Study of Elastic Modulus and Roughness of Porous Alumina Toughened Zirconia

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Abstract. Alumina Toughened Zirconia (ATZ) composite with 20 wt% alumina has been prepared by powder compaction method after stabilized zirconia using 3 mol. of yttria to get the 3Y-TZP compound. A graphite additive (0,10,20,30, and 40) wt.% have been added to produce porous ATZ. The composite has been sintered in the air at 1500 °C. The effect of porosity on physical and structural properties have been investigated. Porosity increased, and bulk density decreased with graphite additives increases in the range (7.5-51.7) % and (5.6-2.8) g/cm 3  respectively for (3Y-TZP/20 wt% Al 2O 3) specimens. The porosity effect is apparent by deteriorating the mechanical properties; the diametric strength decreased from 95.7 to 8.7 MPa, while the young modulus decreased from 159.7 to 27.3 GPa with porosity increases. Surface morphology was detected by atomic force microscope (AFM). The average grain size and roughness of 3Y-TZP/20 wt% Al 2O 3 specimens increased with increasing porosity from 75.44 to 91.9 nm and 2.9 to 18.7 nm, respectively. It was found that porous ATZ was successfully fabricated by using graphite additives. The apparent porosity of 3Y-TZP/20 wt% Al 2O 3 composite after sintering can be controlled by the amount of graphite content in the powder mixture. The presence of porosity greatly influences physical and microstructural properties.

Keywords. Alumina toughened zirconia, Tetragonal stabilized zirconia, Porous ceramics, Diametric strength.

1. Introduction
An Alumina toughened zirconia composite (ATZ) is defined as a composite material with a small magnitude of 1 μm alumina particles after firing in zirconia (nano-sized) tiny particles. A typical ATZ composition is 20 Wt. % Al 2O 3 and 80 Wt.% ZrO 2. Compared to ZrO 2, Al 2O 3 has a lower thermal expansion coefficient and a higher coefficient of thermal conductivity, making it a good additive to improve ZrO 2 thermomechanical performance [1]. Exceptionally high mechanical strength values for ATZ were reported. For hot isostatically pressed (1800-2400 MPa) is the bending strength at room temperature, and at elevated temperatures, the bending strength is more than 800 MPa at 1000 °C. ATZ has very high thermal shock resistance(ΔT = 470 °C) because of the similar thermal expansion coefficient of alumina α = 6.5 - 8.9 10⁻⁶ K⁻¹ and high thermal conductivity (λ = 30 - 39 W m⁻¹ K⁻¹) as compared to zirconia α = 6.8 - 10.6 10⁻⁶ K⁻¹ , λ = 1 - 3 W m⁻¹ K⁻¹ . [2]. ATZ has an economic advantage from replacing part of the zirconia, which is considered an expensive material by alumina as a cheaper material. While properties
with high-performance achieved by high energy-consuming processing of the powders, e.g., by hot isostatic pressing (HIP), are considered an expensive process [3]. ATZ ceramics might be a good replacement for alumina in biomedical applications because while many characteristics, such as mechanical ones, are analogous or better than alumina’s characteristics. Its rigidity (stiffness) lower than alumina’s, ATZ Young modulus around 260 GPa, compared to (380 - 410 GPa) for alumina [4]. Therefore if the porosities are designed appropriately, it can be used in bone replacement applications. It is well known that the porosity can have a profound influence on the (mechanical, thermal, and electrical) of brittle materials. “Shear modulus, Young’s modulus, and Poisson’s ratio” are important parameters in the study of advanced materials [5]. Also, the ceramic macroscopic behavior ranging from quasi-plastic to brittle depending on pores volume; that is why investigating the deformation in a brittle, porous material at different scale levels and the failures depending on the deformation rate, constraints, etc. is of considerable interest in terms of the structural deformation and destruction in similar brittle materials (ceramics) [6]. An important factor affecting the mechanical ceramics mechanical properties is porosity. Thus, the relationship describing the change of the modulus of elasticity (E) with porosity (P) is described as [7]:

\[ E = E_0 e^{-aP} \]  

Where \( E_0 \) is Young’s modulus of material without porosity and \( a \) is a constant, its value is approximately \( a=4 \) for porous ceramics.

