Effect Grain Size on Physical Properties of (Y$_2$O$_3$-ZrO$_2$-MgO-Al$_2$O$_3$) System

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Abstract
The addition of cubic crystalline oxides such as Y$_2$O$_3$ and MgO leads to stability of zirconia phases at high temperature. Y$_2$O$_3$ powder was added to stabilized zirconia and preparing a mixture of MgAl$_2$O$_4$ Spinel by mixing 1 mol of nano-MgO with 1 mol of nano-Al$_2$O$_3$ powders. The spinel was added to the Y$_2$O$_3$-ZrO$_2$ by various weight percentage (5, 10, 15, 20 and 25 wt%), and after the specimens was prepared by axial pressing and sintered at 1550 °C for 4 hours as soaking time.

The grain size was tested by using Atomic Force Microscopy (AFM) and calculated for surface of specimens and it was found to be decreasing (> 0.6 µm) to (~ 108 nm). Linear shrinkage is an important physical characteristic, the addition of clay has led to a decrease in shrinkages from 16.7 % to 9.4 %, and the porosity was low and generally decreased from 4 % to 2.5 % with a clear increase in bulk density from 4.7 g/cm$^3$ to 5.9 g/cm$^3$.

Mechanical tests showed that the diametric strength was increased from 79.3 to 97.1 MPa due to the addition of spinel. The results were explain on the basis of grain size change. After drawing the correlation between strength and (grain size)$^{1/2}$, it was found to correspond to Hall-Patch equation relationship.

Keywords: Zirconia; Magnesia; Alumina; Spinel; Linear shrinkage; bulk density; Porosity; AFM; Diametric Strength; Grain size; Nano ceramics.

Introduction
The addition of oxides soluble in zirconia (CaO, MgO and Y$_2$O$_3$) lowers the tetragonal to monoclinic (t-m) and cubic to tetragonal (c-t) transformation temperatures. These additions are therefore said to stabilize the high temperature phases.

Retention of the tetragonal phase at room temperature is also feasible, providing the t-m transformation is inhibited. This can be achieved by a combination of fine powders, matrix constraint and stabilizing additions. [1] The combination of properties in spinel ceramics enables their use at high temperature and engineering applications. One of the drawbacks of spinel ceramic is its insufficient mechanical properties which limit its practical and potential uses in other fields. Intense research has been intended to improve the mechanical strength of MgO-Al$_2$O$_3$ spinel through combination with other ceramic materials, zirconia and magnesia, that are expected to improve its thermomechanical properties. The optimum characteristics of zirconia–magnesia–spinel composite ceramics should be achieved through controlling the contents of their constituents. [2]

Strength of a sintered body is strongly dependent on particles and grain size distribution [3]. During sintering, the rapid densification regions containing agglomerates can induce stresses within the surrounding compact facilitating the formation of the voids and cracks.

Typically, the strength of ceramics shows an inverse correlation to the average grain size G. The strength can be expressed as:

$$\sigma = (\sigma_0 + k_1 G^{-0.5}) e^{-nP} \ldots \ldots (1)$$

where $\sigma$ is true strength, $\sigma_0$ is strength with no micropores, $k_1$ and $n$ are constants, G is grain size, and P is porosity [4].

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A schematic of the dependence is shown in Fig. 1, where the fracture strength is plotted versus $G^{1/2}$. The simplest explanation for this behavior is that the intrinsic flaw size scales with the grain size, a situation not unlike the one shown in Fig. 2. The flaws form at the grain boundaries, which are weak areas to begin with, and propagate up to about one grain diameter.

**Materials and specimens preparation**

Yttria-Partially Stabilized Zirconia (Y-PSZ) was prepared by adding 8 wt% of yttria to zirconia and different weight percentage of MgO-Al$_2$O$_3$ (5, 10, 15, 20 and 25 wt%) was added to the Y-PSZ mixture. After mixed the composition with 10 wt% of PVA as a binder, the specimens was prepared by pressing for 10 mm as diameter with different thickness by applied hydraulic load for 3 ton at 30 s. All materials were supplied by the companies listed in the table 1.

