wah Chang, U.S.A.). All the powders feature submicron particle sizes. The particle size distribution profile for each alumina powder is presented in Fig. 2.1. Except the TMDAR and ZW-OR, other powders are with lognormal particle size distribution.



Figure 2.1. Particle size distribution profiles of various alumina powders.

The micrographs of the eight raw powders are shown in Fig. 2.2. The TMDAR and CERAC-2003 are almost agglomerate-free while all other powders feature many agglomerates. The agglomerates of GE-1, W-Fluka, and ZW-OR are in flake shape and those of CR-15, CR-6, and TZ3YS are in near-spherical shape. The single particle shape of all the powders is in near-spherical shape.

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Figure 2.2 The raw powder SEM micrograph of a) TMDAR, b) CR-15, c) CR-6, d)

GE-1, e) TZ3YS, f) CERAC-2003, g) W-Fluka, and h) ZW-OR.

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#### **2.2 EXPERIMENTAL FACILITIES**

As discussed in Section 1.3, typical techniques of P/M method include powder mixing, powder characteristics testing, compaction, sintering, mass and volume measurement, and microstructure observation. To perform these steps, various facilities were used.

- The particle size distribution for each grade was measured by a Malvern MicroPlus particle size analyzer (Malvern Instruments Ltd, UK). The measurement range of the instrument is 0.1-1000 μm.
- 2. Powder mixing was processed in a jar mill (U.S. Stoneware 764AVM, U.S.A.) using 12mm diameter alumina and/or zirconia mixing media for 48 hours at a 75 rev/min speed, or by a Speed Mixer DAC 150 (FlackTek, Inc., USA) for 3 minutes (1 minute for each cycle and totally 3 cycles) at the angular velocity of 1700 rad/s.
- 3. Mass was measured by an electronic balance (Adventures AR2140, OHAUS Corp. USA). The resolution is 0.1mg.
- 4. Powder compaction was performed in a single-action die made by 1144 Stress Proof steel. The load to compact powder stacks was in the range of 60 to 210MPa, which was applied by either MTS Insight 300 (MTS Systems Corp. USA) or CARVER 3912 (CARVER INC., USA). Depending on the die dimension, the green samples were of 22.02mm, 19.04mm, or

7.95mm diameter. The compaction speed of MTS Insight 300 was 10mm/min and the stress resolution is 0.013MPa.

- 5. Green compacts were sintered in air (Carbolite-HTF1700, UK). Several different ramp/soak sintering cycles were used based on material properties, which would be discussed in following chapters. The temperature control resolution of the furnace is 1°C, and the ramp rate can set up to 15°C/min.
- 6. The length of samples was measured by a MARATHON electronic digital caliper. The resolution is 0.01mm.
- 7. The volumes of the fully-sintered pieces were measured in water by Archimedes' principle. The resolution is 0.05cm<sup>3</sup>.
- 8. To attain clear micrographs, the fully-sintered samples were polished using polisher (Abramin, Denmark) and thermal-etched in a box furnace (Carbolite-HTF1700, UK). The thermal-etch temperature varied with the materials, which will be discussed in the following chapters.
- 9. Microstructure was observed by Scanning Electron Microscopy (JEOL 6400V, Japan).
- 10. Real time sintering testing was performed using a Thermomechanical Analysor (TMA), SETARAM SETSYS Evoluation 95, with argon gas providing a protective environment.

#### 2.2.1 Introduction of SETARAM SETSYS Evoluation 95

SETARAM SETSYS Evoluation 95 is the most important facility used in my research. It is designed by SETARAM instrumentation, France (<u>http://www.setaram.com/</u>). This machine measures the deformation of a sample under non-oscillating stress against time or temperature with prescribed ramp/soak path. The testing temperature range of SETSYS Evolution 95 is from room temperature to 1750°C [108]. Figure 2.3 shows the front view of this analyzer.



Figure 2.3. The front view of the SETARAM SETSYS Evoluation 95 (1-head cover, 2-furnace side watch, 3-mode changing switch, 4-open/close head switch, 5-side cover, 6-proctective gas inlet and outlet tube).

When the head cover open, the sample can be put in the sample chamber, which is an alumina tube. A probe connected to a displacement transducer is placed in the sample chamber. The position of the probe can be adjusted so its tip can touch the top surface of the sample. In general, a 5-gram load is applied to the probe to ensure its contact to a sample throughout the entire experiment. It has been verified that this small force does not influence the testing results [109]. The displacement transducer equipped in the SETSYS Evolution 95 is characterized by its robustness and high accuracy; it can detect dimension changes as small as 0.01 micron. The transducer uses an electromagnetic system for automatic control of the force applied to the sample, between 0.01 and 1.5 N. The force can be increased by adding weights (up to 200 grams) on a top plate. Transducer calibration and force control are managed automatically by computer [108].

The SETSYS Evoluation 95 has a cylindrical furnace. The heating element is made up of graphite rube and fitted in the centerline of the furnace. The thermocouple is composed of Pt/Pt-Rh and can withstand temperatures as high as 1750°C [108].

With its software, the SETSYS Evolution 95 can be used as a dilatometer to test many material properties, such as the thermal expansion coefficients (CTE), the softening temperature, the glass transition point, and so on. The SETSYS

Evolution 95 is also particularly suitable for measuring controlled-rate sintering. By measuring the displacement of one dimension and performing calculations, this TMA can give the shrinkage rate—sintering temperature curve or densification rate—relative density curve, which will be introduced in Chapter 4. By a set of specially designed probe and support, the SETSYS Evolution 95 also can perform 3-point flexure measurements, which would give the temperature dependence of Young's modulus data of a sample.

### **CHAPTER 3**

# THE PHYSICS OF POWDER METALLURGY: COMPACTION

## 3.1 POWDER MIXING EFFECT ON THE COMPACTION CAPABILITIES OF CERAMIC POWDERS

As discussed in Section 1.3.2.2, the relationship between the compaction capability and powder mixing for ceramic powders may not as simple as the conclusion made by Westman *et al.* [69] and McGeary [81] for sand or metal balls. Therefore, the main focus of this section is to study the compaction of ceramic powders in relation to the powder characteristic and other mixing details.

#### 3.1.1. Materials and Experimental Procedure

In the series of experiments, the four alumina (Al<sub>2</sub>O<sub>3</sub>) powders, TMDAR, CR-15, CR-6, and GE-1 were investigated. The detailed characteristics for the powders have been summarized in Section 2.1. In the selection of the four powders, the study considered CR-15, CR-6, and GE-1, which are all from the same manufacturer, feature near identical chemical components. The size distributions of all CR-15, CR-6 and GE-1 are nearly lognormal. However, due to the difference in particle size distributions and mean particle sizes, the compaction capabilities of these three powders are quite different. TMDAR, on the other hand, was chosen because it is specially treated, both chemically and physically. Its particle size distribution has a very narrow non-lognormal range and it yields a sintered product with very low porosity. These two characteristics yield the well-known high compaction/sintering capability of TMDAR powder. Also, TMDAR is almost agglomerate-free while the other three powders contain agglomerates (Fig. 2.2).

All possible two-powder combinations with the four powders were mixed in various mass ratios, and in total six powder mixture systems were produced. The mixture systems include TMDAR+CR-15, TMDAR+CR-6, TMDAR+GE-1, CR-15+CR-6, CR-15+GE-1, and CR-6+GE-1. In addition to four unmixed powders, each system contains nine powder mixtures, in which the proportions of one powder in the mixtures range between 10% and 90% in 10% intervals. In total, fifty-four powder mixtures were studied. The powders were mixed with Speed Mixer DAC 150 (FlackTek, Inc., USA) for 3 minutes (1 minute for each cycle and totally 3 cycles) at the angular velocity of 1700 rad/s. Six grams of each powder mixture was measured by Adventurer AR 2140 (Ohaus Corp. USA) with a 0.0001g resolution; and then poured into a single-action die made of 1144 Stress Proof steel. The inner diameter of the die, D<sub>in</sub>, is 22.19mm. Before pouring the powders into the die, the die wall was lubricated with graphite powder (Panef

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Corp., USA).

The top surface of the powder was flattened and then the top punch was inserted into the die until it touched the powder. The compaction load was applied on the top punch by MTS Insight 300 (MTS Systems Corp., USA). The speed was 10mm/min and the stress resolution is 0.013MPa. During the compaction, only the top punch moved. The compressive forces applied on the top  $(F_{f})$  and bottom punches ( $F_b$ ) as well as the displacement of the top punch ( $Z_t$ ) were recorded continuously as a function of time by the load sensors. At first, the pre-load of 0.5MPa was applied to set an initial state. The preload is necessary to measure the compact characteristics accurately before starting the main compacting process. After pre-loading, the initial height of each sample, h<sub>i</sub>, was measured. This was done by measuring the total height of the two punches and the pre-loaded compact inside the die, then subtracting the height of the two punches. The measurement was achieved by Marathon electronic digital caliper with a 0.02mm resolution and a 150mm measurement range. Considering the diameter of each compact to be the same as the inner diameter of the die, Din, the initial relative density, *Ri*, can be calculated by the following equation:

$$Ri = \frac{\rho i}{\rho f} = \frac{m/Vi}{\rho f} = \frac{m}{\frac{3.975}{4}\pi Din^{2}hi}$$
(3.1)

where m, V, and  $\rho$  represent mass, volume, and density, respectively, and the



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subscripts *i* and *f* represent initial and theoretically fully value. The theoretical fully-density of alumina was taken as 3.975g/cm<sup>3</sup>.

After obtaining the initial relative density, the die set with pre-loaded compact was put back into the load frame, and then the load of 80MPa was applied to compact samples. The final green samples produced a diameter of 22.19mm and their heights ranged from 7.05mm to 9.1mm. Thus, the height/diameter ratios of compacts were between 0.3 and 0.4. By keeping a low height/diameter ratio, the transmit force applied on the bottom punch and the applied force on the top punch were almost identical in the compaction. The discrepancy between the two recorded forces was less than 0.2%. The masses of the green samples were measured again after compaction. There was always an expected mass change due to the attachment of powders to the die wall and the punches as well as the powder loss during the transport. However, this change was very small, less than 0.4%, and was neglected. Several green samples were coated with nail polish and then their volumes were measured in water by Archimedes' principle. Those values were then compared to the corresponding volumes calculated by the final sample heights, h<sub>f</sub>, and diameter, D<sub>in</sub>, The discrepancies between the two groups of values were minimal, less than 1.1%. Therefore, only the calculated volumes are reported in this investigation.

#### 3.1.2 Relative Density-Stress Relationship for Various Powder Mixtures

By the recorded top punch displacement,  $Z_t$ , and the initial compact height,  $h_i$ , or final compact height,  $h_f$ , the sample height at time t,  $h_t$ , can be calculate,

$$\begin{cases} ht = hi - Zt & (3.2a) \\ ht = hf + Zt & (3.2b) \end{cases}$$

The  $h_t$  calculated by Equation (3.2a) or (3.2b) for any compact was the same. Therefore, two separate measurements,  $h_i$  and  $h_f$ , for each compact were for self-consistency.

From the calculated  $h_t$ , similar to calculating the initial relative density, the relative density at time t, defined as Rt, can be found as,

$$Rt = \frac{\rho t}{\rho f} = \frac{m/Vt}{\rho f} = \frac{m}{\frac{3.975}{4}\pi Din^{2}ht}$$
(3.3)

In Equation (3.3), the sample diameter was assumed to be matching the inner diameter of the die, *D<sub>in</sub>*.

The corresponding stress,  $\sigma t$ , at time *t* can be obtained by the punch diameter,  $D_{in}$ , and the recorded load,  $F_t$ .

$$\sigma t = \frac{Ft}{St} = \frac{Ft}{\frac{1}{4}\pi Din^2}$$
(3.4)

where  $S_t$  is the cross-sectional area of the top punch.

The relative density-stress curves for each powder mixture group were then drawn. Fig. 3.1.a and Fig. 3.1.b show the representative curves for the TMDAR+CR-15 and CR-6+GE-1 powder mixture groups, respectively. For clarity, only six curves were included in each figure.



Figure 3.1 The relative density-stress curves by the compaction for a) CR-15+TMDAR and b) CR-6+GE-1.

Under a constant compaction load or stress, the difference of the relative densities represents the change in the compaction capability in different mixtures. A higher relative density represents improved compaction capability. Even the absolute relative density values continuously increase with the compaction load, the relationship between the relative density and powder proportions remains similar for each powder mixture group as observed in Fig. 3.1. Therefore, one can conclude that the starting powder combination determines the compaction capability of each powder mixture. In addition, the initial relative densities dictated by the starting powder combination can be used to quantify and compare the compaction capability of each powder mixture. The relationships between the initial relative density and the powder proportion are shown in Fig. 3.2 for all six powder mixture groups. For each curve, the left end is the 100% of the fine powder and the right end is the 100% of the coarse powder. The "fine" or "coarse" powder is defined by the average particle size  $\overline{D}$  of the powder. From Table 2.1, we know

$$\overline{D}GE - 1 > \overline{D}CR - 6 > \overline{D}CR - 15 > \overline{D}TMDAR$$
(3.5)



Figure 3.2 The initial relative density – coarse powder proportion for all six powder mixture groups after 0.5MPa pre-load compaction.

Fig. 3.2 shows two kinds of relationships between the initial relative density and the proportion of the coarse powder.

 Linear relationship: TMDAR+CR-15 and CR-15+CR-6 powder mixture groups show this characteristic. The maximum relative density corresponds to 100% of one of the powders. 2) Nearly parabolic relationship: The maximum relative density of some powder groups with this relationship occurs with certain powder mixtures, such as TMDAR+CR-6, CR-15+GE-1, and CR-6+GE-1. This is similar to the conclusion of Westman [69] and McGeary [81]. However, the proportions of coarse powder in the powder mixture that attained the maximum relative density are between 40% and 60%. These values differ from the reported 30% by Westman [69] and McGeary [81] for sand and metal balls. Another powder systems, TMDAR+GE-1, has the maximum relative density at 100% TMDAR.

#### 3.1.3 Relative Density-Strain Relationship for Various Powder Mixtures

In the study of ceramic powders' compaction, Aydin *et al.* [78-80] defined axial true strain  $\overline{\epsilon}_t$  as the following,

$$\overline{\varepsilon}t = \left|\ln(\frac{ht}{hi})\right| \tag{3.6}$$

Fig. 3.3(a) and Fig. 3.3(b) show the representative relative density-strain curves for the TMDAR+CR-15 and CR-6+GE-1 powder mixture groups, respectively. Comparing Fig. 3.3 and Fig. 3.1, the powder mixture with better compaction capability/density in Fig. 3.1 is also with a higher relative density under any strain values in Fig. 3.3.


Figure 3.3 The relative density-strain curves by the compaction for a) CR-15+TMDAR and b) CR-6+GE-1.

The Mircocal Origin and Wolfram Mathematica software were employed to calculate the trend functions of the relative density-strain curves. The relationship exactly fits into the following equation for each powder mixture,

$$Rt = \kappa e^{\overline{\mathcal{E}}t} \qquad (3.7)$$

where k has the same unit as density, g/cm<sup>3</sup>. Table 3.1 displays the k value for the TMDAR+CR-15 powder mixture group.

Table 3.1. The coefficient k in Equation (3.7) for representative TMDAR+CR-15 powder mixture

CR-15	0%	10%	30%	50%	70%	90%	100%
k	1.4228	1.3843	1.29	1.1887	1.0688	0.9622	0.908

Equation (3.7) shows that a powder mixture with a higher density/compaction

capability has a larger k value. Compared the k values in Table 3.1 to the corresponding initial relative density value in Fig. 3.2, they are the same. This indicates the physical meaning of k in Eq. (3.7) is the "initial relative density". From the relative density and strain definitions in Eq. (3.3) and (3.6) as well as Eq. (3.1), the conclusion can be verified as below.

$$Ri = \frac{m}{\frac{3.975}{4} \pi Din^{2}hi}} \left\{ \Rightarrow \frac{Rt}{Ri} = \frac{\frac{1}{4} \pi Din^{2}ht}{\frac{1}{4} \pi Din^{2}hi} = \frac{ht}{hi}} \right\} \Rightarrow Rt = Rie^{\overline{\varepsilon}t} \quad (3.8)$$

$$\overline{\varepsilon}t = \left| \ln(\frac{ht}{hi}) \right|$$

Therefore, the method to compare compaction capability of various powder mixtures from their relative density-strain curves only needs to consider the initial relative density value. In other words, from either the relative density-stress or the relative density-strain curves, one can use Fig. 3.2 to find the difference in the compaction capabilities of powder mixtures.

It is important to emphasize that the initial relative density is dependent on the pre-load. For example, when the pre-load reduced to 0.3MPa, the initial relative density for pure TMDAR was changed to 30.46%. If the stress/strain goes to zero, the initial density goes to the bulk density listed in Table 2.1. However, even the absolute value of the initial density varies, the relationship between the relative

density compa 3.1.4 F ſ Sin elemel the dif studie among ∞mpa chang 'non-d particl 'non-d • requir partic For a value lf <sup>the</sup> in density and strain remains equivalent to Equation (3.7) and the order of compaction capability/relative density remains unchanged.

# 3.1.4 Prediction of Initial Relative Density Versus Powder Proportion Curve

#### Shape from the Characteristics of Powders

Since the four powders used are the same material with nearly identical elements, the linear and parabolic types of curves in Fig. 3.2 may be a result from the difference in the particle size distributions and mean particle sizes. Numerous studies [69, 71, 81] mentioned that if fine particles can fill into the interstices among coarse particles, then the powder mixture should produce a better compaction capability. In this condition, the total volume does not necessary change with the addition of fine powder(s). This will be stated as a "non-disturbance" condition. For a bimodal discrete sphere size system, the particle size of coarse powder is at least 2.4 times of that of fine powder to make a "non-disturbance" powder mixture. More strictly, the condition, Dc/Df > 6.5, is required for the non-disturbance mixing [110], where  $\overline{D}$  represents the average particle size and the subscript, c or f, represent coarse or fine powder, respectively. For a continuous size distribution system, the limitation average particle size ratio value is approximately 3.6 [111, 112].

If the average particle size ratio is less than 3.6, the fine powder cannot fill into the interstices of the coarse powders. The mixing of the two powders only results

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in stacking them together mechanically. Therefore, the relative density-powder proportion curve would be linear. Among the powder mixture systems we employed, TMDAR+CR-15 and CR-15+CR-6 show this trend. The corresponding linear curves in Fig. 3.2 verify this assumption. However, the agglomerates in some powders (Fig. 2.2) may influence the pore/particle size and result in partial filling of fine particles into coarse particles. The agglomerates may be the reason why some parts in those two curves are not perfectly linear.