Equation (1) may be applied to all other mechanical characteristics in terms of behavior, but the constant \( (a) \) will take different values. The objective of this work aims to study the relations between parameters such as porosity, diametric strength, effective Young’s modulus, and structural and surface properties such as grain size, roughness and root mean square of alumina toughened zirconia ceramics. These influencing factors are essential in determining the characteristics of porous ATZ for use as filters and in biological applications.

2. Materials and methods

Fine zirconia commercial powder (Riedel de Haen, Germany, 99% purity, particle size <5 μm) used as starting materials to prepare alumina toughened zirconia composite. A 3 mol% yttria by (sky spring nanomaterials, USA) was added to zirconia to stabilize the tetragonal phase of zirconia and produce (3Y-TZP). Porous (3Y-TZP)/Al₂O₃ specimens were prepared by mixing fine powders of 80 wt.% 3Y-TZP and 20 wt.% nano-sized of laboratory alumina (α-Al₂O₃ purity >99/99%, the average particle size of 13 nm, Sigma Aldrich, USA). 3Y-TZP/20 wt% Al₂O₃ (ATZ) specimens were prepared by mixing the dry powders in a magnetic stirrer with a small amount of distilled water for 3 hrs. to obtain a homogeneous mixture. After that, the mixture has been dried at 100 °C. A total of 5 different powder specimens were prepared after drying by mixing the ATZ powders with graphite particles (32 μm) in different weight percentages (0,10,20,30 and 40) wt% produce sufficient porosity as well as interconnectivity of the pores. Poly (vinyl alcohol) (PVA) sourced by DIDACTIC, Barcelona Espana) is used by 0.5Wt.% as a binder. The powder mixtures have been compacted to form pellets (10 mm diameter and 5 mm thickness) using uniaxial pressing. Steel die using to form specimens with load 255 MPa for 30 seconds to ensure that force is distributed on all areas of the specimen. The pressed pellets then sintered at 1000 °C for 15 min to burnout the graphite particles; only pores were left behind. Followed by sintering at 1500 °C for 2hrs. After sintering, all the specimens turned into white colors due to graphite oxidation, and porous ATZ specimens were produced. After sintering at 1500 °C, the (AP) apparent porosity and (BD) bulk density of ATZ porous composite specimens were calculated by Archimedes principle using ASTM (C373) as follows:

\[ \text{A.P} \% = \frac{W_{w}-W_{d}}{W_{w}} \times 100 \]  

Where \( W_{w} \) is the weight of specimen with water, \( W_{d} \) is the weight of dry specimen, and \( W_{w} \) is the weight of specimen with distilled water.
\[ B.D \ (g/cm^3) = \frac{W_d}{W_{s}-W_i} \]  

(3)

\[ W_d: \text{the mass of the dry specimen, } W_s: \text{the mass of specimen being infiltrated with water, and } W_i: \text{the specimen's mass being immersed in water.} \]

Elastic modulus (Young’s modulus) was measured by using an ultrasonic device (GEUSM 35X). The pulse-echo mode is the operating principle of the device. This test was done using a prob of three different frequencies 1, 2, and 4 MHz. The choice of frequencies was made based on multiples of numbers. The test was carried out by measuring ultrasonic wave flight time within known materials thickness. The processing of data determines the ultrasonic wave velocity. Couplant agent covered the surface of the specimen. Testing was conducted at different spots three times. Elastic modulus has been calculated using the following equation:

\[ E(\text{GPa}) = \frac{V_l \rho (1+v)(1-2v)}{1-v} \]  

(4)

where the elastic modulus is (E), and ultrasonic longitudinal wave velocity (Vl) bulk density is (\( \rho \)), and Poisson’s ratio of the material is (v). Poisson’s ratio for ATZ was taken from literature, which is 0.23 \[8\].

Diametrical strength for porous ATZ specimens was measured by the Brazilian test. The Brazilian test is a disc of the test material loaded across a diameter. The test was done by Hydraulic pressing (Ley Bold Harris NO.36110). The thickness and diameter of the specimens have been calculated. Diametric strength then calculated by using the following equation:

\[ \text{Diametric Strength (MPa)} \quad \sigma_D = \frac{2F}{\pi DL} \]  

(5)

where the applied load (N) is F, the disk diameter is D, and the disk's thickness is L \[9\].