![Figure 1: Schematic relationship between grain size and strength for a number of ceramics.[5]](image1)

![Figure 2: Schematic of cleavage and grain boundary cracks.[5]](image2)

**Table 1: Specifications of materials.**

| Material     | Source                | Purity % | Particle Size |
|--------------|-----------------------|----------|---------------|
| ZrO$_2$      | Riedel de Haen        | 99       | < 5 µm        |
| Y$_2$O$_3$   | Fixanal               | 99.95    | < 5 µm        |
| MgO          | Nanjing Nano Tech.    | 99.9     | 30-40 nm      |
| $\alpha$-Al$_2$O$_3$ | Hongwu I. Group     | 99.9     | < 80 nm       |

**Test Methods**

Grain size was calculated by using Atomic Force Microscopy device (AFM) type SPM-AA 3000 Angstrom (USA).

Shrinkage is a common phenomenon in the sintering process of foam ceramic accompanied by significant weight loss and evolution of gaseous by-products. The shrinkage is caused by the necking...
and grain growth in the densification process. Therefore, the shrinkage is an important parameter which the engineers have to take into account for materials designed in the practice. Total linear shrinkage after drying and firing of ceramic specimens as a percentage of plastic length, is as follows:

\[ L.F.SH\% = \frac{L_0 - L}{L_0} \times 100 \quad \ldots (2) \]

Where, \( L_0 \): plastic length of test specimen (before firing) and \( L \): fired length of test specimen.

The apparent porosity (A.P) and The bulk density (B.D) of the sintered samples were measured by the Archimedes drainage method, using ASTM(C373).

The apparent porosity of such specimens was measured using the traditional Archimedes method. In brief, the dry specimen with mass of (\( W_d \)) was boiled in water for (2) hrs to remove the air trapped in the pores. Then it was cooled down to ambient temperature, and weighed to have the sample mass with water (\( W_s \)) and being immersed in water (\( W_i \)). The apparent porosity was calculated using the following equation:

\[ (A.P)\% = \frac{W_s - W_d}{W_s - W_i} \times 100 \quad \ldots (3) \]

Where, \( W_d \): Mass of the dry specimen, \( W_s \): Mass of specimen being infiltrated with water and \( W_i \): Mass of sample being immersed in water.

The bulk density in (g/cm\(^3\)) of a specimen is the quotient of its dry mass divided by the exterior volume, including pores, the bulk density is calculated as follows:

\[ B.D(g/cm^3) = \frac{W_d}{W_s - W_i} \quad \ldots (4) \]

The Diametral stress distribution should be independent of length as shown in Fig. 3, provided a uniform compression stress applied. The simple theory describing the stress distribution under a uniform diametric load on a disk-shaped specimen predicts a uniform tension field at the center of the disk:

\[ \sigma_D = \frac{2F}{\pi DL} \quad \ldots (5) \]

where F is the applied load (N), D is the disk diameter and L is the thickness of disk. The stress field in the transverse direction is highly dependent on the width of load application and becomes highly compressive. The disk test has therefore been used to attempt to study biaxial stress failure response [6].

![Diagram of Diametral Strength Specimen](Image)

**Figure 3:** Diametral Strength Specimen. [6]

**Results and Discussion**

Grain size was decreased with nano spinel additions increases with range from 624 nm to 109 nm, which is list in table 2.

High shrinkage values of zirconia during sintering are very most difficult problems experienced by manufactures, they can range from 15 to 25%. Generally, the shrinkage rate is often during the phase
transformation of $\text{ZrO}_2$ from monoclinic zirconia ($\text{m-ZrO}_2$) to tetragonal zirconia ($\text{t-ZrO}_2$) at temperature from 970 °C to 1170 °C [7]. Tetragonal zirconia stabilizes by the addition of dopants due to differences in valences and major cause of transformation of monoclinic to tetragonal is due to change in lattice parameters and unit cell volume. Almost 3 to 5 % volume shrinkage leads to tetragonal phase [8]. Fig. 4 shows the shrinkage was decreased with decreasing the percentage of spinel addition. Higher spinel content was found to inhibit the shrinkage of $\text{ZrO}_2$ because large inclusions can effectively retard the matrix densification and affect the composite microstructure characteristics. Low shrinkage can also be beneficial for the near-net shaping for the Y-PSZ-Spinel implants [9]. Surface diffusion normally does not lead to shrinkage of the compacts, whereas surface diffusion increases the particle contacts and decreases surface curvature, thereby eliminating smaller grains and reducing sintering activity [10]. The results showed that the contraction was decreased by 40% when adding 25 wt% of $\text{MgO.Al}_2\text{O}_3$, so that specimens will be more homogeneous in the dimensions when adding the $\text{MgO.Al}_2\text{O}_3$. Porosity is one of the most important factors affecting the characterization and application of ceramics. Increasing the percentage of spinel additions led to decreased the apparent porosity, which is shown in Fig. 5. Generally, the porosity was low and less than 5 %, where reaching a minimum value of 2.5 % when adding 25 % $\text{MgO.Al}_2\text{O}_3$. The reason for the decrease in porosity is explained by the addition of alumina and magnesia in the nano scale size, and therefore the filling of voids between micro Y-$\text{ZrO}_2$ grains. It is also noticeable that porosity was nearly constant when adding more than 15 wt% of spinel [11].