If the average particle size ratio is larger than 3.6, would the mixtures always have better compaction capability than each powder since the fine powder can fill into the interstice of the coarse powders? Based on Table 2.1 and Fig. 3.2, that will not be true. For example, the  $\overline{D}c/\overline{D}f$  of TMDAR+GE-1 powder mixture group equals 57.4. However, its highest density happens with pure TMDAR. This is due to the large difference in the compaction capabilities of the two powders. The initial relative density difference between TMDAR and GE-1 is as large as 12.1%. This shows that even the TMDAR does fill into the interstices of GE-1; the increase in the compaction capability due to the interstitial filling is negligible compared to the excellent compaction capability of TMDAR. Therefore, the excellent compaction capability of TMDAR.

For the remaining three mixture groups with parabolic curves shown in Fig. 3.2,

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the diff 0.87 a small e thus p powde proport When propor capabi excee capab TMDA differe Therei relativ 3.1.5 Th throug initial the difference in the initial relative density between two powders ranges between 0.87 and 5.9%. In the three curves, the difference in the relative densities are small enough to be compensated by filling fine powder into the coarse powder. thus producing mixture(s) that have better compaction capability than the two powders. The Maximum Compaction Capability (MCC) occurs at 40-60% proportion of coarse powder, close to the powder with better compaction capability. When the difference in compaction capability between the powders increases, the proportion of powders at MCC shifts closer to the powder with better compaction capability. Once the compaction capability difference between the powders exceeds a threshold, the peak converts to the powder side with better compaction capability, as shown in TMDAR+CR-6, CR-15+GE-1, CR-6+GE-1, and TMDAR+GE-1 powder mixture aroups. In these four powder mixture aroups, the difference in the initial relative density between two powders ranges 7.1-12.9%. Therefore, we considered the threshold should be around may be in the 7.1-10% relative density difference

# 3.1.5 Discussion about the Limiting Boundaries of Initial Relative Density -

#### **Powder Proportion Curves**

The discussion above allows us to conclude that the straight line passing through both powders' initial relative densities sets the lower boundary for an initial relative density - powder proportion curve. Can the upper boundary also be defined?

In Westman and Hugill's study [69], the reciprocal of relative density of the compact was used to quantify the compaction capability of various sand mixtures. By assuming the fine powder is infinitesimal, one lower boundary was proposed for the curve, as the CO line in Fig. 3.4. By assuming a larger ball immersed in the infinitesimal balls/water, the other lower boundary FN was obtained. The study concluded that the reciprocal of relative density - powder proportion curve should lie in the triangle CFK.



Figure 3.4 The dependence of the reciprocal of relative density on the proportion of coarse powder and its triangle boundary by Westman *et al.* [69].

Corresponding to Westman and Hugill's idea, the O and N points in Fig. 3.4 should convert to the maximum initial relative density of the powders in the initial density versus powder proportion curves. To obtain these maximum initial density values, each powder was put into the die set and then the die set was put on a plane sieves vibrator (Thomas Scientific, USA). The frequency of the vibration was set to 60Hz and the amplitude was set to 4mm. During the vibration, the particles rearranged to an optimal arrangement. The die set was then moved to the MTS machine and the powders were compacted to the 0.5MPa pre-load. Fig. 3.5 shows the dependence of the initial relative densities of the four powders in relation to the vibration time. Clearly, as a result of the particle rearrangement caused by the vibration, the initial relative density increases for each powder. The density increases with vibration duration, and converges to a final value. Each final value is considered to be the maximum initial relative density value for the corresponding powder.



Figure 3.5 Dependence of the initial density on the vibration time for each powder.

The lines,  $FM_C$  and  $CM_f$ , in Fig. 3.6, are obtained by connecting the relative density of the fine powder to the maximum relative density of the coarse powder

and the relative density of the coarse powder to the maximum relative density of the fine powder, respectively. These two lines will build the upper boundaries for the initial relative density-coarse powder proportion curve of CR-15+GE-1 powder mixture group. And the triangle FCK creates the enclosed boundary.



Figure 3.6 Triangle boundaries for the initial relative density-powder proportion curve of CR-15+GE-1 powder group.



Figure 3.7 Triangle boundaries for the initial relative density-coarse powder proportion curves of TMDAR+CR-6, CR-6+GE-1 powder groups.

Fig. 3.7 shows the triangle boundaries for TMDAR+CR-6 and CR-6+GE-1 powder mixture groups. Clearly, as CR-15+GE-1, each initial relative density versus coarse powder proportion curve in Fig. 3.7 also lies within the corresponding triangle.

#### 3.1.6 Discussion about the Maximum Packing/Compaction Relative Density

Brouwers [110] proposed an analytical expression to calculate the void fraction/packing density of continuous particle distribution powders of the lognormal type. The equation is

$$\varphi = \varphi \left(\frac{d \max}{d \min}\right)^{-(1-\varphi_1)\beta/(1+\alpha^2)}$$
(3.9)

where  $\phi$  is the void fraction of the powder with continuous particle size distribution,  $d_{max}$  and  $d_{min}$  represent the maximum and minimum particle sizes, respectively.  $\phi_1$  is the void fraction of assumed uniformly sized particles with the average particle size,  $\alpha$  is the distribution modulus, and  $\beta$  is the scaled gradient of the void fraction. Commonly, both  $\phi_1$  and  $\beta$  can be set as constant, and in Brouwers' study  $\phi_1 = 0.5$  and  $\beta = 0.35$  for fairly angular quartz. The distribution modulus  $\alpha$  is typically between 0 and 0.37 and when  $\alpha$  equals 0, the maximum packing fraction is obtained. Following the Brouwers' parameter setting of  $\phi_1$  and  $\beta$ , the range of maximum relative packing densities of each powder was calculated, as presented in Table 3.2.

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		TMDAR	CR-15	CR-6	GE-1
Calculated	<b>α=0</b>	59.4%	64.2%	64.9%	64.3%
results	<b>α=0.37</b>	58.4%	62.7%	63.3%	62.8
Experimental results	150min vibration	59.8%	52.5%	53.3%	52.7%

Table 3.2. The maximum relative packing density calculated by Brouwers' equation and from the experiments

To attain the maximum compaction density from the experiments, 3g of each powder was vibrated for 150min and then compacted to 220MPa. After 180MPa compaction, the relative densities were convergent to maximum values. Those experimental maximum relative densities are also listed in Table 3.2. For CR-15, CR-6, and GE-1 powder, the experimental values are less than the calculated values. Two reasons contribute to the lower experimental results, 1) the  $\phi_1$  and  $\beta$  may not be exact for our powders, and 2) the agglomerates presented in the powders and the non-perfect spherical-shaped powder particles [113]. However, the order of the relative density/compaction capability among these three powders is the same in both the calculation of Brouwers' equation and the experiments. From this point, the Brouwers' equation has an excellent potential for predicting the compaction capability of various powders.

Contrary to CR-15, CR-6, and GE-1 powders, the experimental result for TMDAR is larger than the calculated result. As mentioned before, Brouwers' equation is suitable for the powder systems with lognormal particle distribution.

However, the particle size distribution of TMDAR is not lognormal. Thus, the Brouwers' equation is not suitable to calculate its compaction capability. The non-lognormal size distribution powder systems have increased maximum packing fractions than lognormal distributed powders [113]. Thus, the compaction capability of TMDAR is improved compared to the other three powders. Therefore, when using Brouwers' equation to evaluate the compaction capability of powders, the particle size distribution of each powder should be lognormal.

#### 3.1.7. Conclusions

Several groups of powder mixtures were produced by mixing four alumina powders. After investigating their compact density versus stress and strain relationships, the initial relative density was determined to be appropriate for quantifying the compaction capability of each powder mixture. The powder mixing process changes the compaction capability of the powder mixtures. The shape of the initial relative density versus proportion of coarse powder curve depends on the ratio of average particle size, and the difference in the initial density of two powders. If the average particle size ratio is less than 3.6, or the average particle size ratio is larger than 3.6 but the initial relative density different is higher than 10%, the curve is linear. If the average particle size ratio is larger than 3.6 and the initial relative density difference is smaller than 10%, the curve is parabolic. The triangle enclosed by the line intersecting the relative density of the fine powder j∎a E

and the maximum relative density of the coarse powder, the line intersecting the relative density of the coarse powder and the maximum relative density of the fine powder as well as the line connecting the relative density of the fine and coarse powder form the boundary of the initial relative density-proportion of coarse powder curve. The experimental results also show Brouwers' equation has excellent potential for comparing the compaction capability of different powders with lognormal particle size distribution.

#### **3.2 DIMENSIONAL VARIATION BY COMPACTION**

In Section 1.3.2.3, it has been introduced that due to the series of operation steps of compaction, the green samples contain two structural inhomogeneities: density distributions as the variation of the internal form and the dimensional variability as manifest in the external shape of the compact [78-80, 82-84]. To investigate the dimensional variation as well as the powder mixing effect on the dimensional variability, the external shapes of several green samples achieved in Section 3.1.1 were measured. The measurements were preformed by Veelo-DEKTAK 6M Stylus Profiler at center for coating and laser application, CCL Fraunhofer. The profilometer is with 0.5nm resolution. A specially designed sample holder was used to support samples as Fig.3.8 shown. The diameter of cave in the holder is the same to the inner diameter of the die. After a sample "sitting" in the sample holder, the probe of the profiler touched the external surface

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of the sample. A 3mg force was applied on the probe and then the probe moved from one edge to the other edge to measure the external surface profile. After one measurement, the sample was rotated 90° and another measurement was performed. Totally four measurements were performed for each sample.



Figure 3.8 The schematics of external shape measurement.



Figure 3.9 The diameter variation along the thickness direction of GE-1 samples

By taking average value of four measurements, the diameter variation along

the thickness direction was obtained for each sample. Fig.3.9 shows the dimensional variation of GE-1 sample. All samples feature the similar barrel lateral shape, which is a result of release of larger residual radial stress at about the middle of the compact after ejection [80].

For GE-1 sample, the difference between the largest diameter and smallest one is  $20.631\mu$ m. This difference varies among samples. Fig.3.10 shows the diameter difference dependence on the powder component for the CR15+GE1 and TMDAR+CR15 groups.



Figure 3.10 Dependence of largest and smallest diameter difference on the powder proportion.

If one compares Fig.3.10 to the lines of corresponding powder groups in Fig. 3.2, it is easy to see that powder mixtures with better compaction capability are with smaller diameter difference. Powders with better compaction capability results shorter green samples if the powder masses are same, resulting a smaller

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residue stress distribution difference insider the green samples hold by the die. Therefore, after the residue stress release by the ejection, the diameter difference is also smaller.

The TMA unit offers a facility to measure Young's modulus of materials (*E*) using the three-point bending method. The Young's modulus of CR-15 compact by 80MPa is 1031.3 MPa, and that of TMDAR is 2155 MPa. The elastic unloading part of the stress-strain curves for the powders is linear, as Fig 3.11 shown. The slope of the elastic unloading part (*m*), the bulk modulus (*K*), the shear modulus (*G*), the Young's modulus (*E*) and the Poisson's ratio (v) have relationship as listed in Equations 3.10-3.12 [114].



Figure 3.11 Stress-strain curve of TMDAR

$$m = K + \frac{4}{3}G \tag{3.10}$$

$$E = \frac{9GK}{3K+G} \tag{3.11}$$

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$$v = \frac{3K - 2G}{2(3K + G)}$$
(3.12)

Therefore, by measured Young's modulus and the calculated slope value, the other moduli and Poisson's ratio can be obtained, as listed in Table 3.3. Table 3.3 also presents the corresponding values by Aydin *et al.* [78-80]. The samples made by Aydin *et al.* have much higher moduli than ours. In their experiments, the alumina powders were mixed with poly PVA bind to enhance the strength. The different processes explain the value difference.

Table 3.3 Material properties for several alumina compacts

Powder	TMDAR	CR-15	Aydin <i>et al.</i> [78]
Young's modulus (MPa)	2155.1	1031.3	9027.4
Unloading slope (MPa)	2498.3	1250.4	11485.9
Shear modulus (MPa)	876.1	410.8	3531.9
Bulk modulus (MPa)	1329.9	702.3	6677.4
Poisson's ratio	0.23	0.255	0.278*

\* assumed value

By Fig. 3.10 one can see the diameter difference for our sample varies from 7 to 23  $\mu$ m. This value in the report of Aydin *et al.* is only 4  $\mu$ m [80]. Since our samples have much lower moduli than theirs, once the die wall restraint was moved, the dimension recovery at radial direction should be larger for our samples. Then with the same residue stress difference along the axial direction, the final dimension recovery difference at the center and the top/bottom surface should be also larger for our samples.

More interesting, the curves in Fig.3.10 have a "mirror image" relationship to the responding curves in Fig.3.2. This relationship is very important, since we can estimate the dimension variation of green samples made by powder mixtures based on the compaction capability relationship in Fig.3.2 and the tested diameter difference of the two ending powders.

## **3.3 DENSITY DISTRIBUTION BY COMPACTION**

#### 3.3.1 Experimental Design

The densities of a green compact are not even everywhere, but with a density distribution. To detect the density distribution insider a compact, Aydin et al [78, 79] designed an experiment, in which they used lead balls as tracers. However, this method only put the tracers in several positions, not in a continuous way. To overcome this disadvantage, we used colored powder as tracer to investigate the density distribution insider green compacts by Powder Metallurgy.

In Section 3.1, we already discovered that powder mixing changes the compaction capability. Therefore, we dyed several powder mixtures by stamp-ink (2000 plus, Red, COSCO, Germany). The mixtures then were put into a furnace (Carbolite-HTF1700, UK) for 4 hours at 70°C to dry out. The remained solids were put into bottles with 12mm diameter alumina mixing media. The bottles were on a jar mill (U.S. Stoneware 764AVM, U.S.A.) for 48 hours to break the solids. Then

the powders were sifted to get colored powder with size less than 0.3mm.

The colored powders were compacted to 0.5MPa to get the initial densities as mentioned in Section 3.1.1. Then the values were compared with five different main powder (mixture): TMDAR, 50/50 TMDAR/CR15, CR15, 50/50 CR15/GE1, and GE1, respectively. The colored powder with the same compaction capability to a powder (mixture) will be used as its compaction indicator.

To investigate the density distribution insider a green compact, the height of the green sample cannot be too small. Otherwise, the density distribution will be in a small range, hard to identify. So in this study, we keep the height/diameter ratio of each green sample around 1.1-1.2. The diameter of the samples is 19.04 mm. In the experiments, we kept the thickness of each main powder layer are identical, also each colored powder layer. And the thickness of colored powder layer is around 1/15 of the main powder layer. Based on these requirements, the powder mass of each layer can be calculated. The main powder is 1.5g for each layer and the colored powder mass is 0.12g for each layer.

Similar to the compaction procedure in Section 3.1.1, the first layer powder, which always is main powder, was pour into the die, which was lubricated with graphite powder (Panef Corp., USA). Then a pre-load of 0.5MPa was applied to compact the first layer to obtain enough stiffness. After the pre-compaction, the die set was moved from the MTS (MTS Insight 300, MTS Systems Corp., USA).

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The layer thickness, measured by subtracting the height of the two punches from the total height of the two punches and the pre-loaded compact inside the die, was recorded. The top punch was then dragged out of the die slowly and then the second layer powder (colored powder) was pour into the die. Flatting the surface of the new layer powder and putting the top punch back to the die, the 0.5 MPa pre-load was applied on the both layer again. Repeat the procedure till the last layer was pre-loaded. Finally the load of 80MPa was applied to compact the whole multi-layered samples.

The green samples were then took out of the die and polished carefully on the lateral surface till to the middle section. Then each sample was placed on the sample holder mentioned in Section 3.2 for photo taking. The photos were taken by a dissection microscope (Wild M5A, Wild Heerbrugg Ltd, Switzerland).

#### 3.3.2 Measurement Results and Discussion

The representative picture of the middle section is shown in Fig. 3.12. Due to the axial symmetric characteristics of the density distribution in the compact, the broken parts in the left edge shown in Fig. 3.12 do not influence the calculation of the density distribution contour.

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Figure 3.12 The photo of the middle section of a TMDAR sample. The bottom side in the picture is also the side contact to the bottom punch in the compaction.

Based on Equations 3.6 and 3.7 in Section 3.1.3, the relative density  $\rho_{t}$  can be calculated as:

$$\rho t = \rho i e^{\left| \ln(\frac{ht}{hi}) \right|}$$
(3.13)

where  $\rho_i$  is the initial density after 0.5MPa, which already is presented in Section 3.1.2 for each main powder. The final height of a position, h<sub>t</sub>, is obtained by analyzing the photo by software Image G. Since each indicator layer is curved after compaction as shown in Fig.3.14, the h<sub>t</sub> varies by positions. Therefore, different position is with different density.



Figure 3.13 The density distribution of TMDAR green sample, zero position is the radial symmetric axel in Fig.3.12.

The density distribution contour was plotted by MatLab, Fig.3.13 shows the contour of TMDAR, in which the 0 position is corresponding to the center axial in the Fig.3.12. All the other four powder compacts feature similar density distribution contour as shown in Fig.3.13, but the density distribution range varies as different powders, as listed in Table 3.4. Similar to the average density relationship in Fig.3.2, powders with better compaction capability have both larger lowest density and highest density. From Fig. 3.13, one can see that the high-density regions exist at the near the bottom central region and on the central axis. And the low-density regions are at the bottom edges and near the top center.

Our results are similar to Aydin et al [78, 79] and others' report [82-84]. However, our samples are with much larger density range than others' report. This should also relate to the lower modulus our samples have. But the material cohesion and internal friction angle difference may also contribute to the density distribution range. This needs to be investigated later.

Powder	Lowest density (g/cm <sup>3</sup> )	Highest density (g/cm <sup>3</sup> )
TMDAR	1.618	2.462
CR-15	1.199	1.662
GE-1	1.203	1.671
50/50 TMDAR/CR15	1.409	2.064
50/50 CR15/GE1	1.414	1.867

Table 3.4 The lowest and highest density in various samples

# **CHAPTER 4**

# THE PHYSICS OF POWDER METALLURGY: SINTERING

Sintering kinetics is dependent on many variables, including material components, green density, porosity, impurities, phase transition, and particle size distribution, and so on [92]. This chapter will focus on how these factors affect sintering kinetics for alumina and zirconia, especially the powder mixing effect on the sintering.

## 4.1 EXPERIMENTS AND DATA CALCULATION

Two Al<sub>2</sub>O<sub>3</sub> powders, TMDAR and CR-15, as well as two ZrO<sub>2</sub> powders, TZ3YS and CERAC-2003 were investigated in this chapter. The particle volume distribution curve of each size class is presented in Fig. 4.1. As shown in Fig. 4.1, both TMDAR and CERAC-2003 powders feature a single-peak powder size distribution profile and the plots of both CR-15 and TZ3YS powders exhibit a dual-peak profile. The second peak of these two plots results from the agglomerates present in these powders. The particle size distribution results are consistent to the Micrograph observation in Fig. 2.2.