Topography and morphological of surface, roughness, and average grain diameter size for prepared Alumina toughened zirconia specimens were analyzed using atomic force microscope type (SPM-AA 3000 Angstrom -USA).

3. Results and discussion

Porosity and bulk density were determined using the Archimedes method. Characterization and application of ceramics affecting by porosity. Graphite is a volatile material, and it is used as a pore-forming agent. The sintering process will burnout the graphite leaving pores behind. Figure (1) shows variations of apparent porosity and bulk density of ATZ composite specimens sintered at 1500 °C with different graphite additives. An increase in the apparent porosity was noted when graphite addition increase. The percentage of porosity was increased from 7.5% (without graphite additive) to 51.7% for 40 wt% graphite additive specimen while bulk density decreased from 4.9 to 2.8 g/cm³.

![Figure 1](image-url)  

*Figure 1.* Variations of apparent porosity and bulk density of ATZ with different graphite additives.
Young modulus for porous media is calculated by the ultrasonic test as a non-destructive method. Figure (2) shows variations of elastic modulus with porosity for ATZ specimens. The results showed that Young modulus for ATZ specimen containing 0 wt. % graphite and 7.5 % porosity is 159 MPa and decreased to 27.9 MPa for ATZ containing 40Wt.% graphite and 51.7% porosity means Increasing graphite additives led to decreased porosity content and caused decrement in young modulus's decrement for the specimen. With a higher porosity structure, the Young modulus will be decreased because pores obstruct the ultrasonic signal's path and retard the ultrasonic waves' speed. This is why the time of flight of specimens will be most significant, and the ultrasonic velocity will be the lowest, leading to a decrease in Young modulus value. The elastic moduli for porous material variation with porosity following a general rule of brittle ceramics contain porosity, as previously reported by researchers [10]. The mathematical relationship between porosity and elastic modulus given by Equation (1) matched the research results, from which we conclude that the value of the constant a=4 is consistent with the literatures [7]. Also, the estimated value of the modulus of elasticity of dense ATZ (without pores) is $E_0=214.97$ GPa, and it is within the specified range for ATZ ceramics.

![Figure 2. Variations of elastic modulus with porosity for ATZ specimens.](image)

Diametrical strength is one of the possible tests for estimating the sintered specimens' durability of mechanical stresses. Figure (3) presented the diametrical strength of ATZ porosity and graphite additives dependence. It is clearly shown that the strength was on a continuous decrease (95.7-8.7 MPa), as the graphite additives increased from (0- 40Wt.%) because increasing graphite leads to increase porosity. Porosities have a significant role in influencing the strength of the sintered composite. The strength is inversely proportional to the porosity because when porosity exists, the load is applied across a smaller cross-section area. It is considered a stress concentration, and residual porosity will have a deleterious influence on both the strength and elastic properties[8]. The strength of porous ATZ is higher than porous TZP; it is believed that the mismatch of thermal expansion coefficient between alumina and zirconia is the reason for the improvement in strength. Another reason is the toughening resulting from crack deflection effected by the secondary nano Alumina particles dispersed in zirconia matrix at the nanoscales and the existing already effect of toughening by the transformation of phase from tetragonal phase to monoclinic phase. These results are compatible with many results of previous articles [1,11]. The mathematical relationship between porosity and diametric strength was described by Ryshkewitch [12] similar to Equation (1). From the relation in Figure (3), it is noted that the constant a= 5.2. The estimated value of the diametric strength of dense ATZ (without pores) is $\sigma_0=99.446$ MPa.
Figure 3. Variations of Young modulus and diametric strength with porosity for ATZ specimen.

