Structural Properties Of Yttria Stabilized Zirconia With Different Nano Alumina - Magnesia Spinel Additions

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Abstract. Micro Y₂O₃ powder (8 wt%) was added to zirconia to prepare Y-PZT, while the mixture of nano (MgO-Al₂O₃) magnesium aluminate spinel (MAS) was prepared by mixing 28.33 wt% of nano-MgO with 71.67 wt% of nano-Al₂O₃ powders. The MAS was added to the Y-PSZ by different weight percentage (5, 10, 15, 20 and 25 wt%), and after homogeneous mixing the specimens was formed by axial pressing and sintered at 1550 °C for four hours as soaking time. X-ray diffraction analysis shows that the three phases of zirconia (m: monoclinic, t: tetragonal and c: cubic) have emerged as a result of the addition of MgO with the formation of MAS. Increasing the percentages additions of MAS was leaded to increase the crystal size from 34 to 48 nm, while the lattice strain was decreased from 0.4 % to 0.3 %. As well as, the grain size was calculated for surface of specimens and it was found to be decreasing from the micro-size (> 0.6 µm) to nano-size (~ 108 nm) with a clear decrease in surface roughness from 6.5 nm to 1 nm due to the nano-MAS additions.

Keywords: Nano-ceramics; Zirconia; Partially stabilized Zirconia; Spinel; X-ray diffraction; AFM; lattice strain; surface roughness; Grain size.

1. Introduction

For a long time zirconia with rare earth oxides as pigment for ceramics, Although low-quality zirconia is used as an abrasive in huge quantities, tough, wear resistant, refractory zirconia ceramics are used to manufacture parts operating in aggressive environments, like extrusion dies, valves and port liners for combustion engines, low corrosion, thermal shock resistant refractory liners or valve parts in foundries. Good chemical and dimensional stability, mechanical strength and toughness, coupled with a Young’s modulus in the same order of magnitude of stainless steel alloys was the origin of the interest in using zirconia as a ceramic biomaterial.[1]

Different oxides, such as yttrium oxide (Y₂O₃), calcium oxide (CaO) or magnesium oxide (MgO), can be added to zirconia to stabilize it, allowing the tetragonal form to exist at room temperature after sintering.[2]

Partially stabilized Zirconia (PSZ) is a mixture of zirconia polymorphs, because insufficient cubic phase-forming oxide (Stabil-ized) has been added and a cubic plus metastable tetragonal ZrO₂ mixture is obtained [3].

Magnesium aluminates spinel MgAl₂O₄ (MAS) an face centre cubic structure (FCC) is one of the most outstanding optically transparent ceramics that exhibits a unique combination of optical and mechanical properties both at ambient and elevated temperatures. The normal composition of spinel is 28% MgO + 72% Al₂O₃, approximately .[4]

2. Experimental Work

A. Materials and sample preparation
From previous studies we have concluded that adding yttria (Y$_2$O$_3$) to zirconia (ZrO$_2$) with percentage ranging from 5 wt% to 10 wt% achieves Y-PSZ. Thus 8 wt% of yttria was added to zirconia. Both materials were supplied by the companies listed in the table 1.

Wet mixing was done by adding water and using magnetic stirrer achieve homogeneous distribution of powders. After drying the mixture at 100 °C, the agate mortar was used to eliminate the aggregates in the powder.

The ceramic powders were used in nano size to preparation the magnesia-alumina spinel, and the specification of Al$_2$O$_3$ and MgO are shown in table 1. The proportion of Al$_2$O$_3$ (71.67 wt%) and MgO (28.33 wt%) was mixed in the same way as the preparation of Y-PSZ. The use of nano size powder is useful to reducing the temperature required for phase transformations completion and the early emergence of the spinel phase. In addition to the high ability to achieve greater diffusion and penetration around Y-PSZ grains.

Different weight percentage of MgAl$_2$O$_4$ spinel (5,10,15,20 and 25 wt%) was added to the Y-PSZ mixture as shown in table 2. The compound was mixed well by the wet method. After obtaining a homogeneous mixture and drying process and 10 wt% of poly (vinylalcohol) (PVA)(sourced by DIDACTIC, Barcelona Espana) as a binder was added to the mixture. The axial pressing method was used to form specimens with diameter (10 mm) and thickness ranging from 3-4 mm by metal mold. The applied load of hydraulic press was 3 ton for 30 s to ensure the distribution of force on all specimen area.