A series of alumina and zirconia powder mixtures was produced, with the proportion of TMDAR in alumina system and CERAC-2003 in zirconia system ranging 0% to 100% in 10% intervals, resulting in a total of 22 powder mixture samples in this study. The powders were mixed using 12mm diameter alumina or zirconia mixing media in a jar mill (U.S. Stoneware 764AVM, U.S.A.) for 48 hours and then compacted in a single-action die under a load producing the pressure of 60MPa. The green samples were 7.94mm in both diameter and height. The real time sintering testing was performed using the TMA (Setaram 95, France) with a protective environment of argon gas. The heating rate was 10°C/min and the final soak temperature was 1475°C. The soak duration was 2 hours. The volume of the fully-sintered pieces was measured in water by Archimedes' principle. To attain clear micrographs, the fully-sintered samples were polished (Abramin, Denmark) and thermal-etched in a box furnace at 1420°C. The microstructure was observed by Scanning Electron Microscopy (JEOL 6400V, Japan).



Figure 4.1. Particle size distributions of the four powders used in this Chapter.

From the TMA testing results, we calculated and plotted densification

rate-relative density curves to describe the sintering kinetics of each powder mixture. Since the TMA can measure the length change in only one direction, to calculate the densification rate based on the results of TMA, Lance et al. [70] defined an anisotropic shrinkage factor  $\alpha$ :

$$\alpha = \frac{(\varphi_f - \varphi_o)Lo}{(L_f - L_o)\varphi_o} \tag{4.1}$$

where  $L_0$  and  $L_f$  are the initial and final height of the specimen, and  $\varphi_0$  and  $\varphi_f$  are the initial and final mean diameters of a specimen. For each of our experimental results,  $\alpha$  was almost 1 (>0.991). It is therefore reasonable to consider the sintering process for our samples to be a self-similar (isotropic) one. Thus, with the 1:1 height to diameter ratio, the temperature dependent relative density can be calculated from the following expression:

$$D(T) = \left[\frac{1 + \frac{L_f - L_o}{L_o}}{1 + \frac{\Delta L(T)}{L_o}}\right]^3 D_f = \left[\frac{L_f}{L_o + \Delta L(T)}\right]^3 D_f$$
(4.2)

where  $D_f$  is the relative density of the fully-sintered sample,  $\triangle L(T)$  is the displacement at temperature *T*, so the  $L_0 + \triangle L(T)$  represents the height of the sample at temperature *T*. Using formulas (1.16) and (4.2), it is relatively easy to derive the expression of densification rate:

$$\dot{\varepsilon}^{s}(T) = \frac{\dot{D}(T)}{D(T)} = \frac{-\Delta \dot{L}(T)}{20[L_{o} + \Delta L(T)]}$$
 (4.3)

where the coefficient 1/20 (3/60) is a result of the conversion to SI units, since the TMA counts time in minutes instead of seconds.

# **4.2 POWDER MIXING EFFECT ON PARTICLES AND SINTERED SAMPLES**

Powder mixing can manipulate the initial powder characteristics and finally affect the dimensions and microstructures of sintered samples.

# 4.2.1 Powder Mixing Effect on Particle Size Distribution Profile



Figure 4.2. Particle size distribution profiles of Al<sub>2</sub>O<sub>3</sub> powder mixtures.

Fig. 4.2 shows the particle size distribution testing results of the representative alumina powder mixtures. Obviously, particle size distribution profiles vary as the proportion of CR-15/TMDAR in the powder mixtures. The width of the particle size distribution increases with the increasing of the proportion of CR-15. As shown in Fig. 4.1, CR-15 has much larger particle size distribution range than TMDAR.

Therefore, increasing the proportion of CR-15 in alumina powder system would results in a wider particle size distribution profile. However, due to the vibration and impact by the medium in the mixing, the large agglomerates were broken. Thus, the width of particle size distribution for TMDAR+CR-15 mixtures is less than that of as-received CR-15.

The particle size distribution of the nine TMDAR+CR-15 mixtures features two peaks. The area fraction of the second peak changes with the varying powder proportions, as seen in Fig. 4.3. This area fraction change corresponds to a change in the volume fraction of agglomerates. Fig. 4.3 shows that the agglomerate volume fraction in the TMDAR/CR-15 powder mixtures increases as the increase of CR-15 at first, once the volume proportion of CR-15 reaches 40%, the agglomerate volume begins to drop as the increase of CR-15 till the volume proportion of CR-15 reaches 90%.

For zirconia powder mixtures, since TZ3YS and CERAC-2003 are different in particle size (Fig. 4.1), the particle size distribution of zirconia powder mixture also changed with the proportion of CERAC-2003/TZ3YS. However, the change is not as obvious as alumina mixtures. The particle size distribution width increases with the increasing of the proportion of CERAC-2003 until 40% CERAC-2003 and then decreases.



Figure 4.3 The area fraction of the second peak in the particle size distribution curves for varying alumina powder mixtures.

## 4.2.2 Powder Mixing Effect on Microstructures of Sintered Samples

For the two alumina powders, TMDAR has as low as 920°C sintering initiating temperature; on the other hand, CR-15, generally used as polishing media, has a much higher sintering-beginning temperature (above 1070°C). Because of these distinct powder characteristics, the sintering capability should increase with the increase of the TMDAR proportion in the powder mixtures. The powder mixing results in the variation of the microstructure of alumina powder mixtures.

Fig. 4.4 shows SEM micrographs of fully-sintered TMDAR and CR-15 samples. From these graphs, one can find:

**Average grain size**: Pure CR-15 sample shows smaller average grain size than TMDAR sample. Fig. 4.5 shows the dependence of average grain size of all 11 fully-sintered alumina samples on the proportion of TMDAR. Because TMDAR is a low-temperature sintering powder, it has a greater potential for grain growth than CR-15 in sintering. Therefore, the final average grain size increases as the proportion of TMDAR powder increases as shown in Fig. 3.5.



Figure 4.4 SEM micrographs of fully-sintered a) TMDAR, and b) CR-15

(Acceleration voltage: 15kV, Working distance: 15mm ).



Figure 4.5. Average grain size of fully-sintered alumina samples.

Pores: Pure TMDAR sample has only few inter-grain pores, while a lot of inter and inner grain pores left in fully-sintered samples containing CR-15. With CR-15
increases, the quantity of pores increases. This phenomenon also related to the high sintering capability of TMDAR. As introduced in Section 1.3.3.1, the single inter-grain pores prove that the sintering of TMDAR has been into the final stage, but all powder mixture with CR-15 only sintered in the intermediate stage.

Grain size distribution: Pure TMDAR sample has very narrow grain size distribution, while fully-sintered samples containing CR-15 have large grain size distribution range. Two reasons result in the large grain size distribution for powder mixture containing CR-15: 1) agglomerates in CR-15 and 2) CR-15 contains very high promoting grain growth elements: Na, K and Si, which are not evenly distributed (Table 2.1).



Figure 4.6. The micrograph of a fully-sintered 40/60 CERAC-2003+TZ3YS sample (Acceleration voltage: 15kV. Working distance: 15mm).

For zirconia system, because TZ3YS and CERAC-2003 have very similar sintering capability, the final sintered zirconia samples have similar microstructure. Fig. 4.6 shows the micrograph of a fully-sintered 40/60 CERAC-2003/TZ3YS samples. Comparing Figs. 4.4 and 4.6, one can see that under the same sintering path, the grain size of zirconia is much smaller than that of alumina. Also the sintered zirconia samples show a relatively uniform grain size, while the alumina powders with CR-15 feature a wide distribution of grain size.

### 4.2.3 Powder Mixing Effect on Dimensions of Sintered Samples

The content of powder mixture dictates its compactability and sinterability, ultimately changing the diameter of the final piece. Fig. 4.7 shows the variation of final diameter with respect to the powder mixtures of alumina and zirconia.



Figure 4.7. The relationship between the final diameters and the percentage of a) CR-15 in alumina system and b) CERAC-2003 in zirconia system under varying compaction load.

Two characteristics of the powder mixtures that influenced the shrinkage of the compacts were the packing density of contents and the particle size distribution.

With a higher proportion of more compactible powders and the optimum particle size distribution, the initial green compacts will attain a higher green density under the same compaction load. They thus shrink less, resulting in a larger final diameter.

For the alumina powders, TMDAR has a much higher compactibility than CR-15 as discussed in Section 3.1. This means that powder compacts containing a higher proportion of TMDAR lead to a larger final diameter under the same load. It is seen from Fig. 4.7(a) that the final diameter of alumina samples increased significantly when the proportion of TMDAR was raised from 0% to 10%. As the proportion of TMDAR increases further, the final diameter increased almost linearly.

In zirconia system, the situation is quite different since the CERAC-2003 and TZ3YS powders have a very similar compactibility. Thus the particle size distribution will be the main factor in determining the final diameter. Table 2.1 shows that CERAC-2003 has a much larger average particle size than TZ3YS. It follows that, in some combination of these two powders, the small TZ3YS particles will fill in the interstitial spaces among the larger CERAC-2003 particles. Powder combinations meeting this criterion have a higher compactibility than either of the pure powders as discussed in Section 3.1.4. As can be seen in Fig. 4.7(b), when the proportion of CERAC-2003 was between 30 and 80%, the final

diameter of full-sintered zirconia pieces was much larger than others.

### 4.3 DENSIFICATION RATE-RELATIVE DENSITY CURVES

### 4.3.1 Alumina Powder System

Fig. 4.8 shows the representative densification rate-relative density curves observed in the alumina powder mixtures. Because of the similarity of the curves for 1) 10%-30% TMDAR powder mixtures, 2) 60%-90% TMDAR powder mixtures, only six densification curves including 0% and 100% TMDAR powders are shown to enhance the clarity of the plots.



Figure 4.8 Densification rate as a function of relative density for TMDAR+CR-15 alumina powder mixtures.

As shown in Fig. 4.8, increasing the proportion of TMDAR enhances both the green density and the final density of the samples. With the exception of the pure CR-15 sample, all of the specimens are nearly fully-sintered (D > 95%). Due to

the high sintering capability of TMDAR, the samples containing a higher proportion TMDAR have higher fully-sintered densities.

In the densification rate-relative density curve, one point of critical importance is the maximum densification rate point. Prior to reaching this point, there is no grain growth and the pores among the grains are parts of interconnected networks. These networks begin to collapse into isolated pores after the powder compact reaches its maximum densification rate, and rapid grain growth begins to occur [74]. From Fig. 4.8, the maximum densification rate for the alumina powder mixtures occurs within the relative density range of 70-84%, consistent with the results of Lance et al. [70] and Lange [115]. Another point of interest is that the increase in the proportion of TMDAR also increases the relative density at which the maximum densification rate occurs. This change is also a result of the increased green density of the samples caused by increased TMDAR proportion.

The ascending and descending parts of a densification curve are the segments before and after the maximum densification point, respectively. Fig. 4.8 shows that the powder mixtures with higher CR-15 proportions have higher densification rates in the ascending section and lower rates in the descending section of the curve. Ting et al. [74, 75] concluded by theoretical calculation that "Prior to the occurrence of grain growth, a maximum densification rate exists as the starting particle size distribution width increases, ... During grain growth, the

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model predicts decreasing densification rate with increasing starting particle size distribution width." Our experimental observations match this conclusion since the increase in the proportion of CR-15 increases the particle size distribution width (Fig. 4.2)

Depending on the powder mixture system, the ascending section for the densification rate-relative density curves can be closely approximated by either one or two straight lines. The 100% TMDAR, agglomerate-free sample, exhibits a single linear segment with one slope. In contrast, systems containing CR-15 demonstrate two linear segments with distinct slopes. Lance et al. [70] obtained similar results by stating, "Agglomerates free alumina powder shows a single slope linear segment and powders with agglomerates show two linear segments."

The length of the first linear part of the curves in Fig. 4.8 varies depending on the proportion of CR-15. It decreases as the proportion of CR-15 decreases from 100% to 90%, then slowly increases until the proportion of CR-15 reaches 40%, then decreases again until the proportion of CR-15 reaches 10%. This length change in relation to the CR-15 proportion is the same as the one outlined previously for the change in the area fraction of the second peak in the particle size distribution for alumina powder mixtures (Fig. 4.3). This similarity can be explained.

Many researchers [104, 116] have pointed out that densification rate is

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inversely proportional to a power of grain size in the initial stage:

$$\dot{\varepsilon}^{S}(T) \propto \frac{1}{G^{n}} \tag{4.4}$$

where *G* is the grain size and *n* is a positive constant that depends on the diffusion mechanism. Therefore, we infer that the small particles within the agglomerates and other free small particles dominate the beginning of the sintering process as they begin to consolidate together. This consolidation causes the first linear part of the curves in Fig. 4.8. The compaction causes contact between the particles within the agglomerates. Once the compaction of the particles inside the agglomerates reaches a critical point, the agglomerates begin to assume the dominant role in the sintering process and the second linear part would begin. Therefore, greater quantity and size of agglomerates will require more time for the agglomerates to finish the consolidation. Hence, the first linear part of the densification curve is extended.

Another important aspect of the densification curves in Fig. 4.8 is that the slope of the first linear segment in the ascending part is nearly constant for all our alumina powder mixtures. It is independent of the green density and the amount of agglomeration in the sample. This result is similar to that of Lance *et al.* [70], but different from that of Rahaman et al. [117]. It is believed that the slope of the first linear part of the densification curve is related to the pore size/particle size ratio [70, 98]. From this result, the pore size/particle size ratio for our CR-15 and

TMDAR powder system is concluded to be the same under the same compaction load. In Lance's experiments, he used several powders with similar pore size/particle size ratio. In Rahaman's study, the compaction load used on a particular powder was varied to achieve the samples with a variety of green densities, and this process changed the pore size/particle size ratio in each sample. The processing method and powders used in each study explains the difference in the three results.

Each powder mixture containing CR-15 features a plateau in the ascending portion in Fig. 4.8. Even though the relative density and densification rate value are different for each powder mixture, the temperature at which the plateau occurs is within the same temperature range (1150-1200°C). This plateau is a result of  $\gamma$ - to  $\alpha$ -phase transition of alumina [96], since 10%  $\gamma$ -phase alumina is present in CR-15 (Table 2.1). TMDAR powder contains only  $\alpha$ -phase alumina and no plateau in the pure TMDAR densification rate-relative density curve.

A plateau in descending section of a densification rate-relative density curve signifies the occurrence of abnormal grain growth [70]. It can be seen that no plateaus exist in that region for any curves in Fig. 4.8. This holds true even for a powder system with agglomerates (such as CR-15), which is known to cause abnormal grain growth. The micrographs in Fig. 4.4 also provide evidence that no abnormal grain growth occurred.

### 4.3.2 Zirconia Powder System

Fig. 4.9 shows the seven representative curves obtained for our zirconia powder system. The 10% and 20% CERAC-2003 systems as well as all the powder mixture systems between 50% and 80% CERAC-2003 exhibit very similar densification rate-relative density curves. The densification rate-relative density curves for each group is presented in Fig. 4.9 as a single curve to allow for clarity.



Figure 4.9 Densification rate as a function of relative density for representative TZ3YS+CERAC-2003 zirconia system.

Fig. 4.9 shows that the green density of zirconia samples increases when the proportion of CERAC-2003 is between 0% and 40%, and begins to decrease beyond 40%. This is because the small TZ3YS particles fill in the interstitial spaces among the larger CERAC-2003 particles as well as the powders of the zirconia system feature very similar compactibility. The similarity in the

sinteribilities of CERAC-2003 and TZ3YS results in a similar final density for various zirconia powder mixtures.

The maximum densification rate for each of our zirconia powder mixtures occurs within the relative density range of 74-82%. This result is consistent with the report of Trunec *et al.* [118]. The higher the green density of a powder mixture, the higher the relative density at which the maximum densification rate occurs. This is the same result found with our alumina powder mixtures. The densification rate in ascent and descent part changes as the proportion of CERAC-2003, which also fit to the Ting's calculation [74]. However, unlike the sintering curves of alumina system, the ascending section of the curves for zirconia powders in Fig. 4.9 cannot be approximated by straight line(s). Using the linear approximation and relating the length of the first linear part to the agglomeration present in the green sample are methods that only apply to alumina powder mixtures. The shapes of densification rate-relative density curves for zirconia system are found to be semi-ellipse.

## 4.4 PHENOMENOLOGICAL CONSTITUTIVE MODELS FOR ALUMINA AND ZIRCONIA SINTERING CURVES

### **4.4.1 Model Equation and Calculation Procedure**

As mentioned in Section 1.3.3.2, one can fit analytical expressions directly

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from the results of sintering experiments to set a phenomenological model to describe the densification kinetics. In this section, the Hsueh's phenomenological model [107] is used to describe the densification rate – relative density curves of alumina and zirconia shown in Fig. 4.8 and 4.9.

The equation of Hsueh's model is:

$$\dot{\varepsilon}^{s} = \Omega(T) [D\infty(T) - D]^{n}$$
(1.18)

where  $D_{\infty}(T)$  is the theoretically possible fully-sintered density at temperature T and  $\Omega(T)$  is related to grain size and activation energy.

To fit the densification rate – relative density curves to Equation (1.18), part-isothermal heating cycle sintering of samples is needed. The part-isothermal heating cycle sintering was first utilized by Dorn in 1957 [119]. The part-isothermal heating cycle used in this study is shown in Fig. 4.10.



Figure 4.10 The part-isothermal ramp/soak sintering cycle used in this study to calculate the phenomenological constitutive models.

Fig. 4.11 shows the part-isothermal sintering test result for 100% TMDAR powder. Each "descending part" is from the isothermal sintering. If one extends each descending part and intersects the extension with the relative density axis, the intersection point gives the  $D_{\infty}$  for the temperature at which the isothermal sintering performed.



Figure 4.11 The densification rate – relative density relationship of the 100% TMDAR powder under the part-isothermal sintering path described in Fig. 4.10.

After obtaining a series of values of  $D_{\infty}(T)$ , the following steps are used to calculate the phenomenological constitutive model for each powder mixture in Figs. 4.8 and 4.9:

1. Taking the natural logarithm for the both sides of Eq. (1.18), a linear relationship can be found:

$$\ln(\dot{\varepsilon}^{S}) = n\ln([D\infty(T) - D]) + \ln(\Omega(T))$$
(4.5)

- 2. Calculating  $D_{-}(T) D$  for the relative density data of each isothermal sintering testing part and then taking the natural logarithm for the densification rate data and the  $D_{\infty}(T) D$ .
- 3. Using the linear function to fit the terms  $\ln(\dot{\varepsilon}^s)$  and  $\ln(D_{\infty}(T) D)$ , a series of linear equations, each of which relates to a specific isothermal sintering temperature are obtained. Table 4.1 shows the linear equations calculated for pure TMDAR powder.