The atomic force microscopy (AFM) is the test used to determine the average grain size and grain size distribution. The device as well as the grain size distribution. Figure 4a shows the grain size statistical distribution of ATZ without graphite specimen, which contains only 7.5 % porosity. Diagram of statistical distribution within nanoscale is narrow to a specific range. The range was from 70 nm to 90 nm, while this specimen's grain size average is 75.44 nm (Figure 5). The apparent porosity in ATZ specimen containing 10 Wt.% graphite additive was 17.6 %, which the distribution of grain size was changed and nanograins amount was decreased in A2 specimen containing 10 Wt.% graphite additive and the porosity content was17.6%. The porosity influence was noted through the extension of granular size distribution from <60 nm to >100 nm, and the symmetrical and bimodal statistical distribution shape was due to the granular size wide range [13]; this is shown in Figure 4b. The increment of the average grain size up to 78.95 nm, as shown in Figure 5, and the porosity amount continue increasing in ATZ with 20% graphite. The amount of nanograins continues decreasing, the distribution of grain size range from 70 to more than 100. The grain size bimodal and symmetrical statistical distribution have been repeated and presented in Figure 4c. The symmetrical distribution means grain size homogeneity was more [8]. The average grain size was 84.6 nm, as shown in Figure 5. In ATZ with 30% graphite, the porous level is 37.7 %, the grain size distribution was also symmetrical but more narrow to a specific value, the distribution of grain size ranged from 80 nm and > 100 nm presented in Figure 4d, and the average grain size diameter is 89.14 nm. In the last specimen, which has a higher amount of porosity, the grain size distribution becomes much more narrow to a specific value. The granular distribution ranges from 90 to more than 100, as shown in Figure 4e. The average grain size is 91.9 nm. The results above noted that grain size distribution deviated from the normal distribution because porosity forming and increasing with graphite additives increases. It was evident from the result showed in Figure 5 that average grain size increases with increasing porosity; this agrees with the fact that large amounts of porosity are challenging to eliminate during densification and then resulted in large grain size after sintering [14].
According to Zhang et al., the addition of alumina to 3Y-TZP restricted grain growth. They studied a small amount of nano Al2O3 effect on zirconia's mechanical properties and noticed that when alumina amount was higher than 0.25 wt.%, the grain size decreased [15]. The effect of porosity on roughness shows in Figure 5, where the roughness increased from (2.9 to 18.7) nm with increases porosity from (7.5-51.7) because the basic assumption of surface roughness is caused by grains or parts of grains have been sheared or pushed out of the surface, the presence of porosity led to pushed the grains out of the surface [14]. This agrees with the fact that in ceramics adding small alumina interstices could be lead to abrasion resistance and hardness[16]. Using AFM, topography images of porous specimens of ATZ have been taken and presented in Figure 6; the range of measurement for all specimens is (2×2 μm). 3D topographies profiles were shown in this figure with different porous levels where the grain size maximum peak has been increased within increasing porosity. In ATZ without graphite containing only 7.5% porosity, the peaks' height is (11.96) nm. The value of peaks increased in which contain 17.6 % porosity; there is a continuous increase in the grains' peaks until it reaches grain size peak to the maximum peak value in ATZ with 40 wt% graphite (78.83) nm specimen, which contains 51.7% porosity. That means there was a high distribution variation of the grain size due to the grain growth caused by porosity.

Figure 4. Grain size distribution of ATZ specimens with different graphite Wt.% content a- ATZ-graphite 0Wt.%, (b) ATZ-graphite 10 Wt.% , (c) ATZ-graphite 20 Wt.%, (d) ATZ-Graphite 30 Wt.%, (e): ATZ-graphite 40 Wt%.
Figure 5. Grain size and roughness variation with porosity for ATZ specimens.

Figure 6. AFM 3D scan data of ATZ specimen with different porosity content.
4. Conclusions
The porous structure of ATZ was successfully fabricated using graphite additives. The apparent porosity of the (3Y-TZP/Al₂O₃) composite after sintering can be easily controlled by the powder mixture's nominal graphite content. Maximum values of the total porosity of porous ceramics (ATZ composite ceramics) prepared with graphite by dry pressing was approx. 52 %. As expected, the porosity had a significant influence on mechanical and structural properties. This influence led to deteriorating mechanical properties. The values of Young modulus and diametrical strength were decreased with increasing pore space volume of alumina toughened zirconia composite, which may correlate with the appearance of multiple cracks in the deformation course of highly porous ceramics. The decrease in mechanical properties with porosity was an exponential change and corresponded to the previous literature's relationships. Porosity decreases the number of nanograins and increases grain growth because eliminating large amounts of porosity during densification is difficult, resulting in large grain size after sintering. The resulting mechanical properties of porous ATZ were acceptable for infiltration applications to produce ceramic-glass composites.

5. References
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