Microstructural and Physical Properties of Yttria Stabilized Zirconia (YSZ) Prepared by Ceramic Injection Moulding (CIM)

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Abstract. Ceramic injection moulding (CIM) is a near net shape process to produce smaller and intricate parts at a competitive cost. However, fine particle size (nano scale) used for such injection moulding process generally leads to agglomeration, higher binder content and critical dimensional shrinkage which results in defects on the sintered components. This study extensively investigates the characteristics of Yttria Stabilized Zirconia (YSZ) for CIM process. YSZ parts were moulded by CIM process that utilized a multi-component binder system using palm stearin (PS) and polyethylene (PE) in 60:40 (vol %) ratio. The powders were characterized using particle size analyzer, pycnometer density and scanning electron microscopic (SEM). The binders were characterized by the pycnometer density, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Powders loading were choosen by the critical powder volume percentage (CPVP) through oil absorption test. YSZ powder was mixed with the binders at different powder loadings ranging from 58 to 60 vol% based on CPVP. The parts were injected moulded, thermal debound, pre-sintered and sintered. The microstructure, green strength and hardness of the sintered part at different powder loadings were investigated. A large porous region was clearly observed at 58 vol% compared to 60 vol%. All samples were sintered at 1350°C, with the highest green strength and hardness were 13MPa and 357.42 HV respectively was given by the sintered part at powder loading of 60 vol.

1. Introduction
Powder Injection Moulding (PIM) has the capability to manufacture products using various types of material such as metals, ceramics, composite and intermetallic compound [1][2]. Ceramic injection molding (CIM) is a process of powder metallurgy forming by using ceramic powders involving four main processes which are mixing, injecting, debinding and sintering [3][4]. These process has been known for more than a century and has managed to get attention as an alternative way to produce various parts in high quality [4]. This process has an advantages in terms of the material usage, shape complexity with a large scale of production, good final products, low cost and much more as compared to other metal forming methods such as forging, casting, and others [5][6]. Preparation of feedstock in powder
injection moulding (PIM) is a very crucial steps where the inadequacies of quality of the feedstock cannot be corrected by subsequence processing adjustment [7]. Characterization of the powders and binders is the first step before proceeding to further processes. Moreover, characterization of the binder provides the parameters used in the mixing, injecting and debinding processes. The homogenous feedstocks were produced by mixing ceramic powder with the binders at the mixing stages monitored by the consistency of torque values. Binders supplied viscosity to the powder, thereby facilitating the process of filling feedstock into the molds during the injection molding stage. Concentration Powder Volume Percentage (CPVP) test is used to obtain the optimum powder loading ratio to ensure the success of PIM [8]. According to Iriany (2002), the common volume powder to binder ratio percentage ranges from 45% to 75% [8]. High powder loading had a low tendency to form high amount of porous due to its low binder content ratio. The porousness occurs when the powder particles do not diffuse completely after the completion of the binder removing process. Furthermore, higher optimum powder loading percentage can minimize shrinkage, prevent cracking, and increase the densities as well as mechanical properties of materials [9]. However, binder that were failed to be removed will contribute to high carbon content in sintered samples which increase the hardness value but reduce their ductility [10].

2. Methods and Materials
The YSZ powders used has 13µm of particle sizes and 5.60 g/cm³ of pycnometer density. YSZ powder was mixed with binders of palm stearin (PS) and polyethylene (PE) at 60:40 vol%. Powder loading of 57, 58, 59, and 60 vol% was chosen in this work based on the concentration powder volume percentage (CPVP). The mixing process was carried out by a Brabender mixer (GmbH & Co.KG) at temperature, time and speed of rotation of 150 °C, 90 minutes and 30 rpm, respectively, to produce feedstock. The samples were injected at 170 °C in rectangular bar shape having the dimension of 55mm (length) x 5mm (width) x 5mm (thickness). This MPIF 15 standard size was applied accordingly to undergo flexural strength of green part. Thermal pyrolysis (debinding) was performed where the parts were embedded in alumina powder that act as a wicking agent, and heated in a furnace at 550 °C. The heating rate was 0.4 °C/min and the samples were soaked for 2 hours in order to remove the binders. The pre-sintering was carried out simultaneously after the debinding process at 1100 °C for 2 hours with a moderate heating rate to initiate the solidification process. The samples were subsequently sintered in the furnace for up to 1450 °C for 3 hours. The microstructures of as-sintered samples for all feedstocks were observed using tabletop microscope (SEM). The relative intensity of the phases was recognized by X-Ray Diffraction (XRD). The density and shrinkage were determined by pycnometer and vernier caliper respectively.