Isothermal temperature (°C)	Linear fitting equations
1020	$\ln(\dot{\varepsilon}^{s}) = 1.638 \ln[0.6118 - D] - 1.6439$
1080	$\ln(\dot{\varepsilon}^{s}) = 1.652\ln[0.6802 - D] + 0.3165$
1140	$\ln(\dot{\varepsilon}^{s}) = 1.648 \ln[0.792 - D] - 0.0657$
1200	$\ln(\dot{\varepsilon}^{S}) = 1.655 \ln[0.973 - D] - 0.5173$
1260	$\ln(\dot{\varepsilon}^{S}) = 1.635 \ln[0.995 - D] - 1.059$

Table 4.1. The linear equations calculated for pure TMDAR powder

- 4. The coefficients in front of ln(D<sub>∞</sub>(T) D) give the value of n in Eq.(1.18).
  From Table 4.1 we can see that the n value is nearly constant for a powder system under different temperature. The n for TMDAR is around 1.65.
- 5. The entries in Table 4.1 give a series value of  $ln(\Omega(T))$ . Thus we can get a relationship between  $ln(\Omega(T))$  and temperature *T*, then use a polynomial to relate  $\Omega(T)$  and *T*. For pure TMDAR, the  $\Omega(T)$  can be expressed as:

$$\Omega(T) = -1.3799 \times 10^{-11} T^4 + 6.0705 \times 10^{-8} T^3$$

$$-8.719 \times 10^{-5} T^2 + 0.037079T + 5.2474$$
(4.6)

6. A series  $D_{\infty}(T)$  values at different temperature T are also obtained. we can fit  $D_{\infty}(T)$  into a hyperbolic tangent function. For the pure TMDAR powder, the expression is:

$$D\infty(T) = \{0.2224 \tanh[8.3785 \times 10^{-3}T - 9.4498]\} + 0.7776$$
(4.7)

7. Combining the result of steps 4-6, The final phenomenological constitutive model for each powder mixture is obtained.

### **4.4.2 Models for Alumina Powder Mixtures**

The calculated phenomenological constitutive function for 100% TMDAR:

$$\dot{\varepsilon}^{s} = [-1.138 \times 10^{-11} (T)^{4} + 0.503408 \times 10^{-7} (T)^{3} -0.72765 \times 10^{-4} (T)^{2} + 0.0319064 (T) + 3.5792]$$
(4.8)  
$$\times \{\{0.2224 \tanh[8.3785 \times 10^{-3} (T+40) - 9.4498]\} + 0.7776 - D\}^{1.5}$$

Fig. 4.12 shows the comparison of the experimental measurement and the calculated result by Equation (4.8) for both the non-isothermal and part-isothermal heating cycles. The correlation between the calculated and experimental results remains very high for both two figures. The errors between the experimental data and the calculated results are less than  $\pm 6\%$ .

The constitutive equations for other alumina powder mixtures were also calculated and several relationships were found.

- 1. The value of *n* is constant for any alumina powder mixture. That is, *n* is only affected by material, and it is a material parameter.
- Ω(7) should be influenced by the apparent activation energy [104].
   However, the Ω(7) values for different alumina powder mixture with a different percentage of TMDAR are very similar, the same Ω(7) in Equation (4.6) was used to simulate other alumina powder mixtures and showed a very good correlation too.
- 3. Since  $D_{\infty}(T)$  is influenced by the green density,  $D_{\infty}(T)$  changes with respect to the proportion of TMDAR present in the powder system. For example, the  $D_{\infty}(T)$  for 50% TMDAR system becomes:



 $D\infty(T) = \{0.2464 \tanh[8.2135 \times 10^{-3}(T+30) - 7.1422]\} + 0.7536$ (4.9)

Figure 4.12 Comparison of the experimental and calculated results for 100% TMDAR under a) non-isothermal and b) part-isothermal heating circle.

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It should also be pointed out that the simulation result from the phenomenological constitutive model does not contain the plateau that occurs in conjunction with the phase change.

### 4.4.3 Models for Zirconia Powder Mixtures

The Hsueh's formula also can be applied to zirconia powder systems. The phenomenological constitutive equations for all zirconia powder mixtures are obtained. For example, the equation to describe the sintering kinetics of pure TZ3YS is:

$$\dot{\varepsilon}^{s} = [1.00465 \times 10^{-9} (T - 150)^{4} + 5.83063 \times 10^{-6} (T - 150)^{3} \\ -1.26736 \times 10^{-2} (T - 150)^{2} + 12.2284 (T - 150) + 51384] \quad (4.10) \\ \times \{\{0.2409 \tanh[9.5305 \times 10^{-3} (T) - 12.259]\} + 0.7444 - D\}^{2.1}$$



Figure 4.13 Comparison of the experimental and calculated results for 100% TZ3YS under a non-isothermal heating circle.

Fig. 4.13 shows the comparison of the experimental and the calculated results by Equation (4.10) during the non-isothermal heating cycle. The errors between the experimental data and the calculated results are less than  $\pm 4\%$ .

Comparing all 11 equations for zirconia, we can find that the *n* value for zirconia is 2.1. The function,  $\Omega(T)$ , for all zirconia powder mixtures is nearly the same too. And  $D_{\infty}(T)$  changes with respect to the proportion of TZ3YS present in the powder system.

### **4.5 CONCLUSIONS**

- Mixing powders is an effective approach to manipulating the characteristics of raw powders, such as compactibility, sinteribility and agglomerates. These parameters finally influence the green and final densities, the sintering kinetics of powder system and the final microstructures.
- 2. Each material has a unique densification rate-relative density curve. The ascent parts of the curves for alumina can be approximated by straight line(s), while the shapes of zirconia powder densification rate-relative density curves are found to be semi-ellipse.
- 3. The powder with wider particle size distribution shows a higher densification rate before the occurrence of grain growth and a lower

one after the densification rate point. This finding verified Ting's theoretical calculation [74, 75].

- 4. Phase transition add a kinetic mechanism for sintering, results in a suddenly change in densification rate.
- 5. Using the part-isothermal heating method, phenomenological constitutive sintering equations were derived for our alumina and zirconia powder mixtures by Hsueh's model [107].
- 6. The variable *n* in Hsueh's model is a material parameter. Even though  $\Omega(T)$  should be influenced by the apparent activation energy, its difference for the powder mixtures in our CR-15/TMDAR alumina system or TZ3YS/CERAC-2003 zirconia system can be ignored.  $D_{\infty}(T)$  is influenced by green density,  $D_{\infty}(T)$  changes with respect to the proportion of TMDAR or CERAC-2003 present in the alumina or zirconia powder system.
- 7. The basic equation of Hsueh's model does not reflect any phase changes that may occur. Despite of the shortcoming, the constitutive models used in this study will be effective in describe most powder sintering processes.

## **CHAPTER 5**

# ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> STEPWISE FGM: MANUFACTURING AND CRACKS PREVENTION

Considering the severe temperature gradients a TPS experiences, FGM is an important candidate for the core material of Perspirable Skin. The first material we considered is ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> FGM. The difficulty remaining in the manufacturing of ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> FGM by P/M is the formation of cracks and/or distortion in the samples. Several reports show that the number of cracks can be reduced by controlling some factors such as heating and cooling rates, layer composition [58, 62]. However, none of these works provided any method to eliminate cracks and camber. Torrecillas et al. [65] studied an FGM system featuring zircon and molybdenum, concluding that a nearly similar transient shrinkage state for each layer can lead to the final fully-sintered specimen being free of cracks.

In this study, the sintering kinetics results for various alumina and zirconia powder mixtures obtained in Chapter 4 were compared. By referring the conclusion made by Torrecillas et al. [65]. Ideal powder mixtures to prevent the cracks and camber in ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> FGM were identified. Other factors affecting the formation of cracks and camber in an Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> FGM, including the compaction load, interface profiles, and ramp/soak sintering cycle, were also varied in order to

determine the optimal experimental parameters. Finally, flat, crack-free three-layered Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> FGM samples were fabricated.

### 5.1 EXPERIMENTAL PROCEDURES

The chosen powder mixtures based on the sintering kinetics curves were compacted in a single-action die and sintered to construct FGM specimens featuring three layers of equal thickness. The top layer is 100% zirconia (denoted as layer *Z*), the bottom layer is 100% alumina (layer *A*), and the middle layer is a mixture of 50% by volume of the alumina powder and zirconia powder (layer *M*). The interface profiles between the layers can be controlled, which will be discussed in Section 5.4. In order to ensure that each layer has the same volume, the mass of alumina and zirconia to be present in each layer needed to be calculated using the theoretical densities, which are  $6.05g/cm^3$  for ZrO<sub>2</sub> and  $3.87-3.98g/cm^3$  for Al<sub>2</sub>O<sub>3</sub> layer depending on the content of CR-15 powder. The mass ratio for each layer can be described as follows.

 $m_A: m_M: m_Z \approx 1:1.24:1.478$  (5.1)

Naturally, in the powder mixture of layer *M*, the mass ratio of alumina to zirconia is nearly 1:1.478.

The load to compact powder stacks was in the range of 60 to 210MPa. The green samples were of 22.02mm diameter and had a height between 4.2 and

4.75mm depending on the compaction load used. Green compacts were sintered in air at 1475°C (Carbolite-HTF1700, UK). Several different ramp/soak sintering cycles were used in order to determine the influence of heating/cooling rate on the sintering process. The microstructure of final samples was observed by Scanning Electron Microscopy (JEOL 6400V, Japan).



A flow chart summarizing the experimental processing is shown in Fig. 5.1.

Figure 5.1 Flow chart detailing the manufacturing process used in this chapter.

### **5.2 POWDERS SLECTION BASED ON SINTERING KINETICS**

To achieve the flatness in the FGM specimen (no significant camber), the essential requirement is that the final diameter of each layer should remain at a similar value. This does not guarantee, however, the survivability of the FGM specimen during co-sintering, since the final diameter of each layer may be the

same but the shrinkage rate at each layer during the co-sintering process can be substantially different. Definitely, a large difference in the final diameter between two layers induces residual stress, resulting in either cracks or camber. Comparing Fig. 4.7 (a) and 4.7 (b), it can be seen that the final diameters of alumina are most often larger than those of zirconia compacted at a same load; only when the proportion of CR-15 in alumina system is higher than 82%, it was possible to achieve similar dimensions of the alumina and zirconia layers. Since the powder combination of 40% CERAC-2003 and 60% TZ3YS yields the largest final diameter for zirconia layer, we fixed this proportion for layer Z in this study. Also, from Figs. 4.8 and 4.9, one can find that most zirconia powder mixtures have higher densification rates than the alumina powder mixtures. In contrast to this trend, the curve of 40%CERAC-2003+60%TZ3YS (Powder Z), the zirconia powder system with the lowest densification rate, lies between 100%CR-15 and 90% CR-15+10%TMDAR curves.

Based on these two comparison results, several alumina powder mixtures were tested with the CR-15 powder varying between 100% and 85%. The TMA testing results revealed that the alumina powder mixtures containing 94% CR-15 and 6% TMDAR (Powder A) has very similar densification rate curve as Powder Z(Fig. 5.2). Also, sintered samples by Powder A and Powder Z had almost the same final diameter. These two powders were mixed in equal volume. The

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resulting powder mixture yielded a similar, not exactly the same, densification curve as Powders *A* and *Z*. This should be due to the change in the particle size distribution. However, considering the excellent sinterability of TMDAR, by making a small adjustment in the TMDAR proportion, the powder system with 46% CR-15, 4% TMDAR, and 20% CERAC-2003, 30% TZ3YS by volume (Powder *M*) shows a nearly same sintering behavior as Powder *A* and Powder *Z* (Fig. 5.2) as well as almost the same final diameter.



Figure 5.2. The densification rate-relative density curves of the three chosen powder mixtures (ramp rate: 10°C/min).

The shape of the three curves in Fig. 5.2 is very similar. One obvious difference is located around  $0.22 \cdot 10^{-3}$ /s densification rate in the ascending portion. The corresponding sintering temperature range is 1150-1200°C. There is a plateau for layer *A* and a drop in slope for layer *M*, but there is no noticeable change for layer *Z* near this region. As explained in Section 4.3.1, the change in

densification rate for layers A and M is a result of  $\gamma$ - to  $\alpha$ -phase transition of alumina [20] since 10%  $\gamma$ -phase alumina is present in CR-15. However, since layer Z does not contain CR-15, there is no plateau or abrupt slope change in its densification rate curve.

The similarity among the sintering kinetics of the three powders results in no obvious difference in shrinkage rate and final diameter among layers during the co-sintering of a FGM sample. Therefore, the Powder *A*, *Z*. and *M* are the potential powders to achieve flat, crack-free three-layered  $Al_2O_3/ZrO_2$  FGM samples.

### 5.3 THE INFLUENCE OF COMPACTION LOAD

The compaction load also affects the final diameter. Fig. 4.7 also depicts this relationship. For any given powder combination, the final diameter and the compaction load are can be seen to be directly proportional. As the compaction load increases, the particles in each specimen pack together more tightly, resulting in an increase in the green density [76]. This decreases the shrinkage, ultimately leading to a larger diameter on the fully sintered samples. However, for a material system under varying compaction loads, the plots seem to display a 'parallel characteristic', suggesting that the change in the compaction load does

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not impact the relation between the final diameter and the content of the powder mixture.

As the compaction load increases, the normal stress being exerted on the powder by the die will increase. Therefore, in the ejection step, there is a larger friction force between the die and the powder. The increase in friction raises the possibility of camber or cracks. In addition, beyond a critical load the yield surface of ceramic powders move out to the shear failure surface [89]. The particles slide against each other, resulting in micro-cracks, which may eventually lead to a crack in the sample.

Table 5.1 The damage characteristics of FGM samples experienced different compaction load

Load (MPa)	Structural Characteristics
>160	Cracks between layers M and A and camber in shape
100–160	Camber in shape, no cracks
60–100	Flat and no cracks
<40	Too fragile to handle for the green piece

In this study, we found that the change in compaction load resulted in various damage characteristics in the sample, as shown in Table 5.1. These observations suggest that it is reasonable to consider that a low compaction load is preferable in order to achieve undamaged and undistorted FGM samples. However, the use of a compaction load lower than 40MPa causes the green bodies to be very weak: either they fracture during ejection from the forming die or they are too fragile to

handle. Due to these findings, we considered a compaction load of 60MPa to be the optimized compaction load.

### **5.4 THE INFLUENCE OF INTERFACE PROFILE**

In the processing of multi-layered FGMs, typically a free and flat interface (natural interface) is used between two successive layers. However, this study finds that with the natural interfaces of the  $Al_2O_3/ZrO_2$  FGM sample, cracks were formed between layer *A* and layer *M* despite of no apparent camber on the sample. This crack formation necessitated the investigation into using more complex interfaces.

Two additional interface profiles were investigated in this study: smooth and occlusive. The smooth profile is obtained by lightly rotating the regular flat punch without any pressure. The smooth interface has a smaller interface area than the natural interface. The occlusive interface profile, so named because it resembles the way in which the cusps of molars from the upper and lower jaw fit together, yields an increase in the interface area. This profile will be obtained by pressing the lower powder layer with a punch featuring a jagged surface as shown in Fig. 5.3 and pouring the powder for the subsequent layer.

Considering the structure of our FGM sample, each interface requires its distinct profile to prevent the formation of cracks. The interfacial crack between

the layers *A* and *M* indicates that the bonding between *A* and *M* was weaker. The interlock structure of the occlusive interface would increase the bonding between these two layers. In addition, the occlusive interface creates a quasi-continuous intergradation, which provides a more continuous material properties transition between these two layers when compared to the other two interface profiles. At the same time, the interface between *M* and *Z* was much stronger as no interfacial crack has been detected.



Figure 5.3 The punch featuring a jagged surface for making the occlusive interface.

For our powder systems, we found that only the combination of a smooth interface between the layers *M* and *Z* and an occlusive one between the layers *A* and *M* prevents the formation of cracks. At this time, the exact reason for this particular interface combination to work is not known. Fig. 5.4 shows the BSE (Back Scatter Electron) micrographs for the two modified interfaces.



Figure 5.4 BSE Micrographs of the two interfaces used in this study, a) the occlusive interface between layer A and layer M and b) the smooth interface between layer Z and layer M (Acceleration voltage: 25kV, Working distance: 39mm).

#### 5.5 THE INFLUENCE OF RAMP/SOAK PROFILE

The mixing proportions of powder have been determined in order to achieve nearly equal final diameters. However, the transient diameter change during the sintering process is also important to yield samples without camber and cracks. Fig. 5.5 shows the change in the shrinkage rate of powder mixture for layer A and layer Z under an isothermal experiment at 1250°C. It is clear that the shrinkage rate of layer Z is higher than that of layer A at this temperature. In fact, this conclusion is suitable for the whole sintering temperature range we used. This sintering mismatch contributes the most important factor in creating cracks or camber as mentioned above.



Figure 5.5 Shrinkage ratio changing profile of Powders A and Z under an isothermal sintering experiment at 1250°C (dh(t) is the height changing ratio and h(t) is the height of sample at time t).

However, considering that alumina has much higher thermal conductivity than zirconia [120, 121], with a faster ramp rate, alumina can be heated up more quickly and may catch up to the shrinkage of zirconia in the co-sintering process. This results in a reduction in the transient mismatch of shrinkage between different layers. From our observation, if the previously determined optimal system of powder mixtures is sintered with a lower ramp rate (less than 7 °C/min), cracks formed on the surface of layer *A*. Final samples were free of cracks and camber if the ramp rate was higher than 10°C/min and a two-hour soak interval was used. This ramp rate is exactly used for the sintering curves shown in Fig. 5.2. However, considering the low thermal conductivity of ceramics, the ramp rate

cannot be set too high. This would cause a large temperature difference within a sample and may create a condition for cracks [58].

Because of the difference in the CTE between layers of a fully sintered sample, a lower cooling rate was preferred to avoid cracks, since the residual stresses can be relaxed in the initial period of cooling [58]. In our experiments, the cooling rate of 4°C/min is low enough to prevent cracks caused by CTE mismatch. The final optimized ramp/soak sintering cycle is shown in Fig. 5.6.



Figure 5.6 Optimal ramp/soak sintering profile for this study.

## 5.6 SHRINKAGE RATE-SINTEIRNG TEMPERATURE CURVES OF CHOSEN POWDERS UNDER OPTIMIZED CONDITIONS

Table 5.2 summarizes the discussion of Sections 5.2 to 5.5 and provides the optimal parameters to yield undistorted, flat three-layered Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> FGM samples without cracks.
- Structure	Layer Z	60% TZ3YS, 40%CERAC-2003	
	Interface Z/M	Smooth	
	Layer M	20% CERAC-2003, 30% TZ3YS	
		46% CR-15, 4% TMDAR	
	Interface M/A	Occlusive	
Γ	Layer A	94% CR-15, 6%TMDAR	
Compaction load		60 MPa	
Rate of temperature change		10°C/min for heating, 4°C/min for coolin	

Table 5.2 Summary of optimized experimental conditions for a 3-layered Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> FGM.



Figure 5.7 Shrinkage ratio-temperature curves for chosen three powder-mixtures under optimized experimental condition ( $h_T$  is the height of sample at temperature T and  $h_o$  is the height of the corresponding green sample).

The densification rate-relative density curves of the three chosen powder mixtures under the optimal parameters have been shown in Fig. 5.2. Alternatively, the shrinkage ratio-sintering temperature curve was also used to express the sintering kinetics of Powders *A*, *M* and *Z*, which is shown in Fig. 5.7. The similarity of the curves can be directly observed, where all three powder mixtures begin

sintering at about 1050°C, and that similar transient shrinkage behavior is exhibited above 1050°C. The similarity of shrinkage rate for those chosen powder mixtures ensures that no significant dimensional mismatch could occur at any time during sintering, thus reducing the possibility to form cracks or camber. The present work verifies the conclusion by Torrecillas *et al.* [65].



Figure 5.8. A representative Backscattered Electron image (BSEI) of the three-layered Al<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub>/ZrO<sub>2</sub> FGM (Acceleration voltage: 22kV, Working distance: 15mm).

Fig. 5.8 shows a representative microstructure of the cut cross-section of the three-layered FGM. Obviously no debonding cracks happened between the conjoint layers. The microstructure observation of the surfaces showed neither channeling in the layer with tensile stress (in this study, alumina layer) nor edge-effect cracks described by Cai [58]. In this study, we fabricated 15 FGM samples by the chosen powder mixtures under the described ramp/soak path, 14 of which are totally crack and camber free. The other one has a small crack

between mixture layer and alumina layer, which may be a result from carelessly handling of the green sample from the die.

### 5.7 PHENOMENOLOGICAL CONSTITUTIVE MODELS

Due to the similarity of the densification rate-relative density curves shown in Fig. 5.2, it is intuitive to investigate and compare the Hsueh's constitutive model [107] describing these three curves. Based on the calculation steps mentioned in Section 4.4.1, we obtain the phenomenological constitutive functions for those three sinter plots.

We a little changed the entire phenomenological constitutive model expression to the form of:

$$\dot{\varepsilon}^{s} = \Omega(T + Ta)[D\infty(T + Tb) - D]^{n} \qquad (5.2)$$

By calculation, the  $\Omega(T + T_a)$  is a 4<sup>th</sup> order polynomial and can be written as:

$$\Omega(T+Ta) = a(T+Ta)^{4} + b(T+Ta)^{3} + c(T+Ta)^{2} + d(T+Ta) + e$$
(5.3)

and  $D_{\infty}(T+T_b)$ , the theoretically possible full-sintered density at temperature *T*, is a hyperbolic tangent function of the form:

$$D\infty(T+Tb) = f \tanh[g(T+Tb) - h] + i \qquad (5.4)$$

Table 5.3 summarizes the coefficients for all three powder mixtures.

From Table 5.3, we can find that the exponent index n is different in each powder mixture. However, the n for layer M is close to the average of the n values

for layer A and layer Z. As of now we cannot give the physical explanation for this relationship. Because the content of layer M is almost equal to the mixture of half layer A and half layer Z, the near-average value of n for layer M seams logical.

Table 5.3 The coefficients used to construct the phenomenological constitutive models for the chosen powder mixtures.

Layer	<i>T<sub>a</sub></i> (°C)	a (·10 <sup>-10</sup> )	b (·10-7)	c (·10-3)	d	е
A	-80	-1.707	7.55112	-1.091475	0.478596	53.688
M	-40	-3.5278	15.60565	-2.224715	0.9891	110.955
Ζ	-20	-5.69	25.1704	-3.63825	1.59532	178.96
Layer	<i>T<sub>b</sub></i> (°C)	f	g (·10-3)	h	i	n
A		0.2365			0.7435	1.65
M	-460	0.2449	8.3885	9.4498	0.7551	1.88
Z		0.2325			0.7675	2.1

Using Table 5.3 and formula (5.3), we can find that  $\Omega(T)$  is entirely different for each layer. This difference is a result of variation of each powder combination's apparent activation energy [104], which is determined by the content of the powder system. By Table 5.3 and formula (5.4), we can find that the coefficient *f* and *i* are different for each layer too. The two coefficients are calculated by the relative green density  $D_g$  and the final relative full density  $D_{f^{\infty}}$  in the following way:

$$\begin{cases} f+i=Df\infty=1\\ -f+i=Dg \end{cases}$$
(5.5)

Since the green density varies for different layer like discussed in Section 4.3, coefficient *f* and *i* also must vary with the powder mixture.

In contrast, the coefficients g, h and  $T_b$  were found to be constant for all three powder mixtures. This results in the terms inside the hyperbolic tangent function being identical for all three cases. In the simulation process, we find that these three coefficients significantly influence the shape of the calculated curve. The similarity of shape of the three plots in Fig. 5.2 results in the same values for g, hand  $T_b$ .



Figure 5.9 The comparison of experimental and calculated densification rate vs. relative density curves ( $R_E$  gives the experimental result and  $R_C$  represents the calculated result).

Fig. 5.9 shows the comparison of the experimental and the calculated densification rate by formula (5.2) for all three powder mixtures. The errors

between the experimental data and the calculated results are less than  $\pm 6\%$ . It should also be pointed out that the simulation result from the phenomenological constitutive model does not display the plateau that occurs in conjunction with the phase change.

#### **5.8. CONCLUSIONS**

In the co-sintering of multi-layered FGMs, matching the compaction and sintering behavior of two distinct materials, each from one type of powder, is not possible. This has been proved by the research of Cai et al. [58]. Mixing powders is an effective approach to manipulating the characteristics of raw powders, such as compactibility, sinterability and agglomerates ratio. These parameters finally influence the sintering kinetics of powder system. By comparing the densification rate-relative density curves as well as the final diameter-powder ratio curve of an alumina powder system containing TMDAR and CR-15 and a zirconia powder system containing TZ3YS and CERAC-2003, we found that 94% CR-15 and 6% TMDAR alumina powder has very similar densification rate curve and final diameter to the 40% CERAC-2003+60% TZ3YS zirconia powder. By mixing these two powders and slightly adjusting the content of TMDAR, we produced a 50 vol% alumina 50 vol% zirconia powder mixture with the similar densification rate-relative density curve and diameter as the other two pure powders. The content of the 50 alumina /50 zirconia mixture is 46% CR-15 and 4% TMDAR/

20% CERAC-2003 and 30% TZ3YS by volume. The shrinkage ratio curves of these three powder mixtures were found to be almost identical. The similarity in the shrinkage ratio for those chosen powder mixtures ensures that no significant dimensional mismatch could occur at any time during sintering, thus reducing the possibility for cracks and camber in the sample. In addition, the effect of the compaction load, interface profiles and temperature ramp/soak cycles were studied. Through a series of experimental processing, the optimal processing parameters were then obtained, which enabled us to produce flat 3-layered Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> FGMs without cracks. Decreasing the compaction load, increasing the ramp rate, selecting an appropriate mixture combination and modifying the interface profile have been found to produce FGM samples free of defects. The shrinkage curves were found to be almost identical. The almost identical densification rate curves of the chosen powder mixtures under the optimized sintering conditions feature the same hyperbolic tangent term in the corresponding three phenomenological constitutive models.

After we successfully fabricated Al<sub>2</sub>O<sub>3</sub>/ ZrO<sub>2</sub> FGMs, we considered replacing reinforced carbon-carbon composite (RCC) by Mullite for the skin of a space shuttle, and manufacturing a ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> FGM core + Mullite skin Perspirable Skin. However, the total weigh of the TPS will increase a lot. If keeping RCC as skin material, because the CTE of either alumina or zirconia is larger than that of

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RCC, there is no gas channel forming at high temperature for a ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> FGM core+ RCC skin structure. Therefore, ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> FGMs are not suitable for the core material of Perspirable Skin. So ceramic with lower CTE is necessary to be investigated for the Perspirable Skin project.

## **CHAPTER 6**

# ZrW<sub>2</sub>O<sub>8</sub> and ZrW<sub>2</sub>O<sub>8</sub>-ZrO<sub>2</sub> COMPOSITES: IN-SITU REACTION AND PHYSICAL PROPERTIES

Since ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> FGMs are not suitable for the core material of Perspirable Skin, ceramic with lower CTE is necessary to be investigated for the Perspirable Skin project. This chapter will present our investigation on ZrW<sub>2</sub>O<sub>8</sub>, a material featuring isotropic negative thermal expansion over the whole solid state, as well as its composites with ZrO<sub>2</sub>.

#### **6.1 EXPERIMENTAL PROCEDURES**

Four powders, W-Fluka, ZW-OR, CERAC-2003, and TMDAR, were used in this study. These powders were mixed in varying proportions as described later using 12mm diameter zirconia media in a mixing jar mill (U.S. Stoneware 764AVM, U.S.A.) for 48 hours. The powder mixtures were compacted in a single-action die under the load producing 80MPa compaction pressure. The green samples for CTE testing were cylindrical with 7.94mm diameter and 6mm height while the *gr*een samples for Young's modulus testing were rectangular parallelepipeds Whose dimension is 16.5mm×5.05mm×3.5mm. Green compacts were sintered in a furnace (Carbolite-HTF1700, UK) under the atmospheric condition in a covered platinum crucible, which can decrease the sublimation of WO<sub>3</sub> at temperatures above 800°C [122]. Several ramp/soak profiles were used in the experiments, which will be described in the following sections. However, a quenching process is necessary for each ramp/soak profile to prevent the decomposition of ZrW<sub>2</sub>O<sub>8</sub> [25, 123]. The volume of each fully-sintered sample was measured in water using Archimedes' principle, which was then used to calculate the relative densities.

Before testing CTE and Young's modulus, the samples were heat-treated (3°C /min for both heating and cooling cycles, and soaking for 60 minutes at 300°C) to cure microcracks induced by the quenching process [25]. The CTE and Young's modulus of the sintered samples were measured using the TMA with the heating and cooling rates of 1°C /min in an argon gas environment. Three samples produced for each material were tested for CTE and Young's modulus. The CTE variation is less than 5% and the maximum discrepancy in the Young's modulus data is 6% in the three samples. Therefore, we considered that the CTE and Young's modulus test results for each material are consistent and each reported value in the paper is the average of the corresponding results of three samples. The sintered samples were then polished (Abramin, Denmark) and thermal etched in the furnace at 600°C for the microstructure observation. The microstructure of each sample was observed using Scanning Electron Microscopy (JEOL 6400V, Japan).

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#### 6.2 SYNTHESIS OF ZrW<sub>2</sub>O<sub>8</sub> SUBSTRATE

From the WO<sub>3</sub> and ZrO<sub>2</sub> bi-phase diagram [123], ZrW<sub>2</sub>O<sub>8</sub> is only present at a temperature higher than 1110°C and stable in the temperature range of 1110 - 1260°C. Therefore, in the processing of ZrW<sub>2</sub>O<sub>8</sub> substrate, the final soaking temperature must be higher than 1110°C and a quenching step is necessary to prevent the decomposition of ZrW<sub>2</sub>O<sub>8</sub>. Based on these two requirements, the ramp/soak profile shown in Fig. 6.1 was used to produce ZrW<sub>2</sub>O<sub>8</sub>. The stoichiometric ratio of WO<sub>3</sub> and ZrO<sub>2</sub> in the reactant is 2:1, which translated into the mass ratio of 1:0.266. The reaction can be expressed as follows:

 $ZrO_2 + 2WO_3 \rightarrow ZrW_2O_8 \tag{6.1}$ 



Figure 6.1 The ramp/soak path used for producing ZrW<sub>2</sub>O<sub>8</sub>.

After quenching in open air, the surfaces of the samples featured small micro-cracks. These micro-cracks disappeared completely after the cure

treatment cycle mentioned above.



Figure 6.2 a) The XRD pattern of the reaction product and b) the standard powder diffraction file of  $ZrW_2O_8$  (JCPDS 13-557).

Fig. 6.2 (a) shows the XRD pattern of the reaction product. The XRD testing was executed with a Scintag XDS2000 4-angle pole figure diffractometer. This pattern was observed to be nearly the same as the standard powder diffraction file of ZrW<sub>2</sub>O<sub>8</sub> (Fig. 6.2 (b), JCPDS 13-557). This verifies that the compound produced is pure ZrW<sub>2</sub>O<sub>8</sub>.



Figure 6.3 The microstructure of the ZrW<sub>2</sub>O<sub>8</sub> substrate.

The final dimensions of the cylindrical  $ZrW_2O_8$  we have produced were 7.51mm in diameter and 5.68mm in height and the final relative density was 90%. The microstructure of the resulting  $ZrW_2O_8$  is shown in Fig. 6.3.



Figure 6.4 The temperature dependence of CTEs of  $ZrW_2O_8$  and CERAC-2003 sintered by ramp/soak path in Fig. 6.1.

The CTE-temperature relationship of the  $ZrW_2O_8$  substrate was measured and presented in Fig. 6.4. The CTE-temperature relationship of the partially sintered CERAC-2003 sample utilizing the ramp/soak path shown Fig. 6.1 is also presented in Fig. 6.4. These two ceramics are the main components for the composites in this study. As expected, the CTE of  $ZrW_2O_8$  is negative and uniform for a wide range of temperature except with a sharp change around 160°C due to the  $\alpha$ - to  $\beta$ -  $ZrW_2O_8$  phase transition. The CTE of the  $ZrW_2O_8$  at room temperature is  $-8.1 \times 10^{-6}$ K<sup>-1</sup>, which matches the report by Mary et al. [20]. The CTE of the partially sintered CEREAC-2003 is  $8.6 \times 10^{-6}$ K<sup>-1</sup> at room temperature.



Figure 6.5 The temperature dependence of thermal conductivity of ZrW<sub>2</sub>O<sub>8</sub>.

The high temperature thermal conductivity of  $ZrW_2O_8$  was measured using the laser flash method (FlashLine 5000, USA) from room temperature to 710°C. The results are shown in Fig. 6.5. Around 160°C, a sharp peak, corresponding to the  $\alpha$  to  $\beta$  ZrW<sub>2</sub>O<sub>8</sub> phase transition can be observed. The room temperature phase is phase  $\alpha$ , and its thermal conductivity is around 0.89 Wm<sup>-1</sup>K<sup>-1</sup>, a result that is very close to the reported value of 0.82 Wm<sup>-1</sup>K<sup>-1</sup> [124]. The high temperature phase  $\beta$  features a nearly constant thermal conductivity at 0.985 Wm<sup>-1</sup>K<sup>-1</sup> between 500 to 710°C. Our data indicates that the thermal conductivity of the phase  $\beta$  is higher than the phase  $\alpha$ . It is known that ZrW<sub>2</sub>O<sub>8</sub> exhibits a crystalline structure, and usually a crystalline material possesses a high thermal conductivity. However, our data show the thermal conductivity of ZrW<sub>2</sub>O<sub>8</sub> is very low (even lower than that of glasses). From the report of Mary et al. [20], the dimension of the unit cell  $ZrW_2O_8$  is extremely large when compared with common ceramics. This structural characteristic provides more phonon vibration modes to hinder the heat flow in solid. Consequently, the thermal conductivity of  $ZrW_2O_8$  is thus very low.

#### 6.3. ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> COMPOSITES

#### 6.3.1 Manufacturing and CTEs

With the ramp/soak path shown in Fig. 6.1 and a higher proportion of  $ZrO_2$ , a  $ZrW_2O_8/ZrO_2$  composite instead of  $ZrW_2O_8$  can be fabricated. Thus, by varying the ratio of WO<sub>3</sub> to  $ZrO_2$ , the resulting composites feature varying ratio between  $ZrW_2O_8$  and  $ZrO_2$ . Table 6.1 shows several WO<sub>3</sub>/ $ZrO_2$  mass ratios used in this study and the corresponding resultant  $ZrW_2O_8/ZrO_2$  volume ratios in the sintered samples.

Table 6.1 The WO<sub>3</sub>/ZrO<sub>2</sub> mass ratios of various green samples and the corresponding resultant  $ZrW_2O_8/ZrO_2$  volume ratios in the sintered samples.

#	WO <sub>3</sub> /ZrO <sub>2</sub> mass ratio	ZrW <sub>2</sub> O <sub>8</sub> /ZrO <sub>2</sub> volume	Final relative
	in reactant powder	ratios in sintered sample	density
1	0.159:1	20:80	77%
2	0.264:1	30:70	79%
3	0.38:1	38.9:61.1	80%
4	0.593:1	51.5:48.5	82%
5	1.096:1	70:30	83%
6	2.307:1	90:10	84%

The temperature-dependent CTE value of each sintered sample is shown in Fig. 6.6. As shown, both Samples 1 and 2 feature positive CTEs, Samples 4-6 exhibit negative CTEs, and the CTE of Sample 3 is nearly zero. Fig. 6.6 shows that the CTE-temperature curves of the composites feature a shape that is very similar to that of pure  $ZrW_2O_8$ . However, the peak caused by phase transition occurs at a lower temperature for the composites. This "peak shift" is possibly a result of phase transition from  $\alpha$ -  $ZrW_2O_8$  (low pressure phase) to  $\gamma$ -  $ZrW_2O_8$  (high pressure phase) [125] due to the thermal stress induced by the CTE mismatch between  $ZrW_2O_8$  and  $ZrO_2$ .



Figure 6.6 The temperature dependent CTEs of the various  $ZrW_2O_8/ZrO_2$  composite samples.

The relationship between the CTEs of various samples and the corresponding volume fractions of ZrW<sub>2</sub>O<sub>8</sub> for both room temperature and 500°C testing

conditions is plotted in Fig. 6.7(a) and 6.7(b), respectively. It can be observed that the CTE values continuously decrease as the volume fraction of  $ZrW_2O_8$  increases in the composites. For the zero CTE  $ZrW_2O_8/ZrO_2$  composite, the volume fraction of  $ZrW_2O_8$  in the final product is about 38.9% (Sample 3).



Figure 6.7 The CTEs of the ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> composite samples and corresponding calculated values from several prediction models at a) room temperature and b) 500°C.

As mentioned in Section 1.2.3.3, the ROM is the simplest method to calculate the effective CTE of a composite. By using the CTE testing results of  $ZrW_2O_8$  and  $ZrO_2$  shown in Fig. 6.4, the effective CTEs of  $ZrW_2O_8/ZrO_2$  composites were calculated based on the ROM and presented in Fig. 6.7. Large discrepancy exists between the experimental results and the calculated values from the ROM for both room temperature and 500°C testing conditions. In fact, the ROM predicts that Sample 4 has a room temperature CTE of nearly zero, but the experimental data showed its CTE to be  $-2.14 \times 10^{-6}$ K<sup>-1</sup>. This discrepancy is due to the porosity of the resulting composites. At the same time, the ROM to predict affective CTE does not include the elastic constants that account for the thermal stress influence between ZrW<sub>2</sub>O<sub>8</sub> and ZrO<sub>2</sub>.

The calculated CTE as a function of v% of  $ZrW_2O_8$  results from Turner model [37], Kerner model [38], Rosen-Hashin Bounds model [39] and Levin model [40] (Equations (1.6-1.9)) also are shown in Fig. 6.7, which take into account the elastic constants into the calculation of CTEs. The values of various elastic constants of  $ZrW_2O_8$  and  $ZrO_2$  necessary for the CTE calculation are calculated based on the experimental data of Young's modulus and the assumed Poisson's ratio. This will be discussed in Section 6.3.2.

Clearly, Equations (1.6-1.9) result in better predictions than the ROM. Among these, the Levin model [40] produces CTE values that are the most similar to the experimental data. The maximum error of Levin model was found to be less than 8%. By studying the series of Al<sub>2</sub>O<sub>3</sub>/NiAl composites, Hsieh et al. [126] concluded "the Kerner [38] and Turner [37] models can be used as the upper and lower bounds for the CTE of two-phase materials, respectively." This conclusion also matches the results from our  $ZrW_2O_8/ZrO_2$  composites. Another interesting finding is that the upper boundary predicted by the Rosen-Hashin Bounds model [39] almost superimposes on the curve form Kerner model [38] for the  $ZrW_2O_8/ZrO_2$  composites.

All of the ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> composites maintained their initial cylindrical shape, with final diameter and height around 7.35mm and 5.57mm, respectively, and they featured final relative densities in the 77-84% range (see Table 6.1). This low density persists mainly because ZrO<sub>2</sub> has not been fully sintered by the ramp/soak path shown in Fig. 6.1. In the representative micrograph of the composites (Fig. 6.8), the large particles surrounded by small ZrO<sub>2</sub> particles are ZrW<sub>2</sub>O<sub>8</sub>. The abundance of pores remaining between the ZrO<sub>2</sub> particles is due to the fact that ZrO<sub>2</sub> is far from fully sintered. In addition, cracks are observed to exist between ZrW<sub>2</sub>O<sub>8</sub> and ZrO<sub>2</sub> grains, resulting from the considerable difference in CTEs for these two component materials. These cracks also contribute to the low final density.



Figure 6.8 The microstructure of a ZrW2O8/ZrO2 composite (Sample 3).

#### 6.3.2. Young's Modulus

The TMA unit offers a facility to measure Young's modulus of materials using the three-point bending method. After sintering and polishing, the samples used in Young's modulus testing are rectangular parallelepipeds (cuboids) with edge lengths 12.6mm, 4.2mm and 2.5mm. The temperature dependent Young's moduli of the fabricated composites as well as that of ZrW<sub>2</sub>O<sub>8</sub> and ZrO<sub>2</sub> are shown in Fig. 6.9.



Figure 6.9. Young's modulus - temperature curves for composites as well as for  $ZrW_2O_8$  and  $ZrO_2$  sintered by ramp/soak path in Fig.6.1.

Since the ZrO<sub>2</sub> in the composites is processed by the ramp/soak path shown in Fig. 6.1, the CERAC-2003 for Young's modulus testing was also partially sintered by the same ramp/soak path. Microcracks formed in the ZrO<sub>2</sub> samples due to the quenching process. The highest testing temperature was set as 650°C in order to avoid the decomposition of  $ZrW_2O_8$ . The room temperature Young's modulus of pure  $ZrW_2O_8$  was found to be 4.31GPa, which nearly matches the value of 4.22GPa reported by Chen et al. [25]. However, these values quite different from the single crystal value of 88.3GPa reported by Drymiotis et al. [127]. Since the  $ZrO_2$  sample was only partially sintered and contains microcracks, its Young's modulus is much lower than that of a fully-sintered sample (~200GPa) and it does not feature a large decrease from 100 to 400°C, which is typical for fully-sintered  $ZrO_2$  [128]. As happened with CTEs, the Young's moduli of the composites and the  $ZrW_2O_8$  feature a value change around 160°C due to the  $\alpha$  to  $\beta$  phase transition.



Figure 6.10. The calculated Young's modulus of  $ZrW_2O_8/ZrO_2$  composites by Mori-Tanaka model and the experimental measurement of composites at a) room temperature, b) 500°C.

From the reports of Drymiotis [127] and Holcome [129], we took the Poison's ratio is 0.3 for both ZrW<sub>2</sub>O<sub>8</sub> and ZrO<sub>2</sub>. Therefore, with the Young's modulus values for ZrW<sub>2</sub>O<sub>8</sub> and partially sintered ZrO<sub>2</sub>, we calculated the elastic constants needed for Mori-Tanaka method (Equation 1.1) and Equations (1.6-1.9) and the Young's moduli of ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> composites by the Mori-Tanaka method. These results are shown in Fig. 6.10 along with the experimental Young's modulus of the composites. It can be seen that the experimental data lies between the two curves predicted by the Mori-Tanaka method. Based on the definition of continuity by Nishimatsu and Gurland [47], we calculated four different continuity values. Since the pores of ZrW<sub>2</sub>O<sub>8</sub> is much less that that of ZrO<sub>2</sub>, only three microstructural interfaces of ZrW2O8-ZrW2O8, ZrW2O8-pores, and ZrW2O8-ZrO2 are needed in the calculation. The summation of interface number of ZrW2O8-pores and ZrW<sub>2</sub>O<sub>8</sub>-ZrO<sub>2</sub> results in the interface number of ZrW<sub>2</sub>O<sub>8</sub>-porous ZrO<sub>2</sub>. The calculation formula we used is

$$C = \frac{2Nzw/zw}{2Nzw/zw + Nzw/p + Nzw/zo}$$
(6.2)

where,  $N_{ZW/ZW}$ ,  $N_{ZW/p}$ , and  $N_{ZW/ZO}$  represent the number of interfaces of ZrW<sub>2</sub>O<sub>8</sub>-ZrW<sub>2</sub>O<sub>8</sub>, ZrW<sub>2</sub>O<sub>8</sub>-pores, and ZrW<sub>2</sub>O<sub>8</sub>-ZrO<sub>2</sub> that crosses the unit line, respectively.

The continuity values are listed in Table 6.2. The curve by Kwon et al. [42] revised Mori-Tanaka method represented in Fig. 6.10 too. As can be seen, the

revised Mori-Tanaka method shows a much better fit to experimental data, even when the volume fraction of  $ZrW_2O_8$  is higher than 0.6. The maximum error of Mori-Tanaka method revised by Kwon *et al.* [42] was found to be only 4%.

Table 6.2 The continuity values obtained by the microstructure observation for  $ZrW_2O_8$ - $ZrO_2$  composite samples with different  $ZrW_2O_8$  volume frictions.

ZrW <sub>2</sub> O <sub>8</sub> volume proportion range (%)	Continuity
0-20	0
20-45	0.3
45-65	0.5
65-90	0.75
90-100	0.98

Here, one point need to be emphasized is that there are voids in the  $ZrW_2O_8/ZrO_2$  composites. If the Young's moduli of the single crystal  $ZrW_2O_8$  and fully-sintered  $ZrO_2$  are used for the Mori-Tanaka method. The third phase of void need to be considered too. However, in our calculation, by taking the measured Young's modulus values of  $ZrW_2O_8$  and  $ZrO_2$  sintered by the same ramp/soak profile to produce the  $ZrW_2O_8/ZrO_2$  composites as the two boundary values, the effect of voids on the Young's modulus has been included. Because the boundary values are exactly for the components of all  $ZrW_2O_8/ZrO_2$  composites in this paper, the calculated curves in Fig. 6.10 can be used to predict the Young's moduli of any other  $ZrW_2O_8/ZrO_2$  composites.

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#### 6.4 ZERO CTE COMPOSITES CONTAINING ZrW<sub>2</sub>O<sub>8</sub>

Fig. 6.6 shows Sample 3 with nearly zero CTE. The dimensions of this composite do not change with the temperature changing. Therefore, it can be used as the ceramic substrate of optical fiber Bragg gratings and some components of microelectronics. One advantage of this kind of composites is to reduce the thermal stress due to the temperature gradient or transient temperature change. Several fabrication methods were developed to produce the ZrW<sub>2</sub>O<sub>8</sub>-containing composites with zero CTE. These methods were then evaluated based on the microstructure, final density, mechanical strength of the sintered samples, and the ability to maintain the shape during the processing.

#### 6.4.1 Method I: In-Situ Reaction of ZrO<sub>2</sub>+WO<sub>3</sub>

By Table 6.1, the reaction of powder mixture of W-Fluka and CERAC-2003 with the 1:2.62 mass ratio produced a  $ZrW_2O_8/ZrO_2$  composite with nearly zero CTE. The volume fraction of  $ZrW_2O_8$  in the final product is 38.9% and the mass ratio between  $ZrW_2O_8$  and  $ZrO_2$  expected to be around 1:1.86. The  $ZrW_2O_8/ZrO_2$  composite fabricated by Method I maintained its cylindrical shape with the final diameter and height of 7.35mm and 5.57mm respectively, and the final relative density of the composite was only 81%. Its Young's modulus at room temperature is 2.26±0.01 GPa. The CTE measurement for this composite is shown in Fig. 6.11.



Figure 6.11 CTE-temperature curves for nearly zero CTE composites fabricated by various processing methods; each data point represents an average of test results for three samples.

### 6.4.2 Method II: Cosintering of ZrO<sub>2</sub> and ZrW<sub>2</sub>O<sub>8</sub>

Considering that no reaction occurs between ZrW<sub>2</sub>O<sub>8</sub> and ZrO<sub>2</sub>, ZW-OR and CERAC-2003 powders were mixed with the mass ratio of 1:1.86. This mass ratio was chosen based on the experimental results of Section 6.4.1. The powder mixture was sintered by the ramp/soak path from Fig. 6.1. The produced ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> composite also exhibits near zero CTE. Fig. 6.11 shows that the CTE curves of the composites fabricated by Methods I and II are almost identical. Fig. 6.12 (b) displays the micrograph of the composite fabricated by Method II. By comparing Figs. 6.12 (a) and 6.12 (b), it can be seen that the microstructures for both composites are very similar. Therefore, Method II produces a very similar composite as Method I. The Young's modulus at room temperature of the

composite by Method II is  $2.27\pm0.01$  GPa. However, due to the relatively high cost of commercially available ZrW<sub>2</sub>O<sub>8</sub> powder, Method II is a more expensive process than Method I.



Figure 6.12 Micrographs of near-zero CTE composites made by Method a) I b) II, c) III and d) IV. The larger grains are ZrW<sub>2</sub>O<sub>8</sub> and the smaller grains are ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (Working distance: 15mm, acceleration voltage: 15KV).

#### 6.4.3 Method III: In-Situ Reaction of ZrO<sub>2</sub>+WO<sub>3</sub>+Al<sub>2</sub>O<sub>3</sub>

In sintering a powder mixture containing ZrO<sub>2</sub>, WO<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub>, a complex chemical reaction occurs when the temperature exceeds 1100°C

$$ZrO_2 + WO_3 + Al_2O_3 \rightarrow ZrW_2O_8 + Al_2(WO_4)_3 + ZrO_2 + Al_2O_3$$
 (6.3)

The melting point of  $Al_2(WO_4)_3$  is 1135°C [130]. Therefore, a liquid phase exists if the soaking temperature is set at 1190°C. The presence of the liquid will promote the densification kinetics, improving the final relative density.

Based on several experiments, one mixture of  $ZrO_2$ ,  $WO_3$ , and  $Al_2O_3$  powders used to produce a near-zero CTE  $ZrW_2O_8/Al_2(WO_4)_3/ZrO_2/Al_2O_3$  composite was with the mass ratio:

$$m_{WO3}:m_{ZrO2}:m_{Al_{2}O_{3}}=1:0.266:1.53$$
 (6.4)

The CTE curve for this composite is also presented in Fig. 6.11. The ramp/soak path used in this method is the same as that of Fig. 6.1. The final relative density of the composite is greater than 95%, which is much higher than those of Methods I and II (81%). The microstructure of the composite produced by Method III (Fig. 6.12 (c)) shows much more compact structure than the microstructures shown in Figs. 6.12 (a) and (b). Very few pores are left among ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> grains in Fig. 6.12 (c), a characteristic attributed to the infiltration of the liquid Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> phase. The average grain size of Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> and ZrW<sub>2</sub>O<sub>8</sub> in Fig. 6.12 (c) is much less than those in Figs. 6.12 (a) and (b). The liquid phase produced in the sintering process for Method III mainly promotes sintering kinetics of ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, resulting a solid ZrO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub> matrix with few pores. In comparison to the porous zirconia matrix produced by Methods I and II, the

 $AI_2(WO_4)_3$  and  $ZrW_2O_8$  phases are tightly integrated into the solid zirconia matrix produced by Method III, which contributes to the small grain growth of  $AI_2(WO_4)_3$ and  $ZrW_2O_8$ . The Young's modulus at room temperature of the composite by Method III is also higher than that by Method I or II. The value is  $38.79\pm0.03$  GPa.

However, the critical problem for Method III is the powder mixture resulting in excessive liquid phase, Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub>, which caused the geometric distortion of the samples. The final shape of the composites fabricated by this method changed substantially from their original cylindrical shape.

#### 6.4.4 Method IV: In-Situ Reaction of ZrO<sub>2</sub>+WO<sub>3</sub>: Another Ramp/Soak Path

Method IV used the same powder mixture to produce pure  $ZrW_2O_8$  (see Section 6.2) with a changed ramp/soak path as shown in Fig. 6.13. The cooling down and the second isothermal soaking part in Fig. 6.13 causes a partial decomposition of  $ZrW_2O_8$ , resulting in a  $ZrW_2O_8/ZrO_2/WO_3$  composite. By using a 2°C/min cooling rate and soaking at 952°C for 37 minutes, a  $ZrW_2O_8/ZrO_2/WO_3$  composite with nearly zero CTE was fabricated, as shown in Fig. 6.11. The final relative density of the composite fabricated by Method IV is only 73%, and the room temperature Young's modulus is 1.89±0.01 GPa. Each value is much lower than the corresponding value of the other three methods. Fig. 6.12 (d) shows the microstructure of the composite fabricated by Method IV, which is less dense than those of the other composites. Because of its loose microstructure, most of the thermal stress due to the CTE mismatch among  $ZrW_2O_8$ ,  $ZrO_2$ , and  $WO_3$  has been released into the larger cracks and pores. Upon heating the composite, only a smaller magnitude of the thermal stress is induced, which deters the  $\alpha$ -to- $\gamma$  phase transition. Therefore, no obvious "peak shift" is observed on the CTE-testing temperature curve for this particular composite as shown in Fig. 6.11. This composite retained the cylindrical shape with the final diameter of 7.49mm and the final height of 5.65mm.



Figure 6.13 The ramp/soak path used in Method IV.

Besides the low final density, another obvious disadvantage of Method IV is the requirement of a very precise control of sintering temperature and time. A small change in the cooling rate or in the duration of the final isothermal cycle (see Fig. 6.13) yields an entirely different CTE result.

#### 6.4.5 Optimal Fabrication Method and Density Improvement

By comparing the four methods, the optimal method is determined for the production of zero CTE composite containing ZrW<sub>2</sub>O<sub>8</sub>. Methods I and II produce

very similar results, where Method II is much more expensive. Method III yields the highest Young's modulus and relative density. However, it could not maintain the sample's shape during sintering. Method IV yields the lowest relative density and Young's modulus. Therefore, it was concluded that the composite is best produced by a new method that combines Methods I and III. By the in-situ reaction of the powder mixture of WO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> with mass ratio 1:0.03:2.61, the optimal nearly zero CTE composite containing ZrW<sub>2</sub>O<sub>8</sub>/Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub>/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> was obtained.



Figure 6.14 The micrograph of near-zero CTE composite made by optimal method (With 0.07 wt% alumina, Working distance: 15mm, acceleration voltage: 15KV).

The CTE-temperature relationship of the optimal composite is almost the same as those of Methods I and II (Fig. 6.11). The optimal composite retains its cylindrical shape and reaches a final relative density of 90%. Its Young's modulus at room temperature is 11.19GPa, which is higher than that of the composites

fabricated by Methods I and II. The microstructure of the composite fabricated by the new optimal method is shown in Fig. 6.14. The microstructure is similar to Figs. 6.12 (a) and (b). However, due to the flow of the liquid phase, the pores among  $ZrO_2$  grains in Fig. 6.14 are much reduced than those in Figs. 6.12 (a) and (b).

Similar method was used to improve density and final mechanical properties of other composites. The 0.07wt% Al<sub>2</sub>O<sub>3</sub> was added into our WO<sub>3</sub>+ZrO<sub>2</sub> powder system, which caused the final relative density to increase from 80 to 90%. Furthermore, the minute amount of TMDAR allowed the samples to maintain their cylindrical shape. The microstructure of these improved-density composites far fewer pores exist between ZrO<sub>2</sub> grains, similar to Fig.6.14.

#### 6.5 CRACKS PROPAGATION?

There are cracks between  $ZrW_2O_8$  and  $ZrO_2$  grains in  $ZrW_2O_8/ZrO_2$  composites as shown in Figs. 6.8, 6.12, and 6.14. An important problem is if those cracks propagate in the thermal cycles a TPS will experience? If the cracks do propagate by the thermal stress, then  $ZrW_2O_8/ZrO_2$  composites cannot be used for the Perspirable Skin. To investigate this issue, we heated and cooled the Sample 3 by the thermal cycles shown in Fig. 6.15 many times. And measured the CTE and Young's modulus of the sample after each thermal cycle.



Figure 6.15 Thermal cycles used to investigate the crack propagation.

From the test results, the CTE of the composite does not change after each thermal cycle. Each measurement is the same to the corresponding curve in Fig. 6.6. There is only very small change of Young's modulus after the first thermal cycle, and then the Young's modulus keeps constant as shown in Fig. 6.16.



Figure 6.16 Young's modulus evolution with the thermal cycles.

The measured CTE and Young's modulus values proof that no obvious physical properties decay by thermal cycles. Therefore, we can conclude that cracks between ZrW<sub>2</sub>O<sub>8</sub> and ZrO<sub>2</sub> may grow, but porous structure of the ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> composites prevent cracks propagate, since once the tips of the cracks reach the porous ZrO<sub>2</sub> region, the energy/stress will release into the grain-bridges.