The process of sintering included several possible options. The most important of which area are:

1- Partially stabilized zirconia or tetragonal zirconia polycrystalline (TZP) formation, as a result of yttria(Y$_2$O$_3$) addition.
2- Acquire the spinel compound (MgAl$_2$O$_4$).
3- Strengthening the grain boundaries of zirconia due to the spread of nano-spinel around it, or the possibility of increased stability of zirconia by magnesia (MgO).

The sintering process was obtained by using an electrical programmable furnace type (NABERTHERM-P310-GERMANY). 3.2, with temperature rising rate 15 °C/min up to 1550 °C at sintering soaking time 4 hr to complete the Process of grain growth and get the required phase.

### B. Test methods

The system was used in x-ray diffraction analysis of specimens is SHIMADZU type-6000. The screening process is conducted for each specimen within the range of angular (2θ=20°-70°). This examination helps us to provide the data necessary to identify the crystal structure of output and phase information.

The lattice constant can be calculated from any plane (hkl) using the relation:

$$a = \sqrt{h^2 + k^2 + l^2} \quad \ldots \ldots \ (1)$$

Where : $2d \sin \theta = n \lambda$

Also, the crystallite size of the structure is estimated by using scherrer's formula:

$$D_c = \frac{K \lambda}{\beta \cos \theta} \quad \ldots \ldots \ (2)$$

Where K=0.94 and $\lambda$ is the wave length of X-Ray used, which is Cu $K_\alpha$ radiation ($\lambda=1.54 \ \text{Å}$) and $\beta$ is the full width at half maximum (FWHM) of the diffraction peak corresponding to a particular crystal plane.

The lattice strain ($\epsilon$) was calculated using the formula:[5,6,7]

$$\epsilon = \frac{\beta}{4 \tan \theta} \quad \ldots \ldots \ (3)$$
The Atomic Force Microscopy device (AFM) type SPM-AA 3000 Angstrom (USA). 3.5a. Atomic force microscopy is used in surface science laboratories to obtain images with atomic resolutions of $10^{-10}$ m or one tenth of nanometer.

Roughness is one of the most important surface characteristics that can be measured with high precision using AFM. Among Height Parameters, the roughness average ($R_a$) is the most widely used because it is a simple parameter to obtain when compared to others. The roughness average is described as follows:

$$R_a = \frac{1}{l} \int_0^l |Z(x)| \, dx \quad (4)$$

Where $Z(x)$ is the function that describes the surface profile analyzed in terms of height ($Z$) and position ($x$) of the sample over the evaluation length "$l$".

The root mean square (RMS) is a statistical measure used in different fields. We cite, as an example, the use of the RMS amplitude applied to harmonic oscillators, such as on an alternating electric current. The root mean square of roughness ($R_q$) is a function that takes the square of the measures. The RMS roughness of a surface is similar to the roughness average, with the only difference being the mean squared absolute values of surface roughness profile. The function $R_q$ is defined as: [8]

$$R_q = \frac{1}{\sqrt{l}} \int_0^l |Z^2(x)| \, dx \quad (5)$$

3. Results And Discussion

Fig. 1 shows the formation of the main phase is tetragonal zirconia (t-ZrO$_2$), and this phase was increased with percentage of spinel additions increases. In addition, there were fewer percentage of the other two phases: monoclinic zirconia (m-ZrO$_2$) and cubic zirconia (c-ZrO$_2$). These phases were formed due to the influence of the addition of micro-Y$_2$O$_3$ or nano MgO. This mains that MgO has contributed to the emergence of the t-ZrO$_2$ phase and the formation of MAS, where the spinel appeared clearly in the x-ray diffraction pattern. These phases appear and increase with temperatures greater than 1300 °C [9]. From the results of x-ray diffraction pattern the crystallite size values were shown in Fig. 2, where the crystallite size was increased with increase the percentage of spinel addition. So, the additions greater than 20 wt% of spinel were less effective in increasing crystallite size and this means that these additives will have less effect in the t-ZrO$_2$ formation. X-ray peak profile analysis (XPPA) is used to estimate the micro and nano structural quantities and correlate them with the observed material properties. XPPA is an averaging method and a powerful tool to estimate the crystallite size and lattice strain. The crystallite size and lattice strain affect the Bragg peak to increase the peak intensity, peak width and shift in the 2θ peak position.[10]