3. Results and Discussions
3.1. Microstructural of the sintered parts
The characterization of the sintered parts is important to analyze the morphologies and crystal structure of the final samples. The goal of microstructure analysis was to ascertain that the particle was diffused with each other to form an as-sintered sample without the presence of other interstitial elements. In order to confirm the phase identified, further investigation was carried out using the back-scattered SEM, equipped with an Energy-Dispersive X-ray Spectrometer (EDX) as shown in previous study [3]. Figure 1 shows an example of the back-scattered SEM image for the surface, prepared at 57, 58, 59 and 60 vol% powder loadings. All samples, regardless of their powder loadings, showed an almost identical microstructure which was identified to be tetragonal zirconia. This was confirmed based on the dominant peaks in XRD results. All sintered samples were not fully diffused in the morphologies studies; the grains overlapped with one another and some of the particles had only started to undergo necking as reported in previous studies using CIM methods with 3mol% YSZ powder [11]. Some of the grains grew where their grain boundaries were neatly attached onto each other with the size up to 30µm. The grain boundaries were able to withstand any external force that was applied on the particular part. By increasing the grain growth, the grain boundaries formed between each grain also increased. Thereby, strengthening the bond between grains builds up resistance to external force [11]. All the samples also showed different amounts of porosity. Lower powder loading had a high tendency to form the highest
amount of porous due to lower powder content and higher binder content [12]. The porosity is known as the fraction of the component volume that is unoccupied by solid. The porosity occurs when the powder particles do not diffuse completely after the binder removing process completes. Thus, porosity is possible to be eliminated completely by controlling discontinuous grain growth and by sintering in hydrogen, oxygen or vacuum [13].

Figure 1. Back-scattered SEM image for the surface, prepared at (a) 57, (b) 58, (c) 59 and (d) 60 vol% powder loadings

3.2. X-ray Diffraction
The XRD patterns in Figure 2 shows that the relative peak intensity of tetragonal and monoclinic phases of sintered samples contained different powder loading (57, 58, 59 and 60 vol%). It was found that the as-sintered samples consisted of monoclinic and tetragonal phases and no apparent differences were identified among the samples from different powder content. The sample was first pre-sintered at 1100 °C for a few hours and the process proceeded with sintering at 1450 °C before cooled down to room temperature. Some of the tetragonal and monoclinic phases were retained during the thermal treatment. The monoclinic phase was spotted on yttrium oxide. The phase was supposed to became tetragonal after being heated in the range of 1170 °C to 2370 °C. However, the monoclinic phase appeared when force was applied on the surface of the sample, such as grinding and polishing before XRD analysis was done [13]. Some small amounts of cubic phases also existed, which seemed to be overlapped by a small peak. According to Chevelier et al., (2004) the presence of cubic zirconia is not desirable in 3Y-TZP for biomedical applications and is caused by uneven distribution of the yttrium stabilizer ions [14]. The cubic grains were enriched in yttrium while surrounding tetragonal depleted and were therefore less stable. A new peak is spotted at 43° and identified as 3Y-TZP [1 0 2] and zirconium yttrium oxide [1 0 2] in their tetragonal phase by referring to the PDF card number 010704434 and 000600502 respectively. The XRD result showed in the present work was slightly different from other previous researchers due to the different sintering profile used, particle size distribution and process of preparing the as-mixed powder [5][15].
Figure 2. Relative peak intensity of tetragonal and monoclinic phases of sintered samples containing different powder loading

3.3 Shrinkage Analysis.
Sintering inherently involved substantial shrinkage, which means the pores were eliminated and all final dimensions were smaller than the starting dimension. Although such shrinkage was a primary goal of sintering, this dimensional change was a source of distortion. Shrinkage is inversely proportional on the green density. Hence, maintaining a high and uniform powder packing density in the feedstock caused the lowering of the shrinkage due to more particle contacts involved in the bonding process. Theoretically, during the sintering process, the particles of ceramic powder bonded together to form a strong bonding. As the ceramic powder particles bonded, the whole structure experienced shrinkage because the reinforcement particles have filled in the crevices after the removal of the binders. The effect of different powder loadings on the volume shrinkage on the as-sintered parts is presented in Figure 3.