#### 6.6. CONCLUSIONS

By the in-situ synthesis of WO<sub>3</sub> and ZrO<sub>2</sub> in a mass ratio of 1:0.266, a ZrW<sub>2</sub>O<sub>8</sub> substrate was fabricated. By increasing the ratio of ZrO<sub>2</sub> in the reactants, the product was found to be ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> composites. Both the CTE and Young's modulus of various samples were measured, and those data were compared with several model predictions, including the rule of mixture (ROM), the Turner model, the Kerner model, the Rosen-Hashin bounds model, the Levin model and the Mori-Tanaka method. Among the model predictions, the revised Mori-Tanaka method by Kwon et al. offers a high degree of agreement to the experimental Young's modulus values and the Levin model shows best correlation to the CTE testing values. To the knowledge of the authors, this research is the first time to apply CTE prediction models to composites containing negative CTE materials. Adding a small amount of Al<sub>2</sub>O<sub>3</sub> into the WO<sub>3</sub>+ZrO<sub>2</sub> reaction system was found to

CTE characteristics formulated in this study can be used to fabricate a specific ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> composite in order to meet given requirements for thermal expansion in an industrial process. Also.  $ZrO_{2}/(WO_{3})/(Al_{2}(WO_{4})_{3})/$ (Al<sub>2</sub>O<sub>3</sub>)/ZrW<sub>2</sub>O<sub>8</sub> composites with nearly zero CTE can be fabricated by various methods. Each method vields some uniqueness in the microstructure. final density, mechanical strength, and ability to maintain shape. By comparing the four methods, the optimal method is found to be the in-situ reaction of powder mixture of WO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub> with mass ratio 1:0.03:2.61. The final relative density of the composite made by this optimal method is around 90%, and the room temperature Young's modulus is 11.19GPa and the sintered sample retains the shape of the green sample. The main advantage of this material is the zero CTE, which reduces the thermal stress under thermal gradient loading and transient temperature change in a structure.

Due to the negative thermal expansion, pure  $ZrW_2O_8$  and some  $ZrW_2O_8/ZrO_2$  composites can be used as the core of Perspirable Skin. However, to accommodate for the temperature gradient a TPS will experiment at reentry, the geometry of a  $ZrW_2O_8$  core or a  $ZrW_2O_8/ZrO_2$  composite core can not to be a simple cylindrical shape. It has to be one that has a bigger radius at the top surface and a smaller radius at the bottom part. The resulting geometry consisted of a frustum of a cone at the top half portion and a cylinder at the bottom half

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portion. When such geometry experiences a temperature gradient, the top surface of the core will shrink significantly due to the endured high temperature, resulting in a large gap at the top surface, while the bottom part of the core will still maintain contact with the RCC skin because of the lower bottom temperature. This designed shape for the core made by ZrW<sub>2</sub>O<sub>8</sub> is shown in Fig. 6.17 [131].



Figure 6.17 Designed geometry for the ZrW2O8 core [131].

The complex shape shown in Fig. 6.17 is hard to achieve by Powder Metallurgy method. Considering the gradient temperature a TPS will experiment at reentry, a cylinder-shaped FGM containing ZrW<sub>2</sub>O<sub>8</sub> and ZrO<sub>2</sub> might be better core material, if the fabrication is possible.

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## **CHAPTER 7**

# ZrW<sub>2</sub>O<sub>8</sub>-ZrO<sub>2</sub> CONTINUOUS FGMs: FABRICATION AND THERMAL EXPANSION GRADIENT CONTROL

As discussed in Section 6.6, the geometry of the ZrW<sub>2</sub>O<sub>8</sub> core or ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> composite core for Perspirable Skin needs to be with very complex shape to accommodate for the temperature gradient it will experiment at reentry. However, it is hard to achieve the complex shape sample by Powder Metallurgy method. Therefore, it is necessary to investigate the possibility of fabrication of FGM containing ZrW<sub>2</sub>O<sub>8</sub>. We employed the same method to that in Chap. 5 and hoped to produce multi-layer FGMs containing ZrW<sub>2</sub>O<sub>8</sub>. Surprisingly, the products turned to be ZrW<sub>2</sub>O<sub>8</sub>-ZrO<sub>2</sub> continuous FGMs. In the following sections, the detailed processing steps and the measurement techniques used will be presented together with the mechanisms that contribute to the formation of the continuous structure. In addition, the influence of the soaking duration on the microstructures, the method used to reduce the distortion in the final FGMs will be discussed.

#### 7.1 EXPERIMENTAL PROCEDURES

The four raw powders used in this study were W-Fluka, CERAC-2003, TZ3YS,

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and TMDAR. A WO<sub>3</sub>+ZrO<sub>2</sub> powder mixture and ZrO<sub>2</sub> powder were stacked layer-by-layer in a single-action die and then compacted under the compaction pressure of 80MPa to form two-layer ZrO<sub>2</sub>/ZrO<sub>2</sub>+WO<sub>3</sub> and three-layer ZrO<sub>2</sub>/ZrO<sub>2</sub>+WO<sub>3</sub>/ZrO<sub>2</sub> green bodies. Each ZrO<sub>2</sub> layer was composed of 0.4g of zirconia powder. With out special explanation, the WO<sub>3</sub>+ZrO<sub>2</sub> powder mixture is the one to produce pure  $ZrW_2O_8$  (Powder A). The stoichiometric ratio of WO<sub>3</sub> and  $ZrO_2$  was 2:1 (the mass ratio is mwO\_3: mZrO\_2 =1:0.266) in the WO\_3+ZrO\_2 powder mixture as discussed in Section 6.2. All powder mixtures were mixed using 12mm-diameter zirconia media in a jar mill (U.S. Stoneware 764AVM, U.S.A.) for 48 hours. Four samples were produced, each featuring a unique mass ratio between the lavers as shown in Table 7.1. Samples 1. 2 and 3 featured a symmetric ZrO<sub>2</sub>/ZrO<sub>2</sub>+WO<sub>3</sub>/ZrO<sub>2</sub> stacking structure and the only variation among them was the mass of the mixture layer. Sample 4 was designed to have an asymmetric ZrO<sub>2</sub>/ZrO<sub>2</sub>+WO<sub>3</sub> stacking structure.

Table 7.1 The mass ratio for each green sample and theoretical thickness/volume ratio and  $ZrW_2O_8$  volume fraction in the sintered samples.

#	Mass ratio	Thickness/volume ratio	Theoretical ZrW <sub>2</sub> O <sub>8</sub>
	Zriconia1:Mixture:Zirconia2	Zriconia1:Mixture:Zirconia2	volume fraction
1	1:1.78:1	1:2.13:1	51.5%
2	1:1.08:1	1:1.28:1	38.9%
3	1:0.65:1	1:0.77:1	29%
4	1:0.54:0	1:0.64:0	38.9%

The diameter of the green compacts was 7.94mm after compaction. Because

the processing ZrW<sub>2</sub>O<sub>8</sub> requires the final soaking temperature higher than 1110°C and a quenching step necessary to prevent the decomposition of ZrW<sub>2</sub>O<sub>8</sub>, as discussed in Section 6.2, these green compacts were sintered in a covered platinum crucible under atmospheric conditions in a furnace (Carbolite-HTF1700, UK). The covered crucible provided a nearly sealed environment in order to decrease the sublimation of WO<sub>3</sub> at temperatures higher than 800°C [122]. The ramp/soak profile used in this study is similar to Fig. 6.1, but the soaking durations was varied from 3.5 hours, 6 hours and 14 hours to investigate its influence on the final microstructures. The volumes of the fully-sintered pieces were measured in water using Archimedes' principle for the calculation of the relative density.

Before the CTE testing, the samples were heat treated (3°C/min for both heating and cooling cycles, and soaking for 60 minutes at 300°C) to cure microcracks induced by the quenching process [25]. The CTE measurements of sintered samples were performed using the Thermomechanical Analyzer (TMA: Setaram 95, France) with argon gas providing a protective environment and using heating and cooling rates of 1°C/min. Three specimens produced for each sample were tested for their CTEs. The CTE variation in the measurement is less than 5%. Therefore, we considered that the CTE testing results for each sample are consistent and each reported value in the paper is the average of the corresponding results of three specimens. The sintered samples were polished

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(Abramin, Denmark) and thermally etched in a furnace at 600°C. Then the microstructure of samples was observed using Scanning Electron Microscopy (JEOL 6400V, Japan).

#### 7.2 CONTINUOUS GRADIENT

In the first attempt to fabricate ZrW<sub>2</sub>O<sub>8</sub>-ZrO<sub>2</sub> FGMs, we used exactly the same ramp/soak path in Fig. 6.1. If the sintering of the green stacks produces multiple layers of ZrO<sub>2</sub>/ZrW<sub>2</sub>O<sub>8</sub> or ZrO<sub>2</sub>/ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub>, as expected, the sintered samples should feature a white/green or white/green/white color distribution since pure  $ZrW_2O_8$  is green and pure  $ZrO_2$  is white. However, the sintered samples were found to exhibit a gradual change in yellow color along the axial direction. This color distribution indicates that ZrW<sub>2</sub>O<sub>8</sub> has infiltrated into the layers that were initially pure ZrO<sub>2</sub>. To investigate the materials distribution, the samples were polished down to observe the cross-sectional microstructures at several positions. The sintered Samples 1, 2 and 3 featured a symmetric microstructure about the mid-plane along the axial direction and Sample 4 remained asymmetric. Also, the proportion of ZrW<sub>2</sub>O<sub>8</sub> was found to vary continuously along the axial direction in each of the four samples. Fig. 7.1 shows the micrographs of several cross-sections of Sample 2. The large ZrW<sub>2</sub>O<sub>8</sub> grains are surrounded by the much smaller ZrO<sub>2</sub> grains. Fig. 7.1 clearly demonstrates the continuous decrease in the concentration of  $ZrW_2O_8$  from the mid-plane shown in Fig. 7.1 (f) to the outer surfaces shown in Fig. 7.1 (a). By the cross section observed, the area fraction of ZrW<sub>2</sub>O<sub>8</sub> is estimated to be around 70% at the mid-plane, but only around 20% on both the top and bottom surfaces.



Figure. 7.1 Micrographs of several cross-sections for sintered Sample 2 with height of 6.2mm from the position of a) the outer surface, b) 2.6mm away neutral plane, c) 1.8mm away neutral plane, d) 1.2 mm away neutral plane, e) 0.6mm away neutral plane and f) the neutral plane. The larger grains are ZrW<sub>2</sub>O<sub>8</sub>, which are surrounded by ZrO<sub>2</sub> (Working distance 15mm, acceleration voltage: 15KV).

Samples 1, 2 and 3 have a similar gradient microstructure. However, the area

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fractions of  $ZrW_2O_8$  at the same positions in Samples 1 and 3 differ from those examined in Sample 2. In Sample 4, the proportion of  $ZrW_2O_8$  continually decreases from the surface initially composed of  $WO_3$ +  $ZrO_2$  to the one initially composed of  $ZrO_2$ .

Fig. 7.1 shows the existence of cracks between ZrO<sub>2</sub> and ZrW<sub>2</sub>O<sub>8</sub> grains, a direct consequence of the significant difference in CTE between the two constituent materials. However, it is important to point out that the interfacial debonding, a typical defect found in multi-layered materials [58], does not appear in our FGMs.



Figure. 7.2 The radial thermal expansion-position relationship for sintering FGMs at room temperature. The 0 position is defined as the mid-plane for Sample 1-3 and the initial  $WO_3$ +ZrO<sub>2</sub> surface for Sample 4 (Soaking duration: 6 hours).

The radial surface of each sample was polished to achieve two parallel planes.

The radial thermal expansions of each sample were then measured at several locations for each sample. It can be seen in Fig. 7.2 that the radial thermal expansions feature a continuously changing profile, providing additional evidence of a continuous gradient of the sintered FGMs.

However, the radial expansions presented in Fig. 7.2 are not the physical properties of cross-sectional CTEs since the values include both the thermal expansion effect and the mechanical constraints exerted from the adjacent parts of the sample. After observing the microstructure of the cross-sections at each testing position, the corresponding ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> area ratio at each position was estimated. Using Fig. 6.7, the corresponding cross-sectional CTE of each testing position was obtained. Fig. 7.3 shows both the radial thermal expansion and the corresponding cross-sectional CTEs for Sample 4. Clearly, the discrepancy between two data is insignificant. However, since the adjacent parts have less ZrW<sub>2</sub>O<sub>8</sub> proportion, the radial thermal expansion of the layers near the initial WO<sub>3</sub>+ ZrO<sub>2</sub> mixture surface show a slightly higher value then the cross-sectional CTEs due to the tension from the adjacent parts. The radial thermal expansion of the parts near the initial ZrO<sub>2</sub> surface are lower than the corresponding cross-sectional CTEs due to the compaction from the adjacent parts, which have more ZrW<sub>2</sub>O<sub>8</sub> proportion. Due to the same reason, for Samples 1, 2 and 3, the central portions' radial CTEs are slightly higher than the cross-sectional CTEs and

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the outer surface parts' radial CTEs are a little lower.



Figure 7.3 The radial thermal expansion and the corresponding cross-sectional CTEs for Sample 4 at room temperature. The sample height is 6.21mm. The 0 position is defined as the initial  $WO_3$ +  $ZrO_2$  surface and the soaking duration was 6 hours.

There are several key processing factors that contribute to the fabrication of continuous FGMs. First, the soaking time was extended to 6 hours in order to fully react the constituent powders, WO<sub>3</sub> and ZrO<sub>2</sub>. This ensures that the WO<sub>3</sub> powders have enough time to diffuse into the zirconia layer(s). Another major contributing factor that is essential to understanding this process is the sublimation of WO<sub>3</sub> at temperatures above 800°C [122]. The sublimation causes the WO<sub>3</sub> gas to diffuse into the whole crucible, providing an additional transport mechanism to form the continuously varying microstructures. The resulting

transport of WO<sub>3</sub> coupled with the chemical reaction between WO<sub>3</sub> and ZrO<sub>2</sub> enables the  $ZrW_2O_8$  grains to appear not only in the initial WO<sub>3</sub>+ZrO<sub>2</sub> mixture layer but also in the ZrO<sub>2</sub> layer(s). In addition, the symmetric distribution of WO<sub>3</sub> about the mid-plane in the green body for Samples 1, 2 and 3 contributed to the final symmetric distribution of ZrW<sub>2</sub>O<sub>8</sub> throughout the sintered samples.

#### 7.3 EFFECT OF SOAKING DURATION ON MICROSTRUCTURES

Considering that the diffusion of WO<sub>3</sub> is one of the major contributing factors in the development of the continuous microstructure of the FGMs, the soaking duration must have a significant influence on the final microstructure. Therefore, two additional soaking durations, 3.5 and 14 hours, were evaluated. The samples sintered in these two new ramp/soak paths were also polished to observe the cross-sectional microstructures at several locations. For the samples sintered with the 3.5-hour soak time, the surfaces also show a gradual change in yellow along the axial direction, similar to the sample processed with the 6 hours soak duration. The outermost surfaces of the initial ZrO<sub>2</sub> layers are now ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> composite structure in yellow color. However, most the other part of the initial ZrO<sub>2</sub> layers exhibited white circular regions surrounded by a yellow ring, in contrast to the whole yellow cross-section found in the previous samples. The microstructure observation showed that the outer ring is composed of both ZrO<sub>2</sub> and ZrW<sub>2</sub>O<sub>8</sub> grains while the white center is composed of only zirconia. For Sample 2, the location of these "white circle + yellow ring" parts is between +2.4mm and +2.8mm and also between -2.4mm and -2.8mm along the axial direction using the origin of the coordinate defined at the center of the mid-plane. The whole height of the sample is 6.2mm and the sample occupies the space between -3.1mm and 3.1mm in the axial direction, and the initial WO<sub>3</sub>+ZrO<sub>2</sub> powder mixture occupies the space between -1.21mm and 1.21mm. The white circle features a diameter of 6.91mm while the diameter of Sample 2 is 7.44mm. The pure ZrO<sub>2</sub> region indicates that the central WO<sub>3</sub> did not diffuse into the whole ZrO<sub>2</sub> layer(s) with the 3.5-hour soaking duration. The average single-direction diffusion path of WO<sub>3</sub> in the ZrO<sub>2</sub> layer(s) for all four samples is only 1.2mm for the 3.5-hour soaking duration. Therefore, the average single-direction diffusion speed of WO<sub>3</sub> from the center part (initial mixture part) to the outer part (initial ZrO<sub>2</sub> part) is 0.343mm/hour. However, as pointed out above, the sublimation provides an additional transport mechanism for WO<sub>3</sub>. This additional transport mechanism induces the formation of the yellow-colored ZrW<sub>2</sub>O<sub>8</sub>+ZrO<sub>2</sub> ring and the ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> composite structure for the outermost surfaces.

For the samples sintered with the 14-hour soaking time, the color distribution of the surfaces is even. The microstructure of each cut surface features a  $ZrW_2O_8/ZrO_2$  composite structure and has nearly the same area fraction of  $ZrW_2O_8$ . This microstructural characteristic indicates the sintered samples are the

even-distributed  $ZrW_2O_8/ZrO_2$  composites. The volume fraction of  $ZrW_2O_8$  for each sample is near to the theoretical value calculated by the mass ratio of  $ZrO_2$ and  $WO_3$  in Table 7.2.

Table 7.2 The room temperature axial CTE of each samples under different soaking durations and of the CTE of the  $ZrW_2O_8/ZrO_2$  composites with the theoretical volume fraction of  $ZrW_2O_8$  calculated by the mass ratio of  $ZrO_2$  and  $WO_3$  in Table 7.1.

Soaking time Sample #	2	6	14	Theoretical
1	-2.11	-2.13	-2.1	-2.14
2	0	0	0.04	0
3	1.87	1.86	1.89	1.86
4	0.02	0	0.05	0

The measured radial thermal expansion also changed with the soaking duration. Fig. 7.4 shows the radial thermal expansion for Sample 2. For the 3.5-hour soaking time, the "flat" sections represent no thermal expansion gradient. These "flat" portions occur at the locations similar to the "white circle + yellow ring." Therefore, the "flat" sections consist of the nearly pure  $ZrO_2$  component. The decrease in the thermal expansion, the radial coordinates between +2.8mm and +3.2mm and also between -3.2mm and -2.8mm, occurs due to the  $ZrW_2O_8$  from the reaction of  $ZrO_2$  and sublimated WO<sub>3</sub>. The radial thermal expansion of the samples with the 14-hour soaking time is nearly constant, which provides further evidence that the samples are evenly distributed  $ZrW_2O_8/ZrO_2$ 

composites. Another important aspect to point out is that the radial thermal expansion values of the samples with the 14-hour soaking time are only slightly larger than the testing results for corresponding  $ZrW_2O_8/ZrO_2$  composites with theoretical  $ZrW_2O_8$  volume fraction calculated by the mass ratio of  $ZrO_2$  and  $WO_3$  (Table 7.1). This is due to the WO<sub>3</sub> that escaped the system as a gas produced by sublimation, resulting in a slight decrease of  $ZrW_2O_8$  fraction in the samples.



Figure 7.4 The CTE-position relationship of Sample 2 for various soaking durations.

#### 7.4 POWDER COMPONENT EFFECT

Varying the component of each layer can also change the microstructure and CTE distribution. For example, we changed the pure  $ZrO_2$  layer to be powder mixture of  $ZrO_2$  and  $WO_3$  with  $m_{WO3}$ :  $m_{ZrO2}$  =1:0.38 (Powder *B*), which produces a composite of  $ZrW_2O_8$  and  $ZrO_2$  with 0 CTE as shown in Section 6.3. And 1.3g

Powder *A* and 1.7g Powder *B* were measured and stacked together. With 6 hours soak duration, the produced continuous  $ZrW_2O_8+ZrO_2$  FGM (Sample 5) was with height of 7.7mm and the he axial CTE of the sample is shown in Fig. 7.5.



Figure 7.5. The CTE-position relationship of Sample 5.

#### 7.5 DISTROTION CONTROL

Initially, only CERAC-2003 powder was used as the zirconia component of the  $WO_3+ZrO_2$  powder mixture and  $ZrO_2$  layer(s). For the 3.5-hour and 6-hour soaking cases, after sintering, the original cylindrical shape of the green bodies changed to a shape similar to a barrel for Samples 1, 2 and 3 and the frustum of a cone for Sample 4. This distortion is a result of the final dimensional mismatch between the two materials. For the cylindrical green body with 7.94mm diameter sintered in the ramp/soak path from Fig. 6.1, the  $ZrW_2O_8$  produced by the in-situ reaction of WO<sub>3</sub> and  $ZrO_2$  mixture (with the Stoichiometric ratio of 2:1) has a final

diameter of 7.51mm while the pure CERAC-2003 yields only a 7.28mm diameter. Due to the variation in the proportion of  $ZrW_2O_8$  along the axial direction, the diameter of the sample changes from the mid-plane (initial WO<sub>3</sub>+ZrO<sub>2</sub> surface) to the outer surfaces (initial ZrO<sub>2</sub> surface).

In Section 4.2.3, we have demonstrated that the final diameters of the sintered samples vary as the content of powder mixtures changes. Based on this finding, CERAC-2003 powders were mixed with TZ3YS in a variety of proportions to form zirconia powder mixtures. And the corresponding final diameters of sintered zirconia samples were compared to the diameter of pure ZrW<sub>2</sub>O<sub>8</sub>, 7.28mm. The relationship is shown in Fig. 7.6.



Figure. 7.6 The relationship between the diameters of zirconia samples sintered by the ramp/soak path of Fig.6.1 and the percentage of Cerac-2003 in zirconia powder mixtures (the diameter of green bodies was 7.94mm).

Fig. 7.6 shows that two mixtures of zirconia have a similar final diameter to the

pure  $ZrW_2O_8$  when the proportion of CERAC-2003 in zirconia system is around 8% or 91%. Through several attempts, the exact proportion of CERAC-2003 in the CERAC-2003+TZ3YS powder mixture has been refined to 11% in order to prevent the distortion in the sintered FGMs.

#### 7.6 DENSITY IMPROVEMENT

The final relative density of all four FGM samples was found to be only near 80%. As discussed in Section 6.3.1, the samples exhibit this low density mainly because ZrO<sub>2</sub> is far from fully-sintered when the final soaking temperature is only 1190°C. This is evidenced by the sample micrograph (Fig. 7.1) from which one can observe that numerous pores remain among the ZrO<sub>2</sub> particles. In addition, the cracks between the ZrO<sub>2</sub> and ZrW<sub>2</sub>O<sub>8</sub> grains due to the significant difference in CTEs between two component materials contribute to the low final density. Similar to the density-improvement method in Section 6.4.5, 0.07% mass ratio of the alumina powder TMDAR was added to each powder mixture. The melting point of Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> is 1135<sup>o</sup>C [130] and therefore a liquid phase exists at the soak temperature of 1190°C. The presence of this liquid will promote the densification kinetics, resulting in an increase in the final relative density from 80 to 90%. Furthermore, the final shape of the samples was not affected, since the added TMDAR only comprises 0.07% of the total mass. The microstructure of the FGMs with 0.07% of Al<sub>2</sub>O<sub>3</sub> remains very similar to that of Fig. 7.1. However, far fewer pores among  $ZrO_2$  grains are evident, which can be attributed to the presence of the liquid  $Al_2(WO_4)_3$  phase during sintering.

#### 7.7 AXIAL CTES

The axial CTE – temperature relation for all four samples (with 0.07% mass ratio TMDAR powder and 6 hours soaking duration) was measured and the data are presented in Fig. 7.7 together with the CTE curve of pure ZrW<sub>2</sub>O<sub>8</sub>.



Figure. 7.7 The axial CTE vs. temperature curve for pure  $ZrW_2O_8$  and samples 1-4 (with 0.07 wt% TMDAR powder by mass and 6 hours soaking duration).

As can be seen, the macroscopic axial CTE is negative for Sample 1, positive for Sample 3 and nearly zero for Samples 2 and 4. The difference in the axial CTEs is due to the thickness variations in each layer for various samples. The CTE curves for all FGMs as well as the pure  $ZrW_2O_8$  feature a sharp change near 160°C due to the  $\alpha$ - to  $\beta$ -  $ZrW_2O_8$  phase transition [20]. However, similar to the  $ZrW_2O_8/ZrO_2$  composites, the peak caused by phase transition occurs at a lower temperature for the FGMs comparing to pure  $ZrW_2O_8$ . This "peak shift" is possibly a result of phase transition from  $\alpha$ - $ZrW_2O_8$  (low pressure phase) to  $\gamma$ - $ZrW_2O_8$ (high pressure phase) [125] due to the thermal stresses caused by the CTE mismatch between  $ZrO_2$  and  $ZrW_2O_8$ .

The axial CTEs of the samples processed under various soak durations are all close to the theoretical CTEs as shown in Table 7.2, which indicates that the average distribution ratio of ZrW<sub>2</sub>O<sub>8</sub> along the axial direction does not change for each soak duration. Based on this observation, we can conclude that even for 3.5-hour soak duration, all WO<sub>3</sub> have already reacted with ZrO<sub>2</sub> mainly in the WO<sub>3</sub>+ZrO<sub>2</sub> layer, thus generating a sharp boundary between ZrW<sub>2</sub>O<sub>8</sub>+ZrO<sub>2</sub> and pure ZrO<sub>2</sub>. For Sample 2, the boundaries were at the ±2.4mm position as discussed before. As the soak duration increases, due to the different concentration of ZrO<sub>2</sub> across the boundary, the ZrW<sub>2</sub>O<sub>8</sub> in the ZrW<sub>2</sub>O<sub>8</sub>+ZrO<sub>2</sub> layer partially decomposes and produces WO<sub>3</sub>. The new WO<sub>3</sub> diffuses toward the pure ZrO<sub>2</sub> layer and reacts with the ZrO<sub>2</sub> to produce new ZrW<sub>2</sub>O<sub>8</sub>. With this decomposition-reaction mechanism, ZrW<sub>2</sub>O<sub>8</sub> advances toward the outer surfaces of ZrO<sub>2</sub> layer(s). Therefore, the processing technique in the fabrication of fully continuous FGMs requires appropriately adjusting soaking duration. However, the gradient of ZrO<sub>2</sub> in the FGMs will drive the decomposition-reaction mechanisms to continue if the soak duration continually increases until the sample becomes the evenly distributed  $ZrW_2O_8/ZrO_2$  composite, as evident by the 14-hour soak duration case. However, due to the loss of WO<sub>3</sub> by sublimation, the CTE values of the samples after the 14-hour soak duration are slightly larger than the theoretical values.

The continuous radial thermal expansion variation of the FGMs can be utilized to reduce the thermal stress induced from a thermal gradient loading that may exist in a structure. Considering the processing method described in this paper, several other ceramic mixture systems such as ZnO+Nb<sub>2</sub>O<sub>5</sub> and Sb<sub>2</sub>O<sub>3</sub>+Al<sub>2</sub>O<sub>3</sub> may also have the potential to produce continuous FGMs.

#### 7.8 CONCLUSIONS

Some research [29-31] on  $ZrW_2O_8/ZrO_2$  composites had been published prior to the work described in this paper. This particular study distinguishes itself from the previous works by reporting on the processing of continuous FGMs containing  $ZrW_2O_8$  and  $ZrO_2$ . The green sample used in this study is not a well-mixed  $WO_3+ZrO_2$  powder compact, but rather multiple layers consisting of  $ZrO_2$  and a  $WO_3+ZrO_2$  powder mixture. Due to the diffusion and sublimation of WO<sub>3</sub> as well as the reaction between WO<sub>3</sub> and  $ZrO_2$  during sintering, continuous FGMs made of  $ZrW_2O_8$  and  $ZrO_2$  were fabricated instead of the expected multi-layer FGMs for several different soaking durations. The continuous structure of the FGM is evidenced by the microstructure observation and the measurement of the radial CTEs. Soaking time influences the final microstructures, mainly the result of the balance between the decomposition of ZrW<sub>2</sub>O<sub>8</sub>, the reaction of WO<sub>3</sub> and ZrO<sub>2</sub> as well as the diffusion of WO<sub>3</sub>. With a short soaking duration, the central WO<sub>3</sub> cannot diffuse throughout the whole structure, leaving some parts as a near pure ZrO<sub>2</sub> structure and others are ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> composite structure. Appropriately adjusting soaking duration will result the final sintered samples being fully continuous FGMs. When the soaking time is long enough, the sintered sample converts to an evenly distributed ZrW2O8/ZrO2 composite. In addition, a small additional amount of alumina powders results in an FGM with a significantly larger final relative density while avoiding shape transformation in the FGM. The thickness of each laver in the processing of FGMs can be varied in order to achieve a variety of gradient in physical properties.







Figure 7.9 The FEA results for the best FGM core design a) gap distance at working condition b) Von Mises stress at working condition c) first stress at room temperature.

The continuous variation in radial thermal expansion of the FGMs can be utilized to reduce the thermal stress induced from a thermal gradient loading. Therefore, continuous  $ZrW_2O_8$ - $ZrO_2$  FGMs are ideal candidates for the core

material of Perspirable Skin. We applied Sample 5 into the design of the Perspirable Skin. The shape of the core is a simple cylinder with semi-circular channels [131], which can be manufactured by P/M directly.

The gap distance and stress analysis for Perspirable Skin with cores shown in Fig. 7.8 were analyzed by finite element software ANSYS. The results are shown in Fig. 7.9 [131]. A larger gap distance at the top surface, 97.7 $\mu$ m, produced, while the bottom part of the core remains in contact with the RCC skin at working condition. The maximum stress at contact is 4.25MPa at room temperature.

## **CHAPTER 8**

### SUMMARY

#### **8.1 CONTRIBUTIONS**

The main contributions of this study are listed below,

- 1. The powder mixing process changes the compaction capability of the powder mixtures. The shape of the initial relative density versus proportion of coarse powder curve depends on the ratio between the average particle sizes as well as the difference in the initial density of two powders. If the average particle size ratio is less than 3.6, or the average particle size ratio is larger than 3.6 but the initial relative density different is higher than 10%, the curve is linear. If the average particle size ratio is larger than 3.6 and the initial relative density difference is smaller than 10%, the curve is parabolic.
- 2. The triangle enclosed by the line intersecting the relative density of the fine powder and the maximum relative density of the coarse powder, the line intersecting the relative density of the coarse powder and the maximum relative density of the fine powder as well as the line connected the relative density of the fine and coarse powder forms the boundary of the initial

relative density-proportion of coarse powder curve.

- After compaction, green samples feature a barrel lateral shape, which is a result of release of larger residual radial stress at about the middle of the compact after ejection than the top/bottom.
- 4. The density distribution in a green compact is not even. The high-density regions exist at near the bottom central region and on the central axis. And the low-density regions are at the bottom edges and near the top center.
- 5. Mixing powders is an effective approach to manipulate the sinteribility and the final microstructures of raw powders. Each powder mixture has a unique densification rate-relative density curve. The ascent parts of the curves for alumina can be approximated by straight line(s), while the shapes of densification rate-relative density curves of zirconia powders are semi-ellipse.
- 6. Using the part-isothermal heating method, phenomenological constitutive sintering equations were derived for our alumina and zirconia powder mixtures by Hsueh's model [107]. The variable *n* in Hsueh's model is a material parameter and D<sub>∞</sub>(T) changes with respect to the proportion of TMDAR or CERAC-2003 present in the alumina or zirconia powder system. The shortcoming of Hsueh's model is it does not reflect any phase changes that may occur.

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7. By comparing the densification rate-relative density curves as well as the final diameter-powder ratio curves of an alumina powder system containing TMDAR and CR-15 and a zirconia powder system containing TZ3YS and CERAC-2003, we found that 94% CR-15 and 6% TMDAR alumina powder has very similar densification rate curve and final diameter to the 40% CERAC-2003+60% TZ3YS zirconia powder. By mixing these two powders and slightly adjusting the content of TMDAR, we produced a 50 vol% alumina + 50 vol% zirconia powder mixture with the similar densification rate-relative density curve and diameter as the other two pure powders. The content of the 50 alumina /50 zirconia mixture is 46% CR-15 and 4% TMDAR/ 20% CERAC-2003 and 30% TZ3YS by volume. The shrinkage ratio curves of these three powder mixtures were found to be almost identical. The similarity in the shrinkage ratio for those chosen powder mixtures ensures that no significant dimensional mismatch could occur at any time during sintering, thus reducing the possibility for cracks and camber in the sintered sample. In addition, the effect of the compaction load, interfacial profiles and temperature ramp/soak cycles were studied. Through a series of experiments, the optimal processing parameters were then obtained, which enabled us to produce flat 3-layered Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> FGMs without cracks. Decreasing the compaction load, increasing the ramp rate, selecting an appropriate mixture combination and modifying the

interfacial profiles have been found to produce FGM samples free of defects. The shrinkage curves were found to be almost identical. The almost identical densification rate curves of the chosen powder mixtures under the optimized sintering conditions feature the same hyperbolic tangent term in the corresponding three phenomenological constitutive models.

8. By the in-situ synthesis of WO<sub>3</sub> and  $ZrO_2$  in a mass ratio of 1:0.266, a ZrW<sub>2</sub>O<sub>8</sub> substrate was fabricated. By increasing the ratio of ZrO<sub>2</sub> in the reactants, the product was found to be ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> composites. Both the CTE and Young's modulus of various samples were measured, and those data were compared with several model predictions, including the rule of mixture (ROM), the Turner model, the Kerner model, the Rosen-Hashin bounds model, the Levin model and the Mori-Tanaka method. Among the model predictions, the revised Mori-Tanaka method by Kwon et al. offers a high degree of agreement to the experimental Young's modulus values and the Levin model shows best correlation to the CTE testing values. To the knowledge of the authors, this research is the first time to apply CTE prediction models to composites containing negative CTE materials. Adding a small amount of Al<sub>2</sub>O<sub>3</sub> into the WO<sub>3</sub>+ZrO<sub>2</sub> reaction system was found to effectively increase the final density of the sintered composites.

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The controllable CTE characteristics formulated in this study can be used to fabricate a specific ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> composite in order to meet given requirements for thermal expansion in an industrial process.

- 9. ZrO<sub>2</sub>/(WO<sub>3</sub>)/(Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub>)/(Al<sub>2</sub>O<sub>3</sub>)/ZrW<sub>2</sub>O<sub>8</sub> composites with nearly zero CTE can be fabricated by various methods. Each method yields some uniqueness in the microstructure, final density, mechanical strength, and ability to maintain shape. By comparing the four methods, the optimal method is found to be the in-situ reaction of powder mixture of WO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub> with mass ratio 1:0.03:2.61. The final relative density of the composite made by this optimal method is around 90%, and the room temperature Young's modulus is 11.19GPa and the sintered sample retains the shape of the green sample. The main advantage of this material is the zero CTE, which reduces the thermal stress under thermal gradient loading and transient temperature change in a structure.
- 10. Continuous FGMs containing ZrW<sub>2</sub>O<sub>8</sub> and ZrO<sub>2</sub> were fabricated. The green sample used is made of multiple layers consisting of ZrO<sub>2</sub> and a WO<sub>3</sub>+ ZrO<sub>2</sub> powder mixture. Due to the diffusion and sublimation of WO<sub>3</sub> as well as the reaction between WO<sub>3</sub> and ZrO<sub>2</sub> during sintering, continuous FGMs made of ZrO<sub>2</sub> and ZrW<sub>2</sub>O<sub>8</sub> were fabricated instead of the expected multi-layer FGMs for several different soaking durations. The

continuous structure of the FGM is evidenced by the microstructure observation and the measurement of the radial CTEs. Soaking time influences the final microstructures, mainly the result of the balance between the decomposition of  $ZrW_2O_8$ , the reaction of  $WO_3$  and  $ZrO_2$  as well as the diffusion of WO<sub>3</sub>. With a short soaking duration, the central WO3 cannot diffuse throughout the whole structure, leaving some parts as a near pure ZrO<sub>2</sub> structure and others are ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> composite structure. Appropriately adjusting soaking duration will result the final sintered samples being fully continuous FGMs. When the soaking time is long enough, the sintered sample converts to an evenly distributed ZrW<sub>2</sub>O<sub>8</sub>/ZrO<sub>2</sub> composite. The thickness of each layer in the processing of FGMs can be varied in order to achieve a variety of gradient in physical properties. The continuous variation in radial thermal expansion of the FGMs can be utilized to reduce the thermal stress induced from a thermal gradient loading.

11. Continuous ZrW<sub>2</sub>O<sub>8</sub>-ZrO<sub>2</sub> FGMs are ideal candidates for the core material of Perspirable Skin. The shape of a ZrW<sub>2</sub>O<sub>8</sub>-ZrO<sub>2</sub> FGM core is a simple cylinder with semi-circular channels, which can be manufactured by P/M directly.

#### **8.2 SUGGESTIONS FOR NEXT STEP RESEARCH**

As mentioned in Section 1.1, from the design idea to the application of Perspirable Skin on the space vehicles, a series of researches are needed: 1) core material selection, 2) materials fabrication, 3) materials properties test, which will be used as the input parameter of Finite Element Analysis (FEA), 4) structure design by FEA, including gap and stress analysis, 5) core pieces and RCC panel assembly, and 6) simulated temperature environment test.

After three and half years, now Steps 1-3 are achieved as discussed in this dissertation. The shape of the core made by  $ZrW_2O_8$ - $ZrO_2$  FGMs was also determined. However, the core dimensions depend on the calculation of thermodynamics and heat transfer. This should be an important research part in the future.

After the determination of core dimensions, the assembly and true-environment test need to be performed to verify the suitability of Perspirable Skin as next-generation TPS.

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