In the case of a stress-free material, the interplanner spacing $d$, for a particular reflection (hkl), is constant from one crystallite to another, when it is deformed elastically, the lattice spacing of the crystallites change from their stress free values, and cause a shift in the Bragg angle. The strain calculated from this shift is termed the lattice strain. [11]

The changes in lattice strain with increasing the percentage of spinel additions are shown in Fig. 3, from which, note the stability of the lattice strain up to 10 wt. The t-ZrO$_2$ transforms to monoclinic to relax the compression stress, a map of lattice strain related to the (101) plane was implemented in the following way. Common strain mapping involves extracting the lattice strain for giving plane for all data points. The shift in t-ZrO$_2$ at (101) peak was
considered for strain calculation, and if strain related to this peak in a particular frame was detected in the interval of less than ± 0.0001.

An interesting result is that at both region where pure tetragonal phase and highly monoclinic phase were observed, there is less strain. In the other words they have less residual stress after fracture. A high fraction of phase transformation and low stress state at the impacted region proves the mechanism of stress relaxation by phase transformation. Although, this mechanism via phase transformation might create some micro cracks that can propagate by fatigue and impacts that total life time of the crown, it shows ZrO$_2$ from failure under the localized compression load. The mechanism helps explain reports about the failure of veneers by chipping without exposing the zirconia support layer. When high stress load is applied to the Y-PSZ-MAS system, high stress state location in ZrO$_2$ undergoes the stress induced phase transformation providing stress relaxation reducing the potential energy for crack initiation and growth in ZrO$_2$ layer rather than the spinel layer [12].

It is depicted that as the crystallite size decrease, lattice strain increases for both pouring temperatures. This is due to the fact that as the crystallite size decrease, the particle diameter is constant and the difference of diameter decreases, and hence lattice distortion increases [13].

The strain of the sintered specimens was varied from 0.28 % to 0.4 % and the crystallite size varied from 34.4 nm to 48.8 nm depending on the percentage of the spinel additions. It was shown that the lattice strain illustrates opposite trend of the crystallite size. The lattice distortion for prepared specimens is relatively high due to the expected large surface / volume ratio values as a direct consequence of small crystallite size. For the sintered specimens, the lattice strain values decreased with reducing ZrO$_2$ content [14].

The statistical distribution of the grain size of the sintered specimens was studied by using atomic force microscopy (AFM) as shown in Fig. 4. When adding a small amount (5 wt%) of nano-MgAl$_2$O$_4$ spinel, no nano size range was shown the grain size distribution of the specimen and in this case the statistical distribution is called positively or right skewed as shown in Fig. 4a.

The highest proportions ranged from 0.5 µm to 0.7 µm. when increasing the percentage of spinel to 10 %, the effect of the addition seems clear in the distribution of granular sizes to extend from 100 nm to greater than 600 nm and the shape of statistical distribution is like to bimodal and symmetrical due to the wide range of granular sizes, as shown in Fig. 4b. The addition of 15 wt% spinel leading to statistical redistribution of positively skewed, but shifted to the right to wards the nano scale size. The granular distribution range extends to less than 100 nm as shown in Fig. 4c. Increasing the percentage of the spinel addition up to 20wt% has led to a continued increase in the amount of the granular nano grains. The statistical distribution diagram more skewed to the right, which is the increase in nano scale and approximation of the exponential distribution. The values of the largest particle size were within the range from 50 nm to 150 nm as shown in Fig. 4d.

The statistical distribution of granular size was repeated by adding 25 wt% of spinel, and this distribution was corresponded to the bimodal and symmetrical with in max nano size granular range less than 100 nm, as shown in Fig. 4e. The symmetry distribution means more homogeneity in grain size and also obtaining uniform surface in granular distribution, and inhibits the continued growth of granular of Y-PSZ compound.