Bulk density increases even though shrinkage decreases due to the change in the structure of the specimens when adding the nano particle size spinel, where nano sized has more effect on increasing the density. As the density of nano particles is greater than micro size. It is also contributes to increasing bulk density. The results of the change in bulk density with increasing the percentage of spinel additions are shown in Fig. 6. Increment of $\text{MgO.Al}_2\text{O}_3$ addition from 5 wt% to 10 wt% was leaded to an increase in bulk density from 4.73 g/cm³ to 4.92 g/cm³, which is an increase of 4 %. While the increase of the spinel up to 25 wt% the density became 5.86 g/cm³, and the increase in density was 24 %. The decrease in grain size was also significant in increasing the bulk density and this is clear in Fig. 7. The reverse relationship between density and porosity has been achieved, as density has increased with porosity decreases. Therefore, this is considered one of the reasons for increasing density.

Diametrical strength is one possible tests to estimate the durability of sintered specimens of mechanical stresses. Fig. 8 shows the dependence of diametrical strength on the addition of the spinel. Increased strength was observed with increasing the amount of spinel additions. Addition of 5 wt% spinel give the strength is 79.3 MPa and became 97.1 MPa at the addition of 25 wt% spinel. The percentage of those increase in diametrical strength is 18%. Several factors influenced the change in strength with spinel additions, so, the most important of which is grain size and porosity. As well as, the large change in grain size made this factors dominant determinant of strength. Fig. 9, shows that the strength was increased monotonically with an decrease in average grain sizes for different nano-$\text{MgO.Al}_2\text{O}_3$ additions. Hall-Petch decrypt the relation between strength and grain size, where, the strength ($\sigma$) increase with grain size ($d$) decreases as given by the following equation, here ($\sigma_o$) is the strength at an infinite grain size, ($K$) is the Hall-Petch constant:

$$\sigma = \sigma_o + K \cdot d^{-1/2}$$

However, it is obvious that this relationship cannot be extrapolated to arbitrarily small grain size and some form of lower limit to this behavior must exist. It has been observed that even if nanocrystalline materials are inherently stronger than their microcrystalline counterparts. The increment in strength falls below the estimated strength based on the Hall-Petch equation [12]. The low porosity values did not have a significant influence on the decrease of strength, in spite of the reverse relationship between them because the effect of the increase due to decreasing grain size was greater.
Fig. 10, shows the specimens after crashing, where broken parts are increase with strength increases, so the decreasing of grain size is led to increasing the cracks baths of grain boundary during applied load.

Conclusions

Decreased grain size with MgO.Al₂O₃ additions led to increasing the density and mechanical properties, this means match the results with Hall-Patch equation.

Specimens were more homogeneous when adding MgO.Al₂O₃ as a result of a decrease in the dimensions shrinkage, this is very important in ceramic products manufacturing processes and to control the exact dimensions.

MgO.Al₂O₃ additions have led to the emergence of a larger amount of nano-grain size and also reduced grain growth during the process of sintering.

Decreasing the porosity and increasing the density due to MgO.Al₂O₃ additions means continued solid-state sintering.

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Table 2: Avg. Grain Size Diameter of Y-PSZ with different MgO.Al₂O₃ additives.
Figure 4: Linear shrinkage of Y-PSZ dependence on MgO.Al$_2$O$_3$ additions.

Figure 5: Variations of apparent porosity with MgO.Al$_2$O$_3$ added to Y-PSZ.
Figure 6: Variations of bulk density with spinel added to Y-PSZ.

Figure 7: The grain size dependence of bulk density for Y-PSZ with different MgO.Al₂O₃ additions.

Figure 8: Variations of diametric strength with MgO.Al₂O₃ added to Y-PSZ.
Figure 9: Variations of diametric strength with (a) mean grain size and (b) inverse of square root of grain size for Y-PSZ with different MgO.Al₂O₃ additions.

Figure 10: Broken specimens after applied diametrical stress; where A, B, C, D and E are Y-PSZ with different MgO.Al₂O₃ additions, 5, 10, 15, 20 and 25 wt%, respectively.