It can be seen that specimens prepared with a powder loading of 57 vol. % (refer to Figure 3) has the highest volume shrinkage compared to 58, 59 and 60 vol. %. Shrinkage is inversely dependent on the green density. The lower the value of green density, the higher the result of the shrinkage gained. Lower powder composition came with higher binder composition which contributes to lower green density. Thus, the samples experience higher shrinkage due to higher removal of the binders. This result is similar agreement to the shrinkage of nano YSZ fabrication via MIM studied by Yu et al., in 2007 [10], where the authors also found that the shrinkage is inversely proportional to green density. Typical weight loss from powder loading corresponded to the amount of the binder. The sintered part in the present work has undergone volume shrinkage ranging from 6% to 7% which was lower than the finding reported by Mohd Foudzi et al., (2013) that ranged from 17% to 21%. In addition, Md Ani et al., (2014) gained the range 6% to 15% whereas 19% to 26% was reported by Yu et al., (2007) [10] [16]. This was due to smaller powder size (nano sized) used for micro size samples which needed more binder composition to cover the powder surfaces.
3.4. Density Analysis

As the dimension of all sintered parts experienced shrinkage, the density of the sintered parts also decreased from its theoretical density. The highest density of the sintered part recorded was 4.31 g/cm³ and the lowest density was 4.04 g/cm³, obtained from 60 vol. % and 57 vol. % specimen respectively. The results of average density from five sintered of 57, 58, 59 and 60 vol. % samples increased linearly to powder loading with 4.04 ± 0.13, 3.90 ± 0.08, 4.21 ± 0.11 and 4.31 ± 0.10 g/cm³ respectively. In comparison to its theoretical density, the decrease in density in percentage recorded for 57, 58, 59 and 60 vol% samples were 31.49%, 25.25%, 24.78% and 22.99% respectively. The green density data from pycnometer test for 57, 58, 59 and 60 vol% samples were 3.90 ± 0.08, 3.94 ± 0.08, 3.97 ± 0.05 and 4.25 ± 0.03 g/cm³ respectively. All data is presented in Figure 4 and Table 1. The difference values of sintered density approaching theoretical density is due to the existence of porosity. The porosity of the specimens is influenced by the factor of binder content in the feedstock. Setasuwon et al., in 2008 who studied the effects of wax/oil binder components for injection moulding found that high green density specimen produces less porosity than low green density specimen and this is agreed by several researchers [11] [17] [18] [19]. This agrees with the findings in this study where 57 vol% specimens have less porosity percentage than 58 vol%, 59 vol% and 60 vol%. This is due to the fact that higher powder loading has greater grain growth number where it can lead to more annihilation of the pores. Pores annihilation occurred due to the effects of densification during sintering when pores reduced in size or even diminished [19]. However, it can also be observed that some of the pores on the samples surface also experienced annihilation.

Table 1. Densities values at different powder loadings.

| Powder loading (vol%) | Green density (g/cm³) | Sintered density (g/cm³) | Comparison to theoretical density (%) |
|-----------------------|-----------------------|--------------------------|---------------------------------------|
| 57                    | 3.90 ± 0.08           | 4.04 ± 0.13              | 68.51                                 |
| 58                    | 3.94 ± 0.08           | 4.18 ± 0.15              | 74.75                                 |
| 59                    | 3.97 ± 0.05           | 4.21 ± 0.11              | 75.22                                 |
| 60                    | 4.25 ± 0.03           | 4.31 ± 0.10              | 77.01                                 |
Figure 4. The green and sintered densities at different powder loadings

4. Conclusions
The samples were successfully injected moulded on all powder loadings from 57 vol% to 60 vol%. Morphological studies showed that all samples incompletely diffused, and some of the particles retained the near spherical grain shape. Abundant void regions were clearly observed at the surface sintered samples at 57 vol% supported by the lowest sintered density value compared to other powder loadings. The XRD pattern showed the relative peaks of tetragonal and monoclinic phases with no apparent differences identified among the samples of difference powder contents. The samples experienced volume shrinkage ranging from 6 to 7% and density ranging from 4.0 to 4.3 g/cm³. The lowest volume shrinkage and highest density were 7.16% and 4.31± 0.10 g/cm³ respectively produced by the sintered samples at the powder loading of 60 vol%.

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