From above, the grain size was decreased with nano spinel additions increases with range from 624 nm to 109 nm as shown in Fig. 5. This decrease leads to increase in surface area of specimens due to the increase in the number of grains per unit area. Grain size also affected on other properties, especially mechanical properties and most important is effective on fracture toughness [15].

The topography images of sintered specimens taken by using AMF were illustrated in the fig. 6, the measurement range for all specimens is (10×10 µm). This figure shows 3D topographies profiles under different MAS additives, where the max high (peak-peak) of the grain size was decreased with spinel additions increases. The value has become 51.37 nm for sintered specimens of Y-PSZ with 5 wt% spinel and listed in Fig. 6a. As well as, the max high
of the grain size was gradually decreasing to 25.78 nm, 18.5 nm, 5.15 nm and 3.62 nm with 10, 15, 20 and 25 wt% of spinel, respectively, as shown in Fig. 6(b, c, d and e).

The roughness was clearly depend on the spinel additions as shown in Fig. 7. The values of roughness were decreased from 6.45 nm to 1.02 nm with spinel additions increases. The results of the root mean square (RMS) and roughness of the surface has been measured by means of atomic force microscopy, and the data have been analyzes statistically to estimate the significance. Additionally, a fractal analysis of the specimens surfaces has been carried out.

The surface roughness of each specimen has been evaluated as the root mean square (RMS) value $R_q$ of the distribution of heights from AFM topographical images [16]. Fig. 8, shows the RMS was decreased with spinel added and the values of RMS dropped from 7.45 nm to 1.2 nm.

4. Conclusions

The crystallite size dependence on the percentage of spinel addition and the lattice strain will depend upon the orientation of the reflecting group of the crystallites with respect to the direction of stress.

At the large amount of spinel additions, the lattice strain become decreases, this means the specimen became more brittle with spinel addition, and this can be reflected on other mechanical properties such as Young's modulus.

MgO-Al$_2$O$_3$ additions have led to the emergence of a larger amount of nano-grain size and also reduced grain growth during the process of sintering.

The decreasing of RMS with spinel addition is leading to decrease the fraction resistance of the materials surface and therefore the specimens will become more resistance to wear when increasing the percentage of spinel.

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Table 1: Specifications of materials.

| Material   | Source          | Purity % | Particle Size |
|------------|-----------------|----------|---------------|
| ZrO2       | Riedel de Haen  | 99%      | < 5 µm        |
| Y2O3       | Fixanal         | 99.95    | < 5 µm        |
| MgO        | Nanjing Nano Tech. | 99.9    | 30-40 nm     |
| α-Al2O3    | Hongwu I. Group | 99.9    | < 80 nm      |

Table 2: Composition of Specimens.

| Specimens | MgAl2O4 wt% | Y-PSZ wt% |
|-----------|-------------|-----------|
| A         | 5           | 95        |
| B         | 10          | 90        |
| C         | 15          | 85        |
| D         | 20          | 80        |
| E         | 25          | 75        |
Figure 1: X-ray pattern of Y-PSZ with different MAS additives; (a) 5, (b) 10, (c) 15, (d) 20 and (e) 25 wt%.

Figure 2: Crystallite size of tetragonal-ZrO$_2$ in Y-PSZ with different MAS additives.
Figure 3: Lattice strain of tetragonal-ZrO$_2$ in Y-PSZ with different MAS additives.
Figure 4: Statistical distribution of grain size for tetragonal-ZrO$_2$ in Y-PSZ with different MAS additives; (a) 5, (b) 10, (c) 15, (d) 20 and (e) 25 wt%.
Figure 5: Variation of the average grain size diameter for Y-PSZ with different MAS additives.
Figure 6: 3D AFM scan data of Y-PSZ with different MAS additives: (a) 5, (b) 10, (c) 15, (d) 20 and (e) 25 wt%.
Figure 7: Variation in roughness average of Y-PSZ as a function of MAS additions.

Figure 8: Variation in root main square of Y-PSZ as a function of MAS